TREATMENT OF PHENOL CONTAINED IN WASTE WATER USING THE HETEROGENIZED FENTON SYSTEM

SeongBo Kim[†]

Environment & Energy Research Center, Korea Research Institute of Chemical Technology, P.O.Box 107, Yusung, Taejeon, 305-606, Korea

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Abstract : Fenton system using homogeneous iron catalyst is very powerful in the degradation of organic compounds, but has a disadvantage to remove Fe ions from water after wastewater treatment. Thus, iron catalyst was bounded to support such as inorganic and polymer materials. The PVP supporting iron catalyst showed a good catalytic performance in degradation of phenol contained in waste water and iron catalyst supported on SO_4^{2-} type PVP (KEX 511) showed the best catalytic performance. Also, reaction kinetic study was carried out in this system. Reaction constants on various catalysts was obtained from the pseudo first order equation. Reaction rate constants with the heterogenized $FeCl_2/PVP$ catalyst is a three-fold smaller than that of $FeCl_2$ catalyst.

Key Words : Phenol, Wastewater Treatment, Fenton system, Heterogenization, Iron Catalyst

INTRODUCTION

The degradation of aromatic pollutants present in waste water generated by industrial process has emerged as an important concern during last decades. Among these aromatic pollutants, the phenol is considered as one of the most toxic pollutants, harmful to human health and to water life, causing an increase in the demand of oxygen in water sources and giving out unpleasant taste and smell in drinking water even when it is found in very small quantities.

Several procedures have been developed to eliminate the organic contaminating compounds found in residual waters, e.g., adsorption processes, biological process, incineration through dry way and processes of wet oxidation. The wet oxidation is currently used and leads to the oxidation of the organic molecules to CO_2 and H_2O.
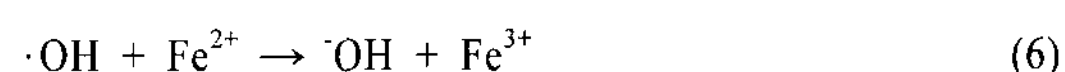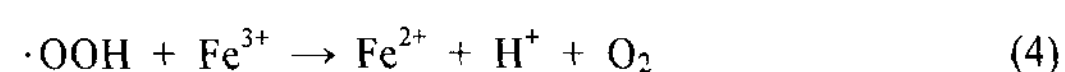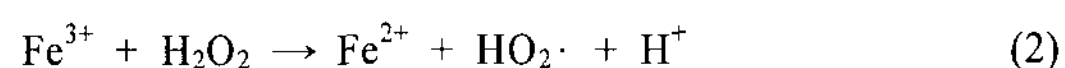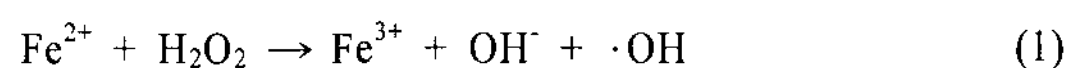
One alternative of special interest is the wet catalytic oxidation with hydrogen peroxide ·OH radicals and the use of their oxidizing capacity. These radicals are not very selective and attack the majority of the organic molecules causing their oxidation up to CO_2 and H_2O. One of the most important processes to generate hydroxyl(·OH) and perhydroxyl (HO_2·) radicals are achived with the Fenton system, which employs iron salts and hydrogen peroxide, Fe(II)-Fe(III)/H_2O_2.[1] Use of this system as an oxidizing agent for the treatment of residual water is very attractive since the iron is an abundant and non-toxic element, the hydrogen peroxide is not harmful to the environment and its decomposition products are oxygen and water, and does not cause additional contamination.

Haber and Weiss[2] proposed the mechanism for oxidation using Fenton reagents and Bard[3] modified this mechanism.

