

# The Role of Magnetite Nano Particle (MNP) to Oxidize Nitrobenzene using Heterogeneous Fenton Reaction

Hong-Kyun Lee, Si-Hyun Do, Sung-Ho Kong\*

**Abstract** — Heterogeneous Fenton system consisting of magnetite nano particle (MNP) catalyst has been developed for the oxidation of nitrobenzene by hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) in aqueous phase. Nitrobenzene was used as probe compound for detecting hydroxyl radical ( $\cdot\text{OH}$ ). The goals of this study were (1) to observe generation of hydroxyl radical in MNP/ $\text{H}_2\text{O}_2$  system using probe compound (nitrobenzene) and (2) compare with commercial magnetite to confirm its activity according to surface area. MNP was characterized by various techniques such as X-ray diffraction (XRD), high resolution transmission electron microscopy (HR-TEM), X-ray photoelectron spectra (XPS), and Brunauer-Emmett-Teller (BET). Degradation of nitrobenzene using MNP/ $\text{H}_2\text{O}_2$  system could be affected by MNP mass, and concentration of  $\text{H}_2\text{O}_2$ . When effects of MNP mass and concentration of  $\text{H}_2\text{O}_2$  were tested, 2.4 g of MNP mass and 1% (294 mM) of  $\text{H}_2\text{O}_2$  were the optimum concentrations for the degradation of nitrobenzene at pH 3. Addition of  $\text{H}_2\text{O}_2$  from 0.25% (73.5 mM) - 1% (294 mM) at 2.4 g of MNP, increased the first-order rate constants for the nitrobenzene degradation ( $0.035$  to  $0.101 \text{ h}^{-1}$ ). The result of different pH value showed that pH 3 was optimum value for Fenton-like degradation of nitrobenzene. Commercial magnetite ( $<5\mu\text{m}$ ) was also tested to compare with MNP. Removal efficiency of nitrobenzene using MNP/ $\text{H}_2\text{O}_2$  system (51%) was greater than using commercial magnetite/ $\text{H}_2\text{O}_2$  system (8%).

**Keywords:** magnetite nano particle (MNP), heterogeneous Fenton system, hydroxyl radical

## I. INTRODUCTION

Recently, the contamination of wastewater and groundwater by organic compounds has been concerned since the Industrial Revolution. These contaminated aqueous streams should be treated for the requirements of human being that increase demand of quality water resource. Physical, biological, and chemical treatment processes can treat organic compounds, which caused environmental problems. Advanced oxidation process (AOP) is the most famous process among chemical oxidation. These are commonly

generating the most powerful oxidant, hydroxyl radical ( $\cdot\text{OH}$ ). Among these, classic Fenton reaction is well known reaction since 1864 [1]. Classical Fenton reaction generates strong, non-selective oxidants, hydroxyl radicals reacting with ferrous salts and hydrogen peroxide ( $\text{H}_2\text{O}_2$ ). Classic Fenton reaction have some disadvantages; 1) to apply to in or ex-situ treatment, extremely low pH was required, and 2) ferrous ion oxidize to ferric ion too fast to reduce, additional ferrous ion have to inject sequentially. In these days, different type of Fenton-like reaction, called 'heterogeneous Fenton catalyst' has been developed. Many researchers have been reported the various heterogeneous Fenton catalyst such as Nafion, polyethylene film, alginate gel beads, Nafion/glass fiber, silica fabrics and layered clays [2-7]. However, these heterogeneous Fenton reaction is too slow to be used itself for degraded organic pollutants. Therefore, heterogeneous Fenton reaction has been developed with UV radiation to accelerate the reaction [8]. Fenton-like reaction cannot be degraded organic compounds as efficient as classic Fenton reaction and modified Fenton reaction. Because the generation rate of hydroxyl radical using surface reaction is much slower than using dissolved iron ion. In these reasons, this research was attempted that iron oxide mineral catalyst (magnetite,  $\text{Fe}_3\text{O}_4$ ) was synthesized nano sized to enhance surface reaction. MNP was used as an iron catalyst in Fenton-like process to enhance the activation of catalyst. These experiments were performed with the synthesis of MNP and determined the generating hydroxyl radicals using probe compounds.

