

# Removal of Ethanolamine (ETA) and COD Produced in a Power Plant Wastewater by Nano-ZVI (Zerovalent Iron) and Hydrogen Peroxide (H<sub>2</sub>O<sub>2</sub>)

Jun Hee Lee, So Yeon Park, and Byoung Ho Lee

**Abstract**—Ethanolamine (C<sub>2</sub>H<sub>7</sub>NO, ETA) is used in a power plant to prevent plumbing system from corrosion by maintaining pH at a certain level. Water flowing inside the plumbing system should periodically be cleaned using ion exchange resin. On the way of regeneration of the resin by sulfuric acid, ethanolamine wastewater is produced.

Removal mechanism of ETA has not been well established because it is very much resistant material in biodegradability, and even in chemical degradation. In this research high concentration of ETA ranging 5,000 ~ 9,000mg/l was successfully removed closely down to zero level using nano sized zerovalent iron powder (nZVI) and appropriate amount of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>). Organic material of high COD concentration (6,000 ~ 13,500mg/l) was also contained in the wastewater along with high concentration of ETA. COD of the wastewater was simultaneously reduced down to 2,500 ~ 6,000mg/l along with ETA when catalytic oxidation of nZVI with hydrogen peroxide takes place, which can be removed further in a biological system of the following process. Removal rate of ETA showed highest at pH 3.

Wastewater produced in a power plant containing high concentrations of ETA and COD could be successfully treated up to the level, from which biological process can be applied for direct discharge to the natural water body.

**Index Terms**—Ethanolamine (ETA), hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), nZVI (nano Zerovalent iron), nuclear power plant, COD.

## I. INTRODUCTION

pH is normally controlled to prevent the water flow line from corrosion in industries where water is used in the circulating system[1]-[3]. To maintain pH at a certain level where chemical potential against corrosion is minimized, various materials have been used such as NH<sub>3</sub>, C<sub>2</sub>H<sub>7</sub>NO (ETA), and C<sub>4</sub>H<sub>9</sub>NO [4]. NH<sub>3</sub> has been widely used for pH control in water pipe lines due to its easier availability. However ETA substituted NH<sub>3</sub> as a pH control agent because NH<sub>3</sub> is highly volatile at higher pH range, thereafter ETA has been used since 2001 in many power plants in Korea[4], [5]. However ETA is known to be highly refractory material in biodegradability and even in chemical oxidation processes [5]. Physicochemical properties of ETA are presented in Table I.

ETA is very stable material at high temperature such that a boiling point is 170.8 °C as shown in Table I. pKa is also formed at high pH 9.496. These two characteristics with the other ones in Table I let ETA be a good pH control agent in the pipe line where hot water or steam flows [6]. The hot water flowing pipe line in a closed system of a power plant is to be cleaned periodically using ion exchange resin [7], which produces ETA wastewater on the way of regeneration of ion exchange resin.

Wastewater produced from a power plant contains high concentrations of ETA (6,000 ~ 9,000mg/l) and COD (6,000 ~ 13,500 mg/L) [8]. Many investigators have tried various technologies to remove ETA [8]-[11] including biodegradation and AOPs.

TABLE I: PHYSICO-CHEMICAL PROPERTIES OF ETA [9]

Molecular weight (g)	61.08
Density	1.0180 (20°C)
Melting/Boiling point (°C)	10.5/170.8
Surface tension (mN/m)	48.3175 (20°C)
Viscosity (mN.S/m <sup>2</sup> )	21.1 (25°C)
Dielectric constant	31.94 (20°C)
Dipole moment (3.3356 x 10 <sup>-3</sup> C.m)	2.27
Conductivity (10 <sup>-4</sup> m <sup>2</sup> .S/mole)	47.2
Diffusivity (10 <sup>-5</sup> cm <sup>2</sup> /s)	1.124
Relative Volatility (25°C)	10 <sup>-2.1</sup>
pKa (25°C)	9.496

Hyun, Rhee, Kwon, Kim, and Cha found that mono ETA could be removed by activated sludge [9]. They could remove 1,000mg/l of ETA in 5days, and 2,000mg/l in 9days [9]. Fredriksen, and Jens tried to figure out the oxidative products of ETA [11]. Vevelstad, Grimstvedt, Elnan, Silva, and Svendsen investigated the effects of oxygen and temperature on ETA degradation. With increasing oxygen concentration and temperature, degradation rate of ETA was increased [12]. In their findings, NH<sub>3</sub>, NO<sup>2-</sup>, and NO<sup>3-</sup> are among the final oxidative products of ETA [11], [12], which should be further removed in the following biological treatment. Fractions of nitrogen produced from ETA could be up to 78% [9].