[†] Corresponding author
E-mail: sbkim@krict.re.kr
Tel: 042-860-7555, Fax: 042-860-7544

When the hydrogen peroxide and iron salts are combined, the hydrogen peroxide decomposes to produce the hydroxyl radical oxidant.[4,5]

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + \cdot OH \qquad (1)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2 \cdot + H^+ \qquad (2)$$

$$\cdot OH + H_2O_2 \rightarrow H_2O + \cdot OOH \qquad (3)$$

$$\cdot OOH + Fe^{3+} \rightarrow Fe^{2+} + H^+ + O_2 \qquad (4)$$

$$\cdot OOH + Fe^{2+} \rightarrow {}^-OOH + Fe^{3+} \qquad (5)$$

$$\cdot OH + Fe^{2+} \rightarrow {}^-OH + Fe^{3+} \qquad (6)$$

When ferrous salts are used, the hydroxyl radicals are produced immediately by the rapid reaction between ferrous ion and hydrogen peroxide (Equation 1, rate constant $k = 63.0 \ M^{-1}s^{-1}$).

With ferric salts, the hydroxyl radicals are produced by a two-stage process with the slow reaction between ferric ion and hydrogen peroxide (Equation 2, rate constant $k = 2.0 \ x \ 10^{-3} \ M^{-1}$) followed by the rapid reaction between the produced ferrous ion and additional hydrogen peroxide. The formed hydroxyl radical have a large electron affinity (136 kcal) and oxidizes most of organic compounds containing hydrogen.

. In a simplified general oxidation mechanisms for hydroxyl radicals and molecular oxygen oxidation suggested by Murphy[6], a hydroxy radical abstracts a hydrogen atom from the organic substrate, producing an organic radical $(R \cdot)$.

$$RH + \cdot OH \rightarrow R \cdot + H_2O \qquad (7)$$

Although the Fenton system is efficient, it presents several disadvantages for its satisfactory application at industrial level: the separation of metal in the reaction media solution at the end of the reaction increases the costs of the process and even so certain metal quantaties remain in the solution as a new pollutant. Nevertheless, these drawbacks can be overcome using a heterogeneous catalytic system.

With this purpose, we studied on the possibility of designing an iron catalyst bound to a solid support. In this paper, we report the results for reaction with phenol, including the effect of counter ion of iron on the efficiency of catalyst. Also, reaction kinetic study was carried out to compare with the each system. We selected the phenol as the standard material in this study, because of good candidates for chemical treatment.

EXPERIMENTAL

Analysis

Gas chromatography analysis was performed on Schimadzu GC-8APT employing a FID detector and a fused capilliary column (SE30). Infrared spectra were measured with Perkin Elmer FT-IR 1640 instrument (KBr pellet).

Preparation of the Catalysts

Preparation of Poly(4-vinyl)pyridine

Poly(4-vinyl)pyridine (PVP) was prepared in accordance with Boyes.[7]

A solution of anhydrous 4-vinyl-pyridine (35 mL) and divinyl benzene (20 mL) added in 250 mL three necked round bottom flask with thermometer and reflux condenser. Aqueous solution of hydroxy ethyl cellulose (1.29 g), 10% NaCl (12.9 g), 0.4% NaOH (1.52 g) and H_2O (129.35 mL) was added in organic soluton and reaction mixture was mixed under nitrogen stream. After mixing for 20 min at room temperature, the temperture was increased to 70 °C and maintained for 12 hr. White poly (4-vinyl) pyridine was obtained. The product was washed twice with hot water, dried at 80 °C for 5 hr. The yield was 94%.

Preparation of iron catalyst bound to various support[7]

To a solution of $FeCl_2$ (1.0 g) in methylene chloride (100 mL) was added to support material (5 g) and this mixture was vigorously stirred at 60 - 65 °C for 15 hr. After that, resultant was filtered and dried under vacuum. Final products were $FeCl_2$ catalysts bound to each supports.

Catalysts Tests

General procedures for degradation of phenol

$FeCl_2$ and $FeCl_2$/support (0.3 g) was added to an aqueous solution containing 10,000 ppm phenol (20 mL), followed by addition of 35% H_2O_2 (1 mL) and the resulting suspended solution was stirred for the reaction time. All the experiments were performed at acidic pH ≤ 3 in order to prevent the precipitation of Fe(III). pH and ionic strength were adjusted with acetic acid. During the course of the experiment, samples were corrected at various reaction times. After removal of the catalyst by filtration, the reaction mixture was treated with saturated sodium bisulfate to decompose unreacted hydrogen peroxide at 0-5°C. Products were analyzed by G.C..

