Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2014.895783

54 (2015) 1038–1043
April

Taylor & Francis
Taylor & Francis Group

Treatment and reuse of electronic wastewater using activated carbon based solid-phase advanced oxidation process

Jinwook Chung[a], Minseok Kim[b], So-Ryong Chae[c], Jong-Oh Kim[d,*]

[a]*Samsung Engineering Co. Ltd, R&D Center 415-10 Woncheon-Dong, Youngtong-Gu, Suwon, Gyeonggi-Do, Republic of Korea*
[b]*Korean Minjok Leadership Academy, Bongwha-ro 800, Anheung-myeon, Hoengseong-gun, Gangwon-do 225-823, Republic of Korea*
[c]*School of Chemical and Biomolecular Engineering, The University of Sydney, Sydney, NSW 2006, Australia*
[d]*Department of Civil and Environmental Engineering, Hanyang University, 222 Wangsimni-ro, Seongdong-gu, Seoul 133-791, Republic of Korea, email: jokim@gwnu.ac.kr*

Received 27 November 2013; Accepted 13 February 2014

ABSTRACT

Herein, the efficacy of catalysts for solid-phase advanced oxidation processes is evaluated in the removal of low-molecular-weight organics from semiconductor wastewater. To investigate and compare the removal efficiency, experiments were conducted by changing the mixing ratio of a catalyst with activated carbon. As a result, the optimal (Cu + Fe) and (Fe + Al) ratios for the removal of acetone and isopropyl alcohol (IPA) were 8:2 and 9:1, respectively, with activated carbon at pH 3. Over 70% acetone removal and almost 100% IPA removal were achieved under acidic conditions. The removal efficiency of both compounds could be maximized using a H_2O_2 concentration of 4.5 mg/L. Solid-phase advanced oxidation processes were believed to be effective methods to overcome the low adsorbability of organics present in electronic wastewater on activated carbon.

Keywords: Acetone; Electronics wastewater; Isopropyl alcohol; Solid-phase advanced oxidation process

1. Introduction

Acetone and isopropylalcohol (IPA) are widely used for the production of liquid crystal displays and semiconductors in the electronics industry. IPA is also used as a dilution agent in the paint industry and as an antifreeze agent in gasoline. However, reports indicate that acetone and IPA exhibit estrogenic activity and alter metabolism kinetics, induce DNA damage, and result in chromosomal aberrations [1]. Considering the widespread application of IPA and the increasing demand for wastewater reclamation, economical and effective techniques for wastewater treatment and reuse are urgently required. The high water solubility and low molecular weight of IPA result in its very low adsorption on activated carbon [2] and incomplete removal by membrane techniques such as reverse osmosis (RO). For example, application of biological treatment to organic compound-containing wastewater discharged from semiconductor manufacturing resulted in the removal of the majority of these com-

---

*Corresponding author.

Presented at the 6th International Conference on the "Challenges in Environmental Science and Engineering" (CESE-2013), 29 October–November 2013, Daegu, Korea

pounds; the remaining substances were readily removed in secondary processes such as RO. However, the RO-treated water contained a small quantity of volatile low-molecular-weight compounds such as acetone and IPA, which adversely affected the water quality for the final use as ultrapure water. As an alternative method, advanced oxidation processes (AOPs) may be more appropriate than adsorption for the removal of compounds with low adsorbability. AOPs are characterized by the production of $OH^{\cdot}$ radicals, which are potent (2.8 V) and unselective oxidants that can oxidize and mineralize organic pollutants in water, yielding CO_2 and other inorganic compounds [3]. Hydroxyl radicals can be generated from H_2O_2 by using activated carbon and Fenton's reagent, among other decomposition catalysts [4–6].

Fenton's reagent utilizes Fe ions as a homogeneous catalyst, producing hydroxyl and perhydroxyl radicals from water (Eqs. (1) and (2)).

