



Zero-valent iron pretreatment for detoxifying iodine in liquid crystal display (LCD) manufacturing wastewater

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ABSTRACT

This study investigated reductive transformation of iodine by zero-valent iron (ZVI), and the subsequent detoxification of iodine-laden wastewater. ZVI completely reduced aqueous iodine to non-toxic iodide. Respirometric bioassay illustrated that the presence of iodine increase the lag phase before the onset of oxygen consumption. The length of lag phase was proportional to increasing iodine dosage. The reduction products of iodine by ZVI did not exhibit any inhibitory effect on the biodegradation. The cumulative biological oxidation associated with iodine toxicity was closely fitted to Gompertz model. When iodine-laden wastewater was continuously fed to a bench-scale activated sludge unit, chemical oxygen demand (COD) removal efficiencies decreased from above 90% to below 80% along with a marked decrease in biomass concentration. On the other hand, the COD removal efficiency and biomass concentration remained constant in the integrated ZVI-activated sludge system. Respirometric bioassay with real iodine-laden LCD manufacturing wastewater demonstrated that ZVI was effective for detoxifying iodine and consequently enhancing biodegradability of wastewater. This result suggested that ZVI pretreatment may be a feasible option for the removal of iodine in LCD processing wastewater, instead of more costly processes such as adsorption and chemical oxidation, which are commonly in the iodine-laden LCD wastewater treatment facility.

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1. Introduction

Molecular iodine and its derivatives have been used in various industries and their primary applications include photographic equipment, pharmaceuticals, animal feed supplements, disinfectants, rosin stabilizers, inks, colorants, and catalysts. Recently, industrial use of iodine has further increased due to continuing demand from electronic and pharmaceutical industries [1]. Demand of iodine will keep growing in electronic industries; in particular, liquid crystal display (LCD) manufactures which typically use iodine as a light polarizing agent.

Even though iodine is less effective than chlorine as a disinfectant, it has been widely used as bactericidal, fungicidal, tuberculocidal, virucidal and sporicidal agents [2]. Iodine-based disinfectant is very effective for inactivating spore-forming *Bacillus* in small dosage [3]. Exact mode of microbial action of iodine is still unknown but it is reported that iodine can penetrate the cell membrane of microorganisms [4], attack key amino acid groups of

proteins, specifically the free-sulfur amino acids such as cysteine and methionine [2,5], nucleotides, and fatty acids [2,6], and lead to the eventual cell death.

Immediately Dangerous to Life or Health Concentration (IDLH) of iodine set by Occupational Safety and Health Administration (OSHA) is 2 mg/L [7]. If iodine is introduced to the wastewater treatment facility in high concentration as in direct discharges from electronic or pharmaceutical plants, it can be detrimental to the proper operation of the wastewater treatment facility due to the potential biocidal effect of iodine toward the microorganisms responsible for biological wastewater treatment.

Physicochemical methods such as UV oxidation, evaporation and membrane filtration were suggested as potential options to remove iodine from the incoming wastewater before it reaches the treatment facility to prevent the inhibitory level of iodine from entering biological treatment processes [8]. Activated carbon sorption is also applicable for iodine detoxication due to its high affinity to iodine [9–11].

These physicochemical processes are potentially selected as a pretreatment method to decrease toxic iodine levels in influent wastewater prior to activated sludge process or as a post-treatment process to polish treated effluents to meet discharge standards.

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However, the downside of these physicochemical processes are that they generally require high operation and maintenance costs, and often generate pollutant-laden hazardous wastes that need to be regenerated or disposed properly.

Elemental iron is one of the many strong reducing agents that received much attention recently for groundwater remediation and wastewater treatment process [12–16]. Despite extensive research and knowledge of its many potential applications, the feasibility of applying iron technology to the treatment of iodine-laden wastewater has not been demonstrated. Thermodynamics predict that iodine should be readily transformed to iodide in the presence of elemental metals such as ZVI ($\Delta G^\circ = -207.6$ kJ/mol). The purpose of this study was to examine the reductive transformation of iodine by zero-valent iron and to evaluate the feasibility of using zero-valent iron to pretreat iodine-containing wastewater prior to conventional biological treatment processes. We hypothesized that reduction with zero-valent iron would convert iodine to products that are less toxic to microorganisms and thus enhance the biological treatment of iodine-containing wastewaters. Inhibitory effects of iodine and its reduction products were examined with batch respirometric studies and bench-scale integrated ZVI-biological wastewater treatment system.