RESULTS and DISCUSSION

Catalytic Activity on Various Iron Compounds

Activation of oxygen is the most important in an oxidation system. Many researchers tried to activate the oxygen. Two developed reaction types using iron catalyst are Fenton system and biomimetic system. Hydroxyl radical is known to the oxidant in Fenton type reaction and oxometal is in biomimetic type system. These two types of systems are depended on nature of solvent and property of catalyst. It is well known that the optimum pH range for homogeneous Fenton process is around 2.5-3.5. Therefore, the pH of the phenolic aqueous solution was controlled by addition of acetic acid.

Kim[8] reported that reactivity showed the different aspects for various counter-ions iron catalyst in the biomimetic oxidation of cyclohexane. Thus, effect of iron catalyst was studied on the degradation of phenol of Fenton type reaction. As shown in Figure 1, effect of iron catalyst in Fenton reaction showed very different aspects for biomimetic system. Although activation of iron compounds in biomimetic system showed the order of $FeCl_3$> $Fe(NO_3)_3$> $FeCl_2$>
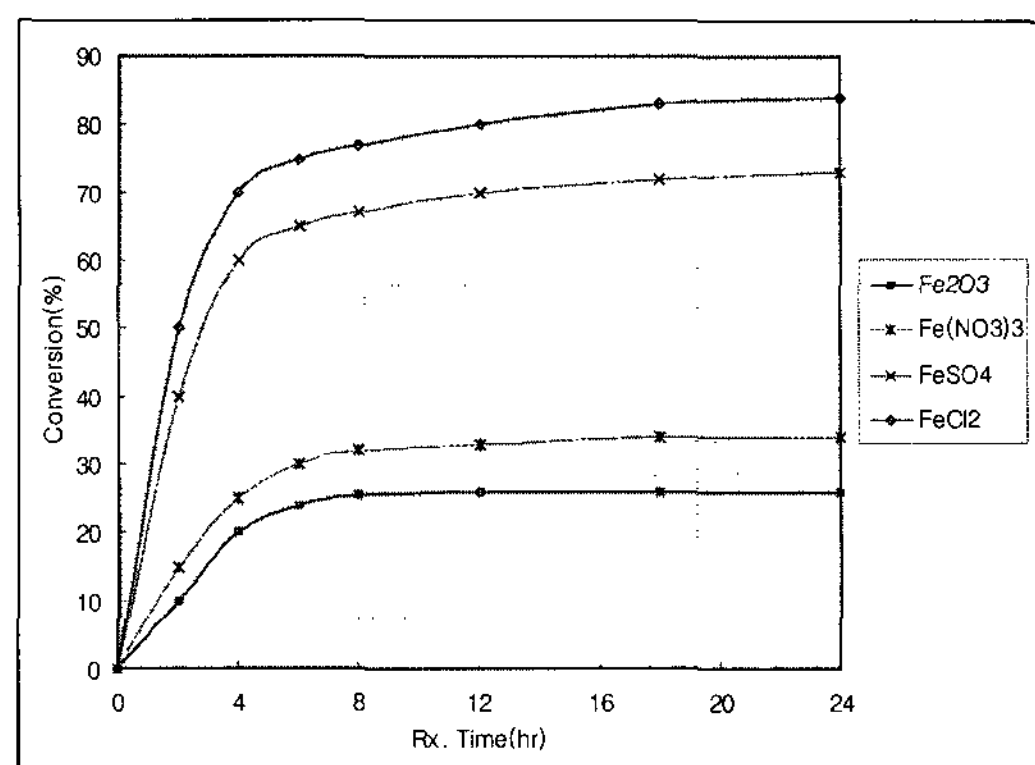

Figure 1. Effect of various catalysts in the decomposition of aqueous phenol solution. (Fe catal.: 0.005 mmole, H_2O_2: 0.7 mole%).

Fe_2O_3, but that order in degradation of phenol in Fenton system showed $FeCl_2$> $FeSO_4$> $Fe(NO_3)_3$ > Fe_2O_3. From these results, it seems the counter ions of iron compounds are the most important factor to determine the reactivity.

Heterogenization of $FeCl_2$ Catalyst on Support

Even though the homogeneous Fenton reaction is very powerful in the degradation of organic compounds, its disadvantage is the requirement to remove Fe ions from water after wastewater treatment. Thus, heterogenization using $FeCl_2$ was tried to overcome draw-back. Iron catalyst was bounded to various supports as shown in Scheme 1 and the loading strength of iron to support was tested and the results were shown in Table 1.