## II. MATERIALS AND METHODS

Magnetite ( $\text{Fe}_3\text{O}_4$ ) nano particle (MNP) used in this study was synthesized by ferric chloride and ferrous chloride, which was a modification of co-precipitation method used in previous study [9]. All other agents were at least reagent grade. The Fenton-like process was conducted in 400 mL serum bottle at atmosphere pressure and room temperature ( $23\pm 5^\circ\text{C}$ ) and sealed with Teflon-faced rubber septa using aluminum cap with center opening. Syringe needle was put into Teflon-faced rubber septa to release pressure of inner sphere of serum bottle. A loss of nitrobenzene was not detected. Total reaction time is 8 h and each sampling times were 1h intervals. In case of variation of MNP and  $\text{H}_2\text{O}_2$  for degradation of nitrobenzene, the reactor was loaded with 400mL of nitrobenzene solution at fixed concentration (5 mM), and initial pH was 3. Tests were carried out by varying

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amounts of MNP (i.e. 2.4 - 9.8 g) and concentration of hydrogen peroxide ( $\text{H}_2\text{O}_2$ , i.e. 0.25% (73.5 mM) - 3% (882 mM)). Control tests were conducted by two cases; i) with/without MNP and ii) with/without  $\text{H}_2\text{O}_2$ . At the results of control tests, degradation portion of nitrobenzene was negligible. Effects of pH experiments were performed at pH values of 3, 5, 7, and 9. Initial concentration of nitrobenzene was 5 mM. 2.4 g of MNP was injected in the reactor and  $[\text{H}_2\text{O}_2]_0$  was fixed with 0.5% (147 mM). The pH was adjusted by 5 N NaOH and 1 N  $\text{H}_2\text{SO}_4$ . For comparison, a commercial magnetite was tested for nitrobenzene destruction. Commercial magnetite (<5 $\mu\text{m}$ ) +  $\text{H}_2\text{O}_2$  test were conducted at fixed concentration (5 mM), and pH 3. To evaluate the effects of iron ion,  $\text{FeCl}_2$  was used as alternative iron ion for modeling.

To characterize MNP, X-ray diffraction (XRD) was obtained with Rigaku D/MAX RINT 2500 X-ray diffractometer operated at 40 kV and 100 mA using Cu  $K\alpha$  radiation. The observation of high resolution transmission electron microscopy (HR-TEM) was performed by JEM3010 (JEOL) operated at 300 kV. BET surface areas were determined with a Micromeritics ASAP 2010 sorption analyzer using a nitrogen adsorption-desorption method at liquid nitrogen temperature. Composition of surface was determined by X-ray photoelectron spectra (XPS) using ESCA 2000 system VG multilab using Al  $K\alpha$  radiation. The residual nitrobenzene was analyzed using Agilent 6890 gas chromatograph (GC) equipped with an electron capture detector (ECD) and Rtx-TNT column (6 m x 0.53 mm, 1.5  $\mu\text{m}$ ). Residual concentration of  $\text{H}_2\text{O}_2$  was measured by titanium sulfate spectrophotometric method (linear range: 1-100  $\text{mg L}^{-1}$ ) [10]. Point of zero charge (PZC) of MNP was measured by the titration method [11]. Rate constants of nitrobenzene were calculated using Mathematica 5.2.