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

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

Fenton processes can also be carried out under heterogeneous conditions by immobilizing the iron catalyst on a support such as activated carbon [7], a brick grain [8], MgO [9], and zeolites [10].

The objective of this study is to investigate the removal efficiency of acetone and IPA from wastewater via oxidation with hydroxyl radicals obtained from hydrogen peroxide by Fenton reactions using different immobilized metal catalysts. To maximize the catalytic oxidation, the combination of metals and their ratios, as well as operational factors such as pH and hydrogen peroxide concentration, were optimized.

2. Materials and methods

2.1. Preparation of catalyst

Metal solutions were prepared using $Fe(NO_3)_3{\cdot}9H_2O$, $Al(NO_3)_3{\cdot}9H_2O$, $Cu(NO_3)_2{\cdot}3H_2O$, and $Zn(NO_3)_2{\cdot}6H_2O$ (Daejung Chemicals and Metals company, Korea, purity 98%). Granular activated carbon (GAC; 8*30 mesh; BET surface area: 860 m^2/g) was used as an adsorbent. The catalyst was prepared as follows: (i) Nitrate-type transition metals were added to 200 mL of distilled water. (ii) Fifty grams of activated carbon was added to the transition metal solution and mixed for 20 min using an ultrasonic device (DH.WUC.D22H, Daehan Science, Korea), during which the transition metals became attached to the pores of the activated carbon. (iii) The supernatant was removed from the mixed solution of metal and activated carbon, 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 carbon 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 calcined at 200°C for 3 h after heating at a rate of 1°C/min using a sintering furnace (YSE-3000, Youl San, Korea) to remove the nitrates. After the synthesis of the catalysts, the residual metal not adsorbed onto the activated carbon or not firmly immobilized on the surface of the activated carbon was washed from the catalysts using a pH 3 solution. The washing steps were repeated until the concentrations of Fe and Al in the wash water were less than 0.05 mg/L. The amount of the extracted active metals was ~55% of the initial metal content, which means ~45% of active metal was solidly attached to the activated carbon.

2.2. Catalyzed oxidation reaction

Batch experiments were performed to examine the efficiency of degradation of low-molecular-weight volatile compounds by the active metals by using 250-mL glass stoppered bottles. The oxidative capacity of the synthesized catalyst using a combination of two metals from the group (Fe, Al, Cu and Zn) 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 200 μg/L of acetone or 400 μg/L of IPA; 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. The removal ratio of acetone and IPA from wastewater in the presence of the metal catalyst was determined at various pH values and H_2O_2 concentrations. The pH was varied from 3.0 to 7.0, and the catalyst loading and H_2O_2 concentration were fixed at 250 mg and 5 mg/L, respectively. The pH was controlled by adding 0.1 N HCl or 0.1 N NaOH. The H_2O_2 concentration ranged from 1.0 to 10 mg/L (1.5, 3.0, 4.5, 6.0, and 7.5 mg/L), and the catalyst loading and initial pH were fixed at 250 mg and 3.0, respectively. In all experiments, acetone and IPA (Daejung Chemicals and Metals Company, Korea, purity 98%)

were used and the concentrations were fixed at 200 and 400 μg/L, respectively.

2.3. Sampling and analysis

Samples were taken from the batch reactors at appropriate intervals and filtered immediately through a glass fiber filter (Whatman, GF/C). For quantitative and qualitative analyses of acetone and IPA, a GC mass spectrometer (Agilent Technologies, 6890 N, USA) equipped with DB-WAX was used. The flow rate of N_2 carrier gas was 40 mL/min, and the temperature of the flame ionization detection system and oven were 120 and 40℃, respectively. A H_2O_2 kit (Chemets, K-5510, USA) was used for determination of the concentration of residual H_2O_2 in the solution after reaction. Transmission electron microscopy–energy dispersive X-ray spectroscopy (TEM–EDS) (Tecani G2 [TF30-ST] FEI) was performed to analyze the metal distribution.