2. Materials and methods

2.1. Chemicals

Iodine crystal (F.W. 253.81, 99.5% purity) was purchased from Fluka (Milwaukee, WI) and used without further treatment. Potassium iodide, potassium iodate, potassium phosphate (mono- and di-basic) and L-glutamic acid were purchased from Fisher Scientific (Pittsburgh, PA). D-Glucose, yeast extract, magnesium sulfate, and sodium chloride were purchased from Sigma (St. Louis, MO). Ammonium chloride and calcium chloride were purchased from Aldrich (Milwaukee, WI). Protease peptone was purchased from Difco laboratories (Detroit, MI). For biochemical oxygen demand (BOD) test, BOD nutrient buffer pillows and BOD seed organisms were purchased from Hach (Loveland, CO). All chemicals were used as received.

Two types of irons were used in this study. High-purity iron powder ($<10 \mu\text{m}$, $>99.5\%$, Aldrich, WI) was used in anaerobic batch reduction experiments. Cast iron granules (10–20 mesh size) used in the column experiments was obtained from Master Builders (Aurora, OH). Both irons were used as received without pretreatment. Elemental composition of Master Builder iron has been reported in previous studies [17–19]. The specific surface area of the Master Builder iron and high-purity iron powder used in this study was $1.29 \text{ m}^2/\text{g}$ [19] and $0.19 \text{ m}^2/\text{g}$ [20], respectively.

2.2. Anaerobic batch reduction experiments

Elemental iodine crystals were dissolved in deionized water, which was previously purged with nitrogen gas to remove dissolved oxygen, for 3 days at room temperature. The residual iodine particles were removed from the stock iodine solution by filtration with a $0.2\text{-}\mu\text{m}$ membrane nylon filter (Millipore, MA). The equilibrium concentration of iodine stock solution made was 300 mg/L . Batch reduction experiments were conducted in 45-mL glass vials containing 2.0 g of pure iron powders and 20 mL of iodine solutions, which has been diluted to give the required final concentration of iodine in each batch reactor. At equilibrium, the iodine solution in control reactor (pH 6.3) consisted of 13.9 mg/L I_2 (0.05 mM), 21.8 mg/L I^- (0.17 mM) and 1.56 mg/L IO_3^- (0.009 mM).

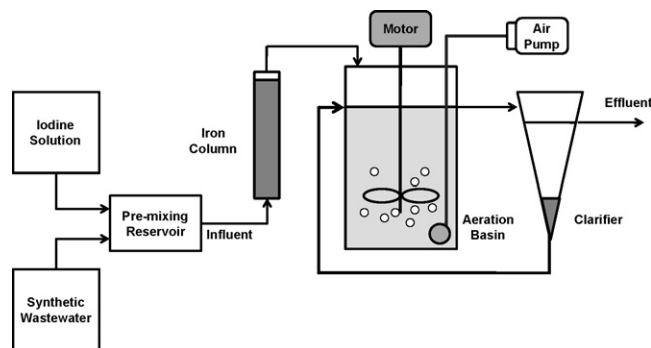


Fig. 1. Schematics of integrated Fe(0)-activated sludge system.

Batch reactors were prepared in duplicate in an anaerobic glove box filled with nitrogen (Bell-Art Products, Pequannock, NJ) to ensure the anaerobic condition inside the batch reactors. Control vials without iron powders were also prepared to determine the volatilization and sorption loss of iodine. All vials were continuously shaken at 150 rpm on an orbital shaker in a horizontal position. Replicate vials were sacrificed at sampling time and the supernatant was filtered through a $0.20\text{-}\mu\text{m}$ membrane filter (Millipore, MA) and filtrates were used for chemical analysis.

2.3. Toxicity assays

Acute toxicity of iodine on microorganisms was measured with Hach BODTrak apparatus (Hach, Loveland, CO). BODTrak measured changes in oxygen partial pressure inside a BOD bottle caused by aerobic respiration and convert them into oxygen consumption.