Table 1. Amounts of dissolved iron from iron supported catalyst for reaction time

Time (hr)	Amounts of dissolved iron (ppm)			
	Silica	Alumina	PVP	Zeolite
24	6.9	4.6	0.23	5.5
48	0.2	0.4	0	1.8
72	0.1	0.2	0	1.2

* Reaction condition
Phenol (0.25 g), Fe/support (1 gr), H_2O (25 mL)

It should be noticed that for a heterogeneous catalyst used for Fenton reaction, besides its catalytic activity, another important property is

its long term stability, which is directly associated with the Fe leaching at a low solution pH. Therefore, to keep stability, a heterogeneous catalyst containing Fe with a negligible Fe leaching is a must. Especially, Fe/PVP-supported catalyst among various catalysts showed the most excellent result. In the Fe/PVP catalyst, the stretching vibration based on the pyridinium ring was observed around 1,645 cm^{-1} and -CH stretching vibration was observed at 3,000 -3,100cm^{-1}.
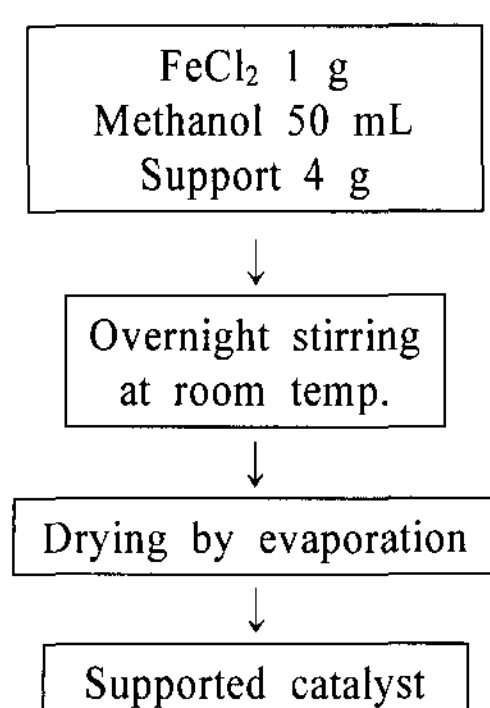
Scheme 1. Preparation of the supported Fe catalyst

Degradation of Phenol by Fe/PVP Catalyst System

$FeCl_2$ was supported on various polyvinyl-pyridines as the method described in Scheme 1. Heterogenized catalyst suppoted on KEX-212 PVP was tested for the degradation of phenol. Heterogenized Fe/PVP showed the lower activity than the unsupported catalyst $FeCl_2$. Catalytic activity represented the similar result at three fold hydrogen peroxide solution. Also, reuse of Fe/PVP catalyst recovered by filtration after reaction showed almost same results as that of the fresh catalyst.

Table 2. Results using the PVP as support in degradation of phenol contained in aqueous solution

Support	Addition of H_2O_2 (mol%)	Conversion(%)
FeCl2	1	100
Fe/PVP(KEX 212)	1	70.0
Fe/PVP(KEX 212)	2	85.5
Fe/PVP(KEX 212)	3	98.8

* Reaction condition
  Rx.Time (3hr), Phenol (10,000 ppm), Fe compound (0.005 mmole)

Also, heterogenized Fe catalysts were prepared using various types of polyvinyl pyridine and their physical properties of prepared catalysts were as Table 3.

Heterogenized Fe catalysts were used to the degradation of phenol. As shown in Table 4, conversion showed the maximum value in the case of Fe/PVP(KEX 202) and Fe/PVP (KEX 511) preparing with SO_4^{2-} type PVP.