3. Results and discussion

3.1. Catalytic oxidation with various combinations of metals

The catalysts were initially screened (Table 1) to determine the most active combination of metals for the degradation of the organic compounds. The initial concentration of active bimetal in the preparation of catalysts was fixed to 1% by weight. The identity and quantity of the active metals in the catalysts influence the generation of ·OH radicals during oxidation [11, 12]. The screening exercise demonstrated that the bimetal catalysts were more effective for degrading acetone compared to the single metal catalysts. These results are not surprising; many studies have reported that, compared to single metals, the presence of metal mixtures in catalysts increase the rate of oxidation [13, 14]. This disparate activity is attributed to the oxidation potential of the metals. The optimal combinations of active metals for removing acetone were Fe + Al or Fe + Cu.

The removal efficiencies of acetone and IPA from wastewater via solid-AOP using various catalyst ratios are shown in Table 2. Acetone removal in the presence of activated carbon alone, which was used as a support, was 20.5%. In comparison, in the presence of the catalysts with immobilized active metals, the removal exceeded 33% regardless of the metal content. Although activated carbon can remove most organic compounds by physical adsorption, low-molecular-weight organic compounds such as acetone are not removed by activated carbon, whereas catalysts on which active metals are immobilized can generate ·OH radicals and effectively remove such compounds by oxidation and adsorption.

Acetone removal achieved using Fe as a single active metal was 41.7%, whereas this value increased to 70.2% when 10% of the total active metal was replaced with Al, suggesting that Al acted as a cocatalyst that enhanced the conversion of Fe^{2+} into Fe^{3+} by ·OH radicals that were generated from hydrogen peroxide [15]. In contrast, when the Al content exceeded 10%, the efficiency of acetone and IPA removal declined, because the amount of generated ·OH radicals decreased owing to the reduction in the quantity of Fe as the major catalyst. In contrast, for the Fe + Cu combination, when the content of Fe decreased, the removal efficiency increased. Fe possibly plays the role of a cocatalyst in this case. The respective optimal ratios of the Fe + Al and Fe + Cu combinations were 9:1 and 2:8.

Notably, when the proportion of Fe in the total active metal was dominant, the acetone removal efficiency was lower than that achieved using Cu as a single active metal. This low efficiency can be explained from the TEM results in Fig. 1. In the Fe +

Table 1
Removal ratio of acetone with various combinations of metals

Sample	Content of active metal (wt. %)	Removal efficiency of acetone (%)	Sample	Content of active metal (wt. %)	Removal efficiency of acetone (%)
Fe	1.03	41.7	Fe + Al	0.56/0.24	54.2
Cu	1.08	38.3	Fe + Cu	0.63/0.54	51.3
Al	0.95	21.8	Fe + Zn	0.53/0.21	44.6
Zn	0.95	27.4	Cu + Al	0.48/0.23	41.7
			Cu + Zn	0.44/0.16	31.5
			Al + Zn	0.23/0.19	23.2

Table 2
Removal ratio of acetone and IPA under reaction conditions (pH 3)

	(Fe + Al)					(Fe + Cu)				
Mixing ratio	9:1	7:3	5:5	3:7	2:8	9:1	7:3	5:5	3:7	2:8
Acetone removal (%)	70.2	53.8	41.7	37.4	36.5	33.1	34.5	41.2	62.5	73.0
IPA removal (%)	99.8	98.2	98.2	93.2	92.2	55.4	59.5	87.4	91.3	99.5

Cu combination sample (Fe:Cu = 7:3), the Cu particles were closely banded and concentrated on the surface of activated carbon; thus, a high content of Fe adversely affected acetone degradation.