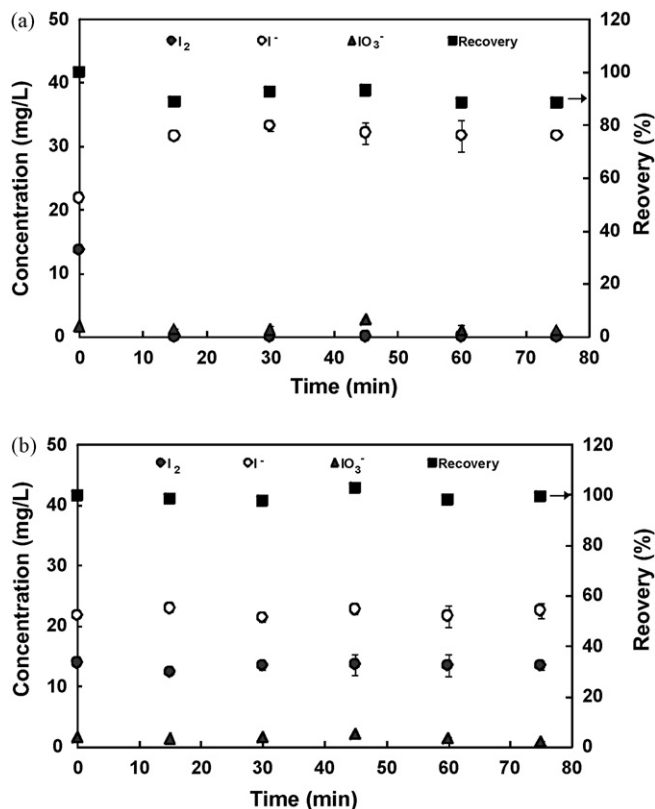


Fig. 2. Aqueous concentrations of iodine species in (a) the presence and (b) absence of zero-valent iron.

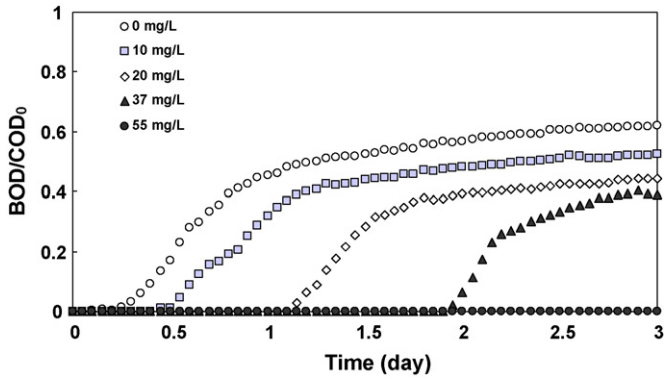


Fig. 3. Effect of iodine on biological oxidation of synthetic wastewater.

The system was interfaced with a PC for automatic data acquisition at fixed time intervals, and cumulative BOD was calculated from the oxygen partial pressure change over time. Total volume of test solution in the bath reactor (600 mL dark borosilicate bottles) was 160 mL, which contained 150 mg/L glucose and 150 mg/L glutamic acid and 5 mL of pH buffer solution (0.5 M phosphate buffer). One capsule of BOD nutrient buffer (Hach) was added into each test bottle to provide micronutrient and buffering capacity. Pre-determined amounts of iodine were spiked to the solutions to give four final concentrations of 10, 20, 37 and 55 mg I₂/L. Hach BOD seed was rehydrated in the buffered deionized water for 1 h on magnetic stirrer. Rehydrated BOD seed solution was then settled for 15 min and 5 mL of the supernatant was collected and used to inoculate the BOD test samples. Aerobic toxicity assays were conducted for 3 days in a temperature-controlled chamber at 25 °C.

One set of test solutions were also pretreated with ZVI in batch reactors prior to toxicity assay to evaluate the toxicity of reduction products of iodine by ZVI. Batch iron reduction of iodine-spiked solutions was conducted in the same manner as the iron reduction experiment described in Section 2.2. After 2 h of reaction time, the supernatant was decanted and vigorously stirred using magnetic stirrer to oxidize the residual Fe(II) in the solution, which may consume oxygen and overestimate BOD values in bioassay. Solutions were then filtered through 0.2-µm membrane filter to remove iron precipitates and used for the toxicity assay.

2.4. Analysis of bioassay data

Cumulative BOD values normalized to initial COD (COD₀) curve from batch bioassay tests were analyzed using the modified Gompertz three-parameter model [21]:

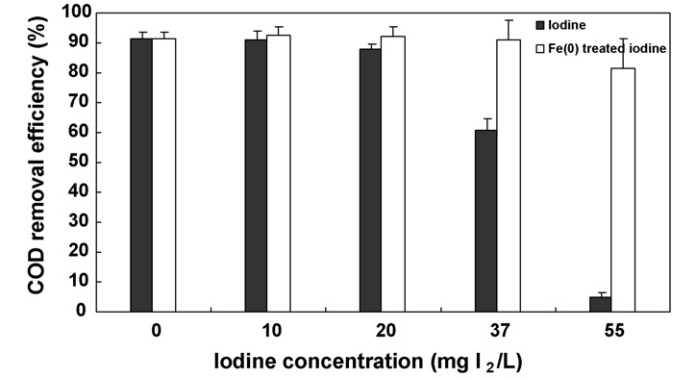


Fig. 5. Effect of iodine and iron-treated iodine on COD removal efficiencies.

