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Degradation of acetone and isopropylalcohol in electronic wastewater using Fe- and Al-immobilized catalysts

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HIGHLIGHTS

- Preparation and characterization of Fe/Al immobilized catalyst.
- Oxidation of low-molecular-weight organic compounds in electronic wastewater.
- Optimal selection and mixture ratio of metals.
- Optimization of operational factors such as pH, H_2O_2 concentration, the amounts of catalysts and various acids.
- Long-term life time of catalyst.

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ABSTRACT

This paper describes a novel technology for the reuse of electronic wastewater by advanced oxidation process (AOP) using an Fe/Al-immobilized catalyst. The metal catalyst in the AOP improved the oxidation of low-molecular-weight organic compounds, such as acetone and isopropylalcohol, in electronic wastewater. The removal efficiency of acetone and isopropylalcohol were 78.5% and 99.9%, respectively. The optimal combination of metal catalysts in the oxidation of acetone was Fe and Al—10% Al in various Fe/Al catalysts. The optimal pH was less than 3, and the proper addition of H_2O_2 and catalysts was an important factor in the AOP. Using optimal metal catalysts, significant amounts of organic compounds were removed from raw electronic wastewater using a continuous flow reactor. We conclude that an AOP with a metal catalyst removes low-molecular-weight organic compounds (91% removal efficiency of isopropylalcohol) and can be implemented as a wastewater treatment and reuse system.

1. Introduction

Electronics manufacturers must innovate and produce at tremendous speed and volume to survive technology cycles. Increasing capacity, reducing costs, and meeting the demand for more complex products require innovative technologies for water reuse as a water-consumable industry [1,2]. With the recent growth of the thin-film transistor-liquid crystal display (TFT-LCD) and organic light-emitting diode (OLED) industries in Korea, water consumption has risen significantly, raising the issue of maintaining sufficient water supplies by reducing and reusing wastewater. However, low-molecular-weight organic compounds, such as acetone and isopropylalcohol, exist in the wastewater that is discharged by electronics industries. Because such organics are not removed completely through reverse osmosis, they limit the reuse of electronic wastewater.

Advanced oxidation processes (AOPs) are used to destroy organic compounds in water by generating hydroxyl radicals ($^{\cdot}OH$) that have much stronger oxidation potentials than agents that are used in conventional oxidation processes. AOPs have been examined with regard to high-energy oxidants, such as ozone and H_2O_2, and photons that generate highly reactive intermediates.

Methods of generating $^{\cdot}OH$ radicals can be classified by Fenton oxidation [3,4], UV oxidation [5,6] and metal-catalyzed oxidation [7,8]. Fenton oxidation requires the continuous addition of ferric chloride and secondary treatment of the sludge that is generated as a byproduct [9]. Also, UV oxidation fails to oxidize many of the persistent organic pollutants into small molecules, such as H_2O and CO_2, and its operating costs are relatively high [10]. These drawbacks can be overcome with heterogeneous catalysts [10–12], the use of which is typically called heterogeneous Fenton oxidation. Transition metals, primarily iron, are used as the active phase. Due to differences in catalytic methods, Fenton's reaction is distinct from other metal- and metal oxide-catalyzed oxidation reactions.

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Iron and copper ions catalyze the dissociation of hydrogen peroxide to ·OH radical and hydroxide ion (Eq. (1)) or to hydrogen ion and hydroperoxy radical (Eq. (2)) [13]:

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

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + H^+ + HOO^{\cdot} \quad (2)$$

Homogeneous Fenton's reaction is used in industrial wastewater purification [13]. Several studies support the combination of Fenton's catalyst and various carriers, such as brick grain [14], MgO [15], SiO_2 [16], and zeolite [13]. Further, copper- and iron-containing pillared clays are used as Fenton's catalysts [9,17].

In this study, activated carbon, which increases the active surface area of a catalyst due to its large specific surface area, was used as a carrier. To maximize the oxidation by catalysts, the proper combination of metals and their ratios were determined in screens. Operational factors, such as pH, hydrogen peroxide concentration, and the amounts of catalysts and various acids, were examined in the degradation of isopropylalcohol using the optimal combination of metals. A continuous upflow reactor was operated using raw electronic wastewater to evaluate the application potential of an Fe/Al catalyst.

2. Materials and methods

2.1. Preparation of catalyst

The metal catalyst was prepared by incipient wetness impregnation of activated carbon (SLS-100, 8–30 mesh, Samchully Activated Carbon Co., Korea) with an aqueous solution of metal nitrate—for example, $Fe(NO_3)_3{\cdot}9H_2O$ (SHOWA) and $Al(NO_3)_3{\cdot}9H_2O$ (JUNSEI).