3.2 Effect of pH and H_2O_2 concentration

Generally, the pH influences the oxidation reactions in the Fenton process—the optimal pH for the homogeneous Fenton process is ~2.8 when the Fe that is in solution exists as Fe(III) and $Fe(III)(OH)^{2+}$, which are photoactive species [16,17]. Fig. 2 shows a comparison of the catalyst performance for acetone and IPA degradation with pH variation. When the optimized catalysts were applied, greater than 70% acetone removal and almost 100% IPA removal were achieved at pH 3 and 4, respectively. However, as the pH approached neutral conditions, the removal ratios decreased, implying that high pH values stabilize hydrogen peroxide, which decomposes rapidly into molecular oxygen without generating appreciable amounts of $^{\cdot}OH$ radicals.

In the previous experiment, it was found that IPA was oxidized more easily than acetone using the Fe/Al catalyst. Thus, only IPA was used in the subsequent evaluation of the effect of varying the concentration of hydrogen peroxide on oxidation using the Fe/Al catalyst. As shown in Fig. 3(a), the oxidation rate increased as the amounts of hydrogen peroxide increased up to 4.5 mg/L, indicating that the amount of $^{\cdot}OH$ radicals generated by the catalyst was sufficient to degrade 400 μg/L of IPA. When the hydrogen peroxide concentration exceeded 6.0 mg/L, the removal of IPA decreased because of the well-known scavenging effect of $^{\cdot}OH$ radicals [18,19].

$$H_2O_2 + {}^{\cdot}OH \rightarrow H_2O + HO_2^{\cdot} \qquad (3)$$

Reaction (3) reduces the probability of attack by $^{\cdot}OH$ radicals on organic molecules, causing the oxidation rate to fall. Although other radicals (e.g. $OH_2^{\cdot}$) are also produced, their oxidation potential is much lower than that of $OH^{\cdot}$ species impairing the removal of organic

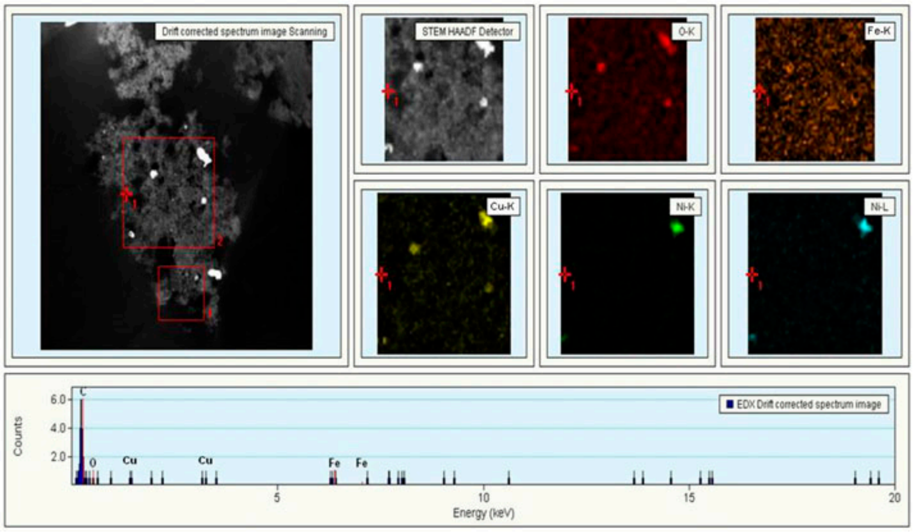

Fig. 1. TEM-EDS images of Fe + Cu combination sample (Fe:Cu = 7:3).

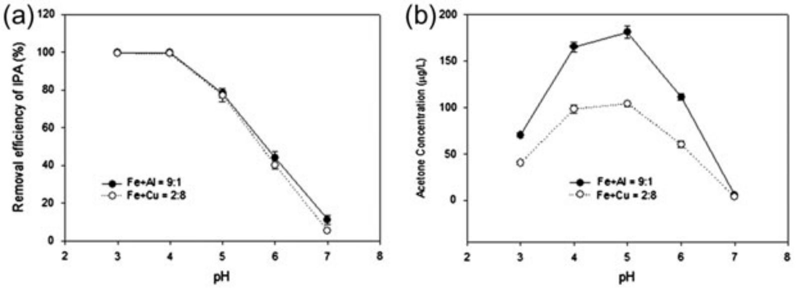

Fig. 2. Effect of pH on oxidation of (a) IPA and (b) acetone.