where $B(t)$ is the BOD/COD₀ at time t , B_{max} the BOD/COD₀ at the end of incubation time, R the specific BOD/COD₀ increase rate (d⁻¹), e the $\exp(1) = 2.71828$ and λ is the lag phase (d). The three parameters of B_{max} , R and λ were determined by curve-fitting using Sigma plot version 9.0.

$$B(t) = B_{max} \exp \left\{ -\exp \left[\frac{R \cdot e}{B_{max}} (\lambda - t) + 1 \right] \right\}, \quad (1)$$

2.5. Integrated Fe(0)-activated sludge system

The feasibility of integrated Fe(0)-activated sludge system to treat the iodine-laden wastewater was investigated with laboratory-scale continuously stirred tank reactor (CSTR) systems.

Fig. 1 shows the lab-scale integrated Fe(0)-activated sludge system. Three different wastewaters (iodine-laden, iron-pretreated iodine and no iodine) were used as influents. Each bench-scale unit consisted of an aeration basin and a secondary clarifier. All aeration basins and clarifiers were constructed from a transparent acrylic polymer. The aeration basins were cylindrical, CSTRs with a working volume of 3.4 L, and were constantly stirred by impeller mixers. The flow from the aeration basin to the secondary clarifier was by gravity. The settled solids in the clarifier were pumped continuously back to the aeration basin using peristaltic pump. Each system was operated at 10-h hydraulic retention time (HRT) and 10-day mean cell residence time (MCRT).

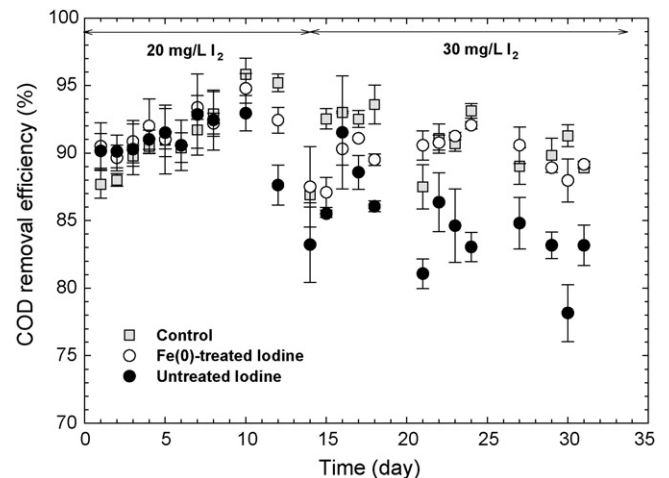


Fig. 6. COD removal efficiencies in the bench-scale activated sludge systems.

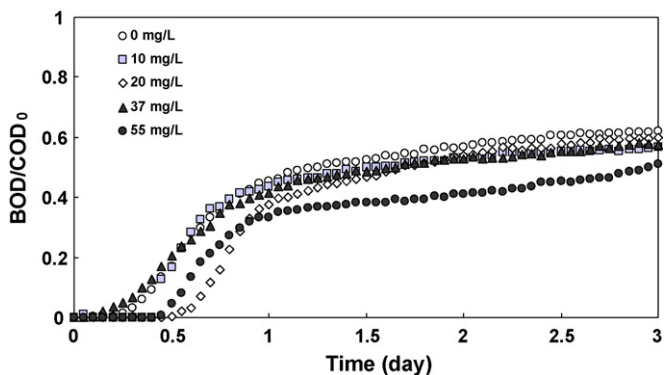


Fig. 4. Effect of iron treatment on biooxidation of iodine-dosed wastewater.

Table 1
Calculated parameter values (Gompertz model) and observed values for respirometric bioassay data

I_2 conc. (mg/L)	Control		No iron pretreatment				Iron pretreatment			
	0		10	20	37	55	10	20	37	55
B_{max}^a	0.59		0.50	0.42	0.38	–	0.53	0.56	0.55	0.44
B_{max}^b	0.62		0.52	0.44	0.39	–	0.57	0.60	0.58	0.51
R (d^{-1})	0.66		0.59	0.74	0.82	–	0.85	0.66	0.55	0.60
λ (d) ^a	0.23		0.47	1.12	1.91	–	0.31	0.49	0.15	0.38
λ (d) ^b	0.05		0.59	1.18	1.93	–	0.25	0.49	0.23	0.44
R^2	0.99		0.99	0.99	0.99	–	0.98	0.99	0.99	0.97

^a Calculated value.