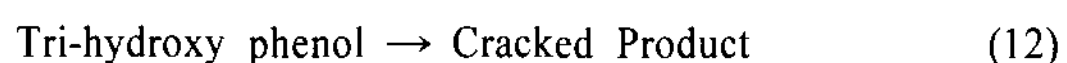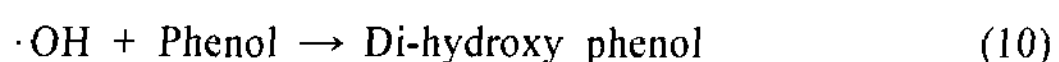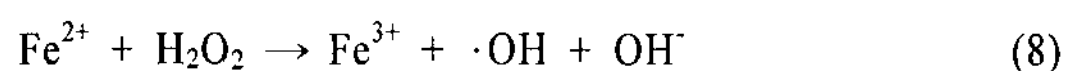Table 4. Results on the degradation of phenol using various $FeCl_2$/PVP

Catalyst	Conversion (%)
Fe/PVP (KEX 316)	90.52
Fe/PVP (KEX 212)	98.78
Fe/PVP (KRICT)	99.21
Fe/PVP (KEX 202)	99.23
Fe/PVP (KEX 511)	-100

* Reaction condition
  Rx. Time (3 hr), Phenol (10,000 ppm), Fe compounds (0.005 mmole), H_2O_2 (3.0 mmole)

REACTION KINETIC STUDY

From these results, it was evident that reaction rate was largely related to the decomposition of hydrogen peroxide. Decomposition of phenol can be represented as the Scheme 2.

Table 3. Specification of various polyvinyl pyridine used in degradation of phenol

PVP	KEX*-316	KEX*-212	KEX*-202	KEX*-511	KRICT**
Type	-	-	SO_4^{2-}	SO_4^{2-}	-
Bulk density	0.60	0.75	0.64	0.68	0.65
Water content	0.5-2.0	32-38	35-40	38-41	0.5-1.0
Particle size (mesh)	60	16-50	10-50	10-50	60-80

* KEX: Koei chem Co. product
** KRICT: prepared in our laboratory

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \cdot OH + OH^- \qquad (8)$$

$$\cdot OH + Fe^{2+} \rightarrow Fe^{3+} + OH^- \qquad (9)$$

$$\cdot OH + Phenol \rightarrow Di\text{-}hydroxy\ phenol \qquad (10)$$

$$\cdot OH + Di\text{-}hydroxy\ phenol \rightarrow Tri\text{-}hydroxy\ phenol \qquad (11)$$

$$Tri\text{-}hydroxy\ phenol \rightarrow Cracked\ Product \qquad (12)$$

Scheme 2. Reaction mechanism in the degradation of phenol.

If we assume a steady state concentration for the ·OH radical species, the rate equation can be expressed as the pseudo first order with respect to the substrate (phenol) as shown in following equation.[9]

$$-\frac{d[phenol]}{dt} = k[phenol]\,[\cdot OH]$$

$$-r_A = k\,[phenol]$$

$$-\ln\left[\frac{C_A}{C_{Ao}}\right] = kt\ ;\ 1st\ order\ reaction$$

The pseudo first order rate constant (k_{obs}) were determined from the slopes of regression lines in the ln $[C_A]/[C_A]_0$ vs time plots.

As shown in Table 5, the reaction rate constants with the heterogenized $FeCl_2$/PVP catalyst is three fold smaller than the unsupported $FeCl_2$ catalyst.

Table 5. Reaction rate constants for various iron catalysts in the Fenton reaction of phenol

Catalyst	$k(hr^{-1})$
$FeCl_2$	8.5
$FeSO_4$	7.9
FeF_3	2.1
Fe/PVP (KRICT)	2.9

Reaction condition
Temperature: 15°C, Phenol: 10,000 ppm
Fe compound: 0.1 mmole, H_2O_2: 50 mmole, H_2O: 100 mL

CONCLUSIONS

Heterogenization of iron compounds on various supports was tried for the degradation of phenol using hydrogen peroxide. $FeCl_2$ showed a good acitivity among various iron compounds and was supported on various supports such as inorganic and polymer material. Iron compound supported on the PVP was found to be an efficient catalyst on the degradation of phenol usimg aqueous hydrogen peroxide. $FeCl_2$ supported on poly(4-vinyl)pyridines was less active than unsupported $FeCl_2$. But, recovered catalyst by filtration after the reactions showed almost the same results as those by the original catalysts.

Also, reaction rate constants with the heterogenized $FeCl_2$/PVP catalyst is a three fold smaller than that of unsupported $FeCl_2$ catalyst.

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