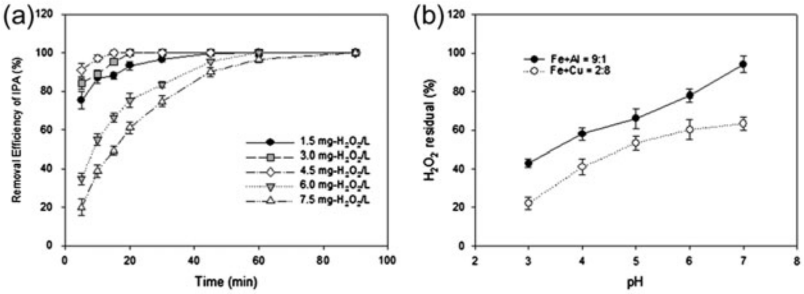

Fig. 3. IPA oxidation at various H_2O_2 concentrations (a) and residual H_2O_2 under various pH conditions (b).

compounds [18]. Thus, in subsequent experiments, 4.5 mg of H_2O_2/L was used.

The experimental results indicate that the acidic pH range, especially pH 3, is more favorable than alkaline pH for the removal of organic compounds by solid-AOPs. These findings are attributable to the increase in the number of surface active sites for H_2O_2 decomposition and formation of hydroxyl radicals at low pH. However, there was no significant difference in the IPA removal with increasing Fe content in all cases.

Several preceding studies have shown that activated carbon promotes H_2O_2 decomposition, probably via the formation of hydroxyl- and hydroperoxyl-type radicals. It is plausible that these radicals can also promote oxidation of organic compounds such as acetone and IPA [20]. In contrast, Fenton's reagent does not significantly affect the porous structure, surface area, or surface chemical properties of the activated carbon. Consequently, solid-phase advanced oxidation processes are believed to be effective methods to overcome the low adsorbability of organics present in electric wastewater on activated carbon.

Summary

The removal of acetone and IPA using AOP employing several catalysts prepared from Fe, Cu, Al, and Zn support on activated carbon resulted in an enhanced decomposition of organics relative to the activated carbon alone. Optimal acetone removal and IPA removal from wastewater were achieved using a catalyst ratio of (Cu + Fe) = 8:2 or (Fe + Al) = 9:1 with the activated carbon at pH 3. Greater than 70% acetone removal and almost 100% IPA removal were achieved in the pH range 3~4. The use of 4.5 mg/L of H_2O_2 resulted in the highest removal efficiency for IPA. Solid-phase advanced oxidation processes are believed to be effective methods to overcome the low adsorbability of organics present in electronic wastewater on activated carbon.

Acknowledgement

This study was supported by a National Research Foundation of Korea (NRF) grant funded by the Korean Government (NRF-2013R1A2A1A09007252).

References

[1] European DG ENV, Towards the establishment of a priority list of substances for further evaluation of their role in endocrine disruption-preparation of a candidate list of substances as a basis for priority setting, BKH Consulting Engineers, 2000.

[2] M.A. Fontecha-Cámara, M.V. López-Ramón, M.A. Álvarez-Merino, C. Moreno-Castilla, Effect of surface chemistry, solution pH, and Ionic strength on the removal of herbicides diuron and amitrole from water by an activated carbon fiber, Langmuir 23(3) (2007) 1242–1247.

[3] A. Zapata, T. Velegraki, J.A. Sánchez-Pérez, D. Mantzavinos, M.I. Maldonado, S. Malato, Solar photo-Fenton treatment of pesticides in water: Effect of iron concentration on degradation and assessment of ecotoxicity and biodegradability, Appl. Catal. B 88 (2009) 448–454.

[4] L.B. Khalil, B.S. Girgis, T.A.M. Tawfik, J. Chem. Technol. Biotechnol. 76 (2001) 1132–1140.