Even with results of invaluable investigations by many researchers, their works have some limitations to be applied in a real wastewater treatment plant because their works have been performed in Lab scale, and for a pure ETA solution. Wastewater produced in a power plant contains very high concentrations of ETA unlike the ones which above mentioned researchers used, and other complex materials such as high concentration of COD material, and other toxic

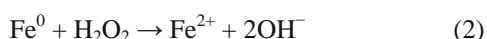
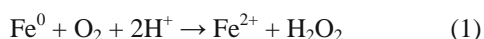
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material of hydrazine (N<sub>2</sub>H<sub>4</sub>). Hydrazine is used to remove oxygen in water, which suppresses corrosion in water flowing pipe line. Hydrazine is toxic to human and environment, as well as nitrification microorganisms [13]. OH\* radical has been used to remove chemical toxic pollutants [14], [15]. Sun suggested that application of nZVI was a good technology in decolorization of cationic dye methylene blue [14]. Bremner investigated the degradation of the model pollutant phenol with hydroxyl radicals generated from zerovalent iron and hydrogen peroxide [15]. OH\* radical is assumed to be generated by the following (1) ~ (3) processes [8].



Due to highly refractory, toxic, and complexity of power plant wastewater, treatment processes of ETA have not been clearly established yet even though ETA is not allowed to discharge into natural water body at all by law [5], [6].

In this paper, removal mechanisms of ETA contained in power plant wastewater have been suggested using nZVI and H<sub>2</sub>O<sub>2</sub>. Oxidation potential of highly reactive OH\* radical is used in removing ETA, COD, and other material such as hydrazine.

## II. EXPERIMENTAL METHODS

### A. ETA Wastewater Sample

Wastewater produced in a nuclear power plant in Korea was collected under strict surveillance of the authority. Taken sample was stored in polyethylene vessel. Concentrations of ETA, and COD of the wastewater sample were measured according to standard methods. COD was estimated by the standard dichromate method ASTM D1252 (ASTM D1252-06(2012)). ETA was analyzed using ion chromatography (DIONEX ICS-5000 DP) equipped with CG-12A (guard column) and CS-12A (analytical column).

### B. nZVI (Nano Size Zerovalent Iron)

nZVI having 99.8% purity were purchased from DittoTechnology Co., Ltd. They exhibited an average particle size of 70 nm. nZVI sample was stored not to be exposed to atmospheric air. And bottle of nZVI was open, and appropriate amounts of samples were taken just before it was used.

### C. Raw Water Characteristics

Raw water characteristics were varied with some range, which is shown in Table II.

	Unit	Concentrations
ETA	mg/l	5,000 ~ 9,000
COD	mg/l	6,000 ~ 13,500
T-N (Total Nitrogen)	mg/l	2,000 ~ 3,500

pH range of the wastewater was 0 ~ 1.5.

After screening test, experiments have been performed at pH 3, which is turned out to be the optimum pH for removing ETA in wastewater. Experimental setup is shown in Fig. 1. (a) represents raw wastewater, (b) is after pH adjustment to 3, (c) is after nZVI addition, and (d) is shown after H<sub>2</sub>O<sub>2</sub> addition. Salinity of wastewater was about 4 ~ 6‰.

After pH adjustment to 3, CaSO<sub>4</sub> (gypsum) was settled on the bottom of the vessel as it may be seen in (b) of Fig. 1. As soon as nZVI is added in the wastewater, vigorous oxidation reaction of nZVI took place like (c). After addition of H<sub>2</sub>O<sub>2</sub> in the nZVI added sample, even more vigorous reaction took place like (d). The reactor vessel was placed for 24 hours for sufficient reaction period.

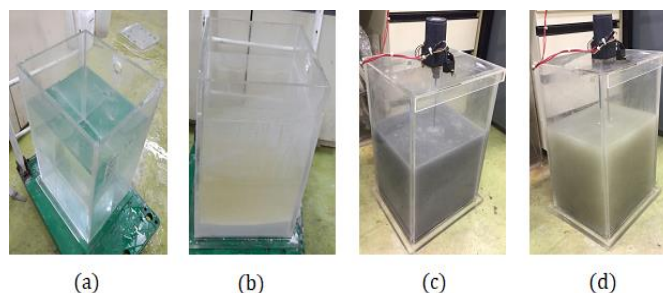


Fig. 1 Experimental set up.