### III. RESULTS AND DISCUSSIONS

#### 3.1. Characterization of magnetite nano particle (MNP)

A typical XRD pattern of MNP showed that it matched well with the standard pattern of  $\text{Fe}_3\text{O}_4$  (JCPDS no. 19-0629). Moreover, the peak position and relative intensities of MNP with those XRD patterns of MNP in the literature [12]. The XRD patterns did not change after the reaction. The XPS patterns of MNP were shown as O 1s (529.9 eV) and Fe 2p ( $2p_{3/2}$  710.6 eV and  $2p_{1/2}$  724.1 eV) and it matched well with  $\text{Fe}_3\text{O}_4$  [13]. A HR-TEM image indicated the structure and size of particle. The diameter of MNPs was approximately 6 nm. The BET surface area and total pore volume of MNP were 130.5  $\text{m}^2 \text{g}^{-1}$  and 0.189  $\text{cm}^3 \text{g}^{-1}$ , respectively. MNP had much larger surface area compared to commercial magnetite (BET surface area of 6.2  $\text{m}^2 \text{g}^{-1}$  and a pore size of 0.013  $\text{cm}^3 \text{g}^{-1}$ ), which was in agreement with previous work [14]. The point of zero charge (PZC) value of MNP was pH 7.

#### 3.2. Degradation of nitrobenzene using MNP/ $\text{H}_2\text{O}_2$ system

Magnetite nano particle (MNP) was tested with  $\text{H}_2\text{O}_2$  to

evaluate ability of generating hydroxyl radicals due to the surface reaction of MNP. Fig. 1 demonstrated the removal efficiencies of nitrobenzene by MNP/ $\text{H}_2\text{O}_2$  system at pH 3 using 0.5%  $\text{H}_2\text{O}_2$ , along with variation of MNP.

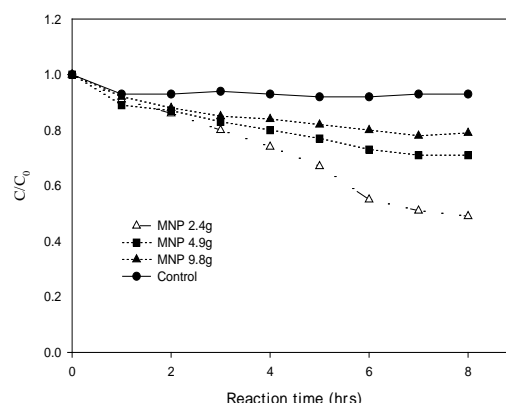


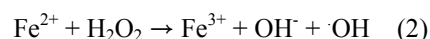
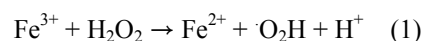
Fig. 1. Degradation of nitrobenzene (5mM) using MNP/ $\text{H}_2\text{O}_2$  system with  $\text{H}_2\text{O}_2$  0.5% at pH 3 (●, control; △, MNP 2.4 g; ■, MNP 4.9 g; ▲, MNP 9.8 g).

The degradation follows the first-order kinetics:

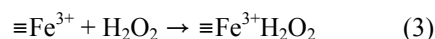
$$\ln (C/C_0) = -kt$$

Where  $k$  is the first-order rate constant,  $C_0$  is initial concentration of nitrobenzene and  $C$  is the concentration at time ' $t$ '. The rate constants were determined from the slope of liner plots of  $\ln (C_0/C)$  vs.  $t$ . The best removal efficiency of nitrobenzene was 51% at MNP 2.4 g. The nitrobenzene removal decreased with increased MNP mass 2.4g to 9.8 g. The degradation rates of nitrobenzene were 0.094  $\text{h}^{-1}$  (2.4 g) and 0.041  $\text{h}^{-1}$  (9.8 g). However, Kwan and Voelker (2003) reported that quantity of hydroxyl radical is proportional to the product of concentrations of surface area and  $\text{H}_2\text{O}_2$  [15].

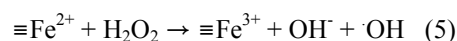
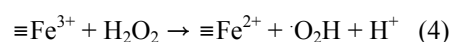
Walling and Goosen (1973) have suggested ferric ion catalyzed decomposition of  $\text{H}_2\text{O}_2$  (Eq. 1-2) [16].



Recently, Kwan and Voleker (2003) suggest a reasonable explanation for the mineral-catalyzed Fenton reaction on the surface (Eq. 3) [15];

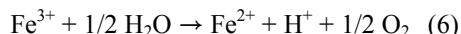


Following reaction occurred with  $\text{H}_2\text{O}_2$  sorbed to the iron mineral surface indicating the rate-limiting step (Eq. 4-5).