[5] A. Georgi, F.D. Kopinke, Interaction of adsorption and catalytic reactions in water decontamination processes, Appl. Catal. B 58 (2005) 9–18.

[6] V.P. Santos, M.F.R. Pereira, P.C.C. Faria, J.J.M. Órfão, Decolourisation of dye solutions by oxidation with H_2O_2 in the presence of modified activated carbons, J. Hazard. Mater. 162 (2009) 736–742.

[7] F. Lücking, H. Köser, M. Jank, A. Ritter, Iron powder, graphite and activated carbon as catalysts for the oxidation of 4-chlorophenol with hydrogen peroxide in aqueous solution, Water Res. 32 (1998) 2607–2614.

[8] S. Chou, C. Huang, Y.H. Huang, Heterogeneous and homogeneous catalytic oxidation by supported γ-FeOOH in a fluidized-bed reactor: Kinetic approach, Environ. Sci. Technol. 35 (2001) 1247–1251

[9] D.W. Pak, W.S. Chang, Decolorizing dye wastewater with low temperature catalytic oxidation, Water Sci. Technol. 40 (1999) 115–121

[10] S.G. Huling, R.G. Arnold, P.K. Jones, R.A. Sierka, Predicting fenton-driven degradation using contaminant analog, J. Environ. Eng. 126 (2000) 348–353.

[11] K. Pirkanniemi, M. Sillanpää, Heterogeneous water phase catalysis as an environmental application: A review, Chemosphere 48 (2002) 1047–1060.

[12] J. Deng, J. Jiang, Y. Zhang, X. Lin, C. Du, Y. Xiong, FeVO4 as a highly active heterogeneous Fenton-like catalyst towards the degradation of Orange II, Appl. Catal. B 84 (2008) 468–473.

[13] J.C. Moreno-Piraján, V.S. Garcia-Cuello, L. Giraldo, The removal and kinetic study of Mn, Fe, Ni and Cu ions from wastewater onto activated carbon from coconut shells, Adsorption 17 (2011) 505–514.

[14] J.G. Carriazo, E. Guelou, J. Barrault, J.M. Tatibouët, S. Moreno, Catalytic wet peroxide oxidation of phenol over Al–Cu or Al–Fe modified clays, Appl. Clay Sci. 22 (2003) 303–308.

[15] T. Ohyashiki, T. Karino, S. Suzuki, K. Matsui, Effect of aluminum ion on Fe^{2+}-induced lipid peroxidation in phospholipid liposomes under acidic conditions, J. Biochem. 120 (1996) 895–900.

[16] J. Barrault, M. Abdellaoui, C. Bouchoule, A. Majesté, J.M. Tatibouët, A. Louloudi, N. Papayannakos, N.H. Gangas, Catalytic wet peroxide oxidation over mixed (Al–Fe) pillared clays, Appl. Catal. B 27 (2000) 225–230

[17] J.H. Ramirez, F.J. Maldonado-Hodar, A.F. Perez-Cadenas, C. Moreno-Castilla, C.A. Costa, L.M. Madeira, Azo-dye Orange II degradation by heterogeneous Fenton-like reaction using carbon-Fe catalysts, Appl. Catal. B 75 (2007) 317–328.

[18] C. Walling, Fenton's reagent revisited, Acc. Chem. Res. 8 (1975) 125–131.

[19] J. De Laat, T.G. Le, Effects of chloride ions on the iron (III)-catalyzed decomposition of hydrogen peroxide and on the efficiency of the Fenton-like oxidation process, Appl. Catal. B 66 (2006) 137–146.

[20] V. Gomez-Serrano, M. Acedo-Ramos, A.J. Lopez-Penido, Tratamiento de un carbon activado con peroxide de hidrogeno, Efecto sobre la masa de muestra [Treatment of activated carbon with hydrogen peroxide – Effect on the mass of the sample], Information Tecnologica 7 (1996) 61–65.