## III. RESULTS AND DISCUSSION

Due to relatively easier measurement, COD was used as an index parameter in the study. After finding the optimum condition of a catalytic oxidation of nZVI and H<sub>2</sub>O<sub>2</sub> in removing COD, ETA was measured at the final stage assuming that ETA is removed highest at the same optimum condition.

### A. Screening Test for Finding an Optimum pH

Experiments have been performed in various pHs to figure out the optimum pH for the catalytic oxidation of nZVI and H<sub>2</sub>O<sub>2</sub>. And the optimum pH was decided at which COD removal was highest. Lee et al. reported the optimal pH in catalytic oxidation of nZVI and H<sub>2</sub>O<sub>2</sub> was 3 for maximum COD removal [8]. In screening test, Fig. 2 shows that the lowest COD concentration was obtained at pH 3 after treated by nZVI and H<sub>2</sub>O<sub>2</sub> oxidation, so that it was decided that the optimum pH was 3. Otherwise specified experiments have been done at pH 3 in the study. Original pH of wastewater was close to zero. COD concentration of power plant wastewater was 9,500mg/l.

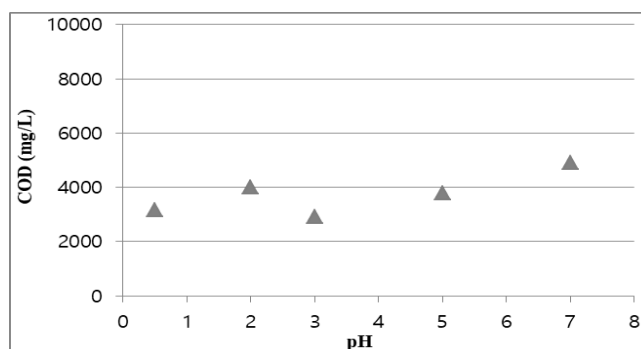


Fig. 2. Screening test for finding optimum pH on COD removal (nZVI (10mg/L) + H<sub>2</sub>O<sub>2</sub> (50ml/L)).

**B. Effect of Hydrogen Peroxide (H<sub>2</sub>O<sub>2</sub>) Concentration**

Effect of H<sub>2</sub>O<sub>2</sub> concentration was investigated in the oxidation. COD removal was increased with H<sub>2</sub>O<sub>2</sub> concentration up to about 150ml/L as shown in Fig. 3. 35% of H<sub>2</sub>O<sub>2</sub> was used in the test. H<sub>2</sub>O<sub>2</sub> used in the experiment was manufactured in Taegwang co. LTD, Korea. COD was removed down to 2,800mg/l from 9,500mg/l by nZVI 1g/L, and 150ml/L of H<sub>2</sub>O<sub>2</sub> for about 24 hours. At the same condition, COD was removed to 3,400mg/l by 50ml/L of H<sub>2</sub>O<sub>2</sub>. Both concentrations of COD may be removed by the following biological treatment process up to the dischargeable level to a natural water body. 50ml/L of H<sub>2</sub>O<sub>2</sub> may be an optimum dose in economic point of view.

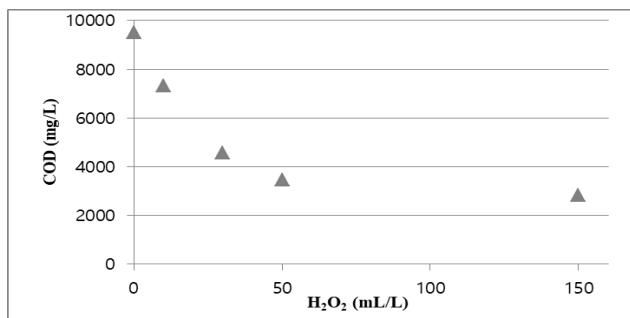


Fig. 3. Effect of H<sub>2</sub>O<sub>2</sub> concentration on ETA degradation (nZVI 1g/L, pH 3).