The catalyst was prepared as follows: (i) Nitrate-type transition metals (Table 1) were added to 200 mL distilled water. (ii) 50 g of activated carbon was added to a transition metal solution and mixed for 20 min using an ultrasonic device (DH.WUC.D22H, Daehan Science, Korea), during which the transition metals attached to the pores of the activated carbon. (iii) In the mixed solution of metal and activated carbon, the supernatant was removed, and the mixture of residual activated carbon and transition metals was rinsed five times with distilled water to remove the remaining transition metal solution that did not attach to the activated carbon. (iv) The moisture in the mixture of activated carbons and transition metals was removed by drying the mixture at 60 °C for 12 h in an oven (WOF-155, Daehan Science, Korea). (v) The mixture was calcinated at 200 °C for 3 h at 1 °C/min using a sintering furnace (YSE-3000, Youl San, Korea) to remove nitrates.

After the catalysts were synthesized, the residual metal that adsorbed onto the activated carbon or was not firmly immobilized on the surface of activated carbon was washed from the catalysts using pH 3 solution. The wash steps were repeated until the concentrations of Fe and Al were less than 0.05 mg/L. The amount of extracted active metals was approximately 55% of the initial metal content – i.e., approximately 45% of active metal was solidly attached to the activated carbon.

Table 2
Removal rates of acetone at various ratios of Fe and Al.

Sample	Fe (g)	Al (g)	Al/(Fe + Al) (%)	Removal rate of acetone (%)
1	0.295	0.015	5	57.6
2	0.276	0.034	11	71.1
3	0.264	0.047	15	47.5
4	0.248	0.062	20	53.9
5	0.217	0.093	30	54.9
6	0.186	0.124	40	51.0
7	0.155	0.155	50	41.8
8	0.093	0.217	70	44.4
9	0.034	0.277	89	37.8
Activated carbon				20.5

2.2. Oxidative reaction by catalyst

Batch experiments were performed to examine the efficiency of active metals in degrading low-molecular-weight volatile compounds using 250-mL glass stopped bottles. The oxidative capacity of the synthesized catalyst using 1 or 2 of 7 possible metals (Fe, Cu, Co, Mn, Al, Ce, and V) was evaluated under the following conditions: (i) initial pH of 3.0 using nitric acid (Showa, Japan); (ii) 250 mg of catalyst, based on preliminary experiments; (iii) an initial target compound concentration of 300 μg/L acetone or 400 μg/L isopropylalcohol; and (iv) 5 mg/L of H_2O_2, which was the appropriate stoichiometric amount to degrade all acetone to CO_2 and H_2O. These experiments were performed at 25 ± 1 °C. Also, in a control experiment, activated carbon (SLS-100) was added to the same solution, and the acetone that was removed only by the carrier was measured.

The removal rates of acetone and isopropylalcohol by the Fe/Al catalyst were determined at various pHs, H_2O_2 concentrations, catalyst doses, and acids. The catalyst that was used in these batch experiments was Sample 3 in Table 2. The pH varied from 2.7 to 5.0, and the dose of the catalyst and H_2O_2 was fixed at 250 mg and 5 mg/L, respectively. The pH was controlled with HCl or NaOH. H_2O_2 concentration ranged from 1.5 to 10 mg/L (1.5, 3.0, 4.5, and 10.0 mg/L), and the catalyst and initial pH were fixed at 250 mg and 3.0, respectively. The catalyst doses were 0.1, 0.2, 0.3, and 0.4, and the H_2O_2 concentration and pH were fixed at 5 mg/L and 3.0, respectively. Finally, nitric acid, hydrochloric acid, perchloric acid, sulfuric acid, and phosphoric acid were used to adjust the solution's pH to 3, and the catalyst and H_2O_2 were fixed at 250 mg and 5 mg/L, respectively.

2.3. Continuous flow column test

The raw electronic wastewater was collected from a cleaning process in an OLED manufacturing system. The main components of the raw wastewater were isopropylalcohol, tetra-methyl ammonium hydroxide (TMAH), and monoethanolamine (MEA). The ini-

Table 1
Removal rates of acetone with various combinations of metals.

Sample	Content of active metal (wt.%)	Removal rate of acetone (%)	Sample	Content of active metal (wt.%)	Removal rate of acetone (%)
Fe	1.03	41.7	Fe + Al	1.01/0.44	68.6
Cu	1.12	37.5	Fe + Co	0.63/0.04	50.4
Co	0.43	25.8	Fe + Cu	0.43/0.23	53.3
Mn	0.41	33.9	Fe + Mn	0.61/0.01	48.3
Al	0.40	21.6	Fe + V	0.34/0.11	36.5