Surface area was a key factor of production of hydroxyl radical, however if excess quantity of MNP which was consisted of ferrous ion and ferric ion (mole ratio = 1 : 2) was presented,  $\text{H}_2\text{O}_2$  was sorbed to MNP (Eq. 3) and then reacted

with iron (ferric iron) mineral surface (Eq. 4). Thus, if excess quantity of MNP was existed, Eq. 4 might be predominant reaction. Therefore, most hydrogen peroxide was decomposed to perhydroxyl radical ( $\cdot\text{O}_2\text{H}$ ) (Eq. 4) or oxygen ( $\text{O}_2$ ) (Eq. 6).



The degradation of nitrobenzene with MNP/ $\text{H}_2\text{O}_2$  system at different  $\text{H}_2\text{O}_2$  concentrations was studied. Addition of  $\text{H}_2\text{O}_2$  from 0.25% (73.5 mM) - 1% (294 mM) at 2.4 g MNP increased the first-order rate constants for the degradation (0.035 to 0.101  $\text{h}^{-1}$ ) (Table 1). 1% (294 mM) of  $\text{H}_2\text{O}_2$  was the optimum concentrations for the degradation of nitrobenzene. At  $\text{H}_2\text{O}_2$  dosage above optimum level the decrease in removal rate is due to hydroxyl radical scavenging effect of  $\text{H}_2\text{O}_2$  [17]:

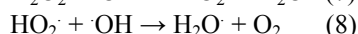
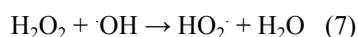


Table 1. Removal efficiency (%) of nitrobenzene (5mM) and first-order rate constants ( $k_{\text{obs}}$ ) for various MNP mass and concentration of  $\text{H}_2\text{O}_2$  at pH 3

$\text{H}_2\text{O}_2$ (%)		MNP mass(g)		
		2.4	4.9	9.8
0.25%	R.E. (%)	27	24	24
	$k$ ( $\text{h}^{-1}$ )	0.035	0.029	0.031
0.5%	R.E. (%)	51	36	29
	$k$ ( $\text{h}^{-1}$ )	0.094	0.054	0.041
1%	R.E. (%)	61	52	45
	$k$ ( $\text{h}^{-1}$ )	0.101	0.085	0.071
2%	R.E. (%)	53	52	53
	$k$ ( $\text{h}^{-1}$ )	0.094	0.089	0.087
3%	R.E. (%)	51	58	43
	$k$ ( $\text{h}^{-1}$ )	0.076	0.095	0.057

\* R.E.: Removal efficiency (%)

The effect of initial pH on the MNP/ $\text{H}_2\text{O}_2$  system degradation of nitrobenzene was investigated (Table 2). Increasing pH from 3 to 9, degradation of nitrobenzene was observed at only pH 3, its first-order rate constant was 0.094  $\text{h}^{-1}$  (Table 2). However, degradation of nitrobenzene at pH from 5 to 9 was negligible.

pH 3 was optimum for Fenton-like degradation of nitrobenzene (51%) (nitrobenzene 5 mM, MNP 2.4g, and  $\text{H}_2\text{O}_2$  0.5%). Khan and Watts (1996) reported that the most effective pH regime for the mineral-catalyzed oxidation was pH 3. It was attributed to increase soluble iron dissolution [18]. In addition, Walling and Goosen (1973) reported that ferric ion could be generated oxidants reacting with  $\text{H}_2\text{O}_2$  under low pH (Eq. 1-2) [15]. In further study, the effect of dissolved iron ion from MNP will be tested.