**C. Effect of Nano Zerovalent Iron (nZVI) Dose**

Effect of nZVI concentration on COD removal by the oxidation with H<sub>2</sub>O<sub>2</sub> was investigated. As shown in Fig. 4, nZVI concentration was not sensitive as much as H<sub>2</sub>O<sub>2</sub> does. It is believed that nZVI acts as catalyst in the oxidation reaction [15], so that if concentration of nZVI is over in some level, nZVI effect on COD removal was not increased very much with increasing its concentration. Optimum dose of nZVI was revealed to be 1g/L in the experiment like in Fig. 4. From the experiment result, nano ZVI was used 1g/L throughout the remaining experiment.

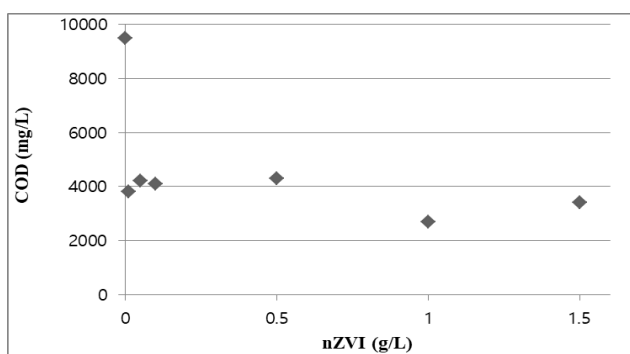


Fig. 4. Effect of nano zerovalent iron (nZVI) concentration (H<sub>2</sub>O<sub>2</sub> 50ml/L, pH 3).

**D. Effect of Reaction Time**

Oxidation reaction of nZVI and H<sub>2</sub>O<sub>2</sub> has completed in about 10 hours as shown in Fig. 5. Economic reaction time may be about 5 hours. In 5 hours, most of COD contained in wastewater was reduced to its minimum level.

**E. ETA Removal**

About 7,500mg/l of ETA was removed 99% to 51mg/L by catalytic oxidation of nZVI with H<sub>2</sub>O<sub>2</sub>. ETA was effectively

removed if nZVI was used with H<sub>2</sub>O<sub>2</sub> as it can be seen in Table III. Even if ETA was known to be very much refractory material in power plant wastewater [8], it was proved that nZVI catalytic oxidation with H<sub>2</sub>O<sub>2</sub> could be a solution for direct discharge of the treated water to the natural water body after following biological processes.

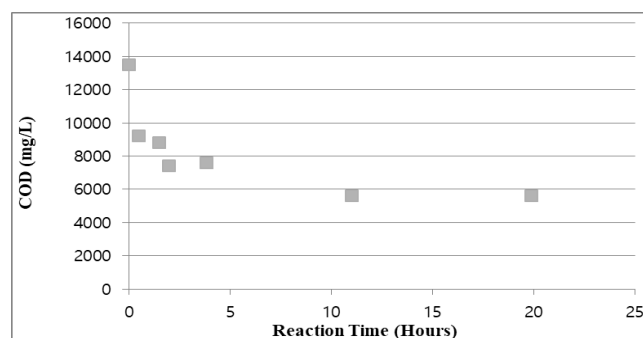


Fig. 5. Effect of reaction time on oxidation reaction (nZVI = 1 g/L, H<sub>2</sub>O<sub>2</sub> = 50 ml/L, pH = 3).

TABLE III: ETA REMOVAL BY NZVI AND H<sub>2</sub>O<sub>2</sub> OXIDATION

Item	ETA (mg/L)	Removal Rate (%)
Wastewater	7,465	-
nZVI added	51	99.3

(nZVI = 1.5 g/L, H<sub>2</sub>O<sub>2</sub> = 50 ml/L, pH = 3, Reaction time = 24 hrs)

**IV. CONCLUSION**

Wastewater containing high concentrations of ETA and COD is produced in power plant. ETA is regulated not to be discharged to the natural water body at all. Due to its highly refractory characteristics, mechanisms to treat ETA have not been clearly figured out. In this paper, wastewater containing ETA taken from a nuclear power plant was treated using nZVI and H<sub>2</sub>O<sub>2</sub>. 9,800mg/l of ETA was removed down to about below 290mg/l by the catalytic oxidation of nZVI (1g/L) with H<sub>2</sub>O<sub>2</sub> (150ml/L). COD was also removed from 13,500mg/l to 6,100mg/l by the same oxidation reaction. It was found that ETA wastewater produced in power plants could be treated successfully by nZVI catalytic oxidation with H<sub>2</sub>O<sub>2</sub>.

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