Table 2. Removal efficiency (%) of nitrobenzene (5 mM) and first-order rate constants ( $k_{\text{obs}}$ ) for various pH

MNP (g) $\text{H}_2\text{O}_2$ (%)		pH			
		3	5	7	9
2.4 g 0.5%	R.E. (%)	51	4	0	2
	$k$ ( $\text{h}^{-1}$ )	0.094	-	-	-

\* R.E.: Removal efficiency (%)

Consequently, the optimum conditions for degradation of nitrobenzene were MNP 2.4g and  $\text{H}_2\text{O}_2$  1% at pH 3. However, 1%  $\text{H}_2\text{O}_2$  was not appropriate to observe degradation of nitrobenzene varying other conditions for due to high concentration. The remainder experiments were conducted by 0.5%  $\text{H}_2\text{O}_2$ .

### 3.3. Compared with commercial magnetite ( $\text{Fe}_3\text{O}_4$ )

When commercial magnetite was used in the catalyzed  $\text{H}_2\text{O}_2$  system, it showed that removal efficiency of nitrobenzene using commercial magnetite/ $\text{H}_2\text{O}_2$  was less than MNP/ $\text{H}_2\text{O}_2$  system at the same condition. Comparing removal efficiencies between MNP and commercial magnetite at the same mass (2.4g) were 51% and 8% (Fig. 2). It might be explained that MNP was more efficient than commercial magnetite in case of injection same mass due to expansion of surface area.

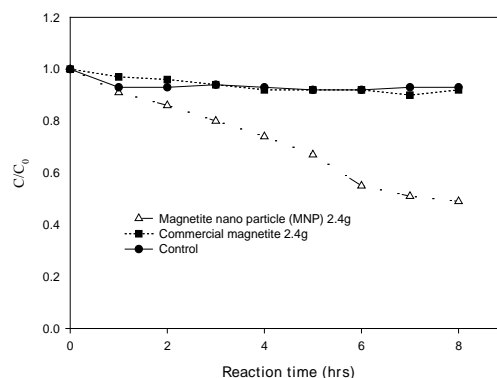


Fig. 2. Degradation of nitrobenzene (5mM) compare commercial magnetite ( $\text{Fe}_3\text{O}_4$ )/ $\text{H}_2\text{O}_2$  system with MNP/ $\text{H}_2\text{O}_2$  system with  $\text{H}_2\text{O}_2$  0.5% at pH 3 (●, control; □, commercial magnetite 2.4 g; △, MNP 2.4 g).

## IV. CONCLUSION

Magnetite nano particle (MNP) was synthesized by co-precipitation method. A Fenton-like reaction with a MNP catalyst was developed for the degradation of nitrobenzene. Nitrobenzene was used as probe compound for detecting hydroxyl radical ( $\cdot\text{OH}$ ). X-ray diffraction (XRD), high resolution transmission electron microscopy (HR-TEM), X-ray photoelectron spectra (XPS), and BET analysis were used to characterize MNP. HR-TEM image demonstrated that the diameter of MNP was approximately 6 nm. Moreover, BET analysis showed that surface area of MNP was much larger than commercial magnetite, approximately twenty-two fold.

Degradation of nitrobenzene using MNP/ $\text{H}_2\text{O}_2$  system could be affected by MNP mass, concentration of  $\text{H}_2\text{O}_2$ , and pH value. When effects of MNP mass and concentration of  $\text{H}_2\text{O}_2$  were tested, 2.4 g of MNP mass and 1% (294 mM) of  $\text{H}_2\text{O}_2$  were the optimum concentrations for the degradation of nitrobenzene at pH 3. Addition of  $\text{H}_2\text{O}_2$  from 0.25% (73.5 mM) - 1% (294 mM) at 2.4 g MNP increased the first-order rate constants for the degradation (0.035 to 0.101  $\text{h}^{-1}$ ). Further

increased of H<sub>2</sub>O<sub>2</sub> above 1% (294 mM) decreased the nitrobenzene degradation. pH 3 was optimum for Fenton-like degradation of nitrobenzene. Comparing removal efficiencies between MNP and commercial magnetite at the same mass (2.4g) were 51% and 8%. It might be explained that MNP was more efficient than commercial magnetite in case of injection same mass due to expansion of surface area.

#### ACKNOWLEDGEMENT

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