^b Observed value.

The activated sludge used in this study was obtained from wastewater treatment plant in Kennett Square, PA. Primary effluent from Elkton Wastewater Treatment Plant (Elkton, MD) supplemented with synthetic wastewater at 1:1 ratio was used as influent. The Elkton wastewater was selected as the influent for this bench-scale system because it consisted of mostly domestic wastewater and its proximity to our laboratory. The composition of synthetic wastewater are as follows: 160 mg/L peptone, 110 mg/L yeast extract, 106 mg/L NH_4Cl , 28 mg/L K_2HPO_4 , 7 mg/L $NaCl$, 4 mg/L $CaCl_2 \cdot 2H_2O$, and 2 mg/L $MgSO_4 \cdot 7H_2O$. The synthetic wastewater and iodine stock solution (300 mg/L) were blended in a pre-mixing reservoir (0.2 L) prior to iron column. The flow rate of the iodine stock solution was adjusted to control iodine concentration in the synthetic wastewater.

For integrated Fe(0)-activated sludge system, the iodine-laden synthetic wastewater was passed through an iron column prior to entering the aeration basin. Iron column was a 9.5 mL of glass column filled with 1:1 (v/v) mixture of scrap iron and 20–30 mesh sized Ottawa quartz sand (Fisher scientific, Fair Lawn, NJ). The iron column was operated in an up-flow fashion with a contact time of 5.4 min.

2.6. Analytical methods

Aqueous concentration of iodine was determined according to Hach method 8031 using Hach DR3000 spectrophotometer (Loveland, CO). Iodide and iodate was determined by a Dionex DX 500 ion chromatograph (Dionex, Marlton, NJ) equipped with AS 11 column and a guard column. Chemical oxygen demand (COD) was determined according to Hach method 8000 using Hach DR3000 spectrophotometer (Loveland, CO). Total suspended solids (TSSs) and volatile suspended solids (VSSs) in mixed liquor and effluent

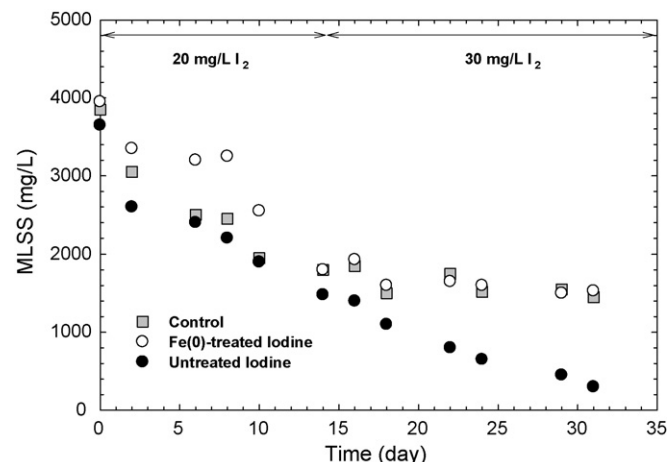


Fig. 7. MLSS concentrations in the bench-scale activated sludge systems.

samples were determined in accordance with the Standard Methods [22]. The surface morphology of the cast iron was observed with a field-emission scanning electron microscope (FE-SEM, Hitachi, S-4100, 15 kV) at a magnification of 50,000.

3. Results and discussion

3.1. Anaerobic batch reduction experiment

Aqueous concentrations of iodine, iodide and iodate in batch reduction bottles were determined every 15 min for 75 min in the presence of iron and the results are shown in Fig. 2(a). Iodine disappeared completely in 15 min in the presence of elemental iron and the majority of iodine was converted to iodide ion as follows:



Overall reductive reaction of iodine by elemental iron is as follows:



About 90% of added iodine was accounted for in the iron system. The loss of 10% may be attributed to the formation of intermediates such as iron-iodide which was not analyzed in this study. In the absence of iron (control reactor), iodine species remained the same throughout the 75-min experimental period indicating that no volatilization and sorption loss occurred (Fig. 2(b)).

3.2. Biological toxicity assessment

Acute toxicity of iodine and iron-treated iodine was compared by examining the effects of these compounds on microbial oxidation of synthetic wastewater. Fig. 3 shows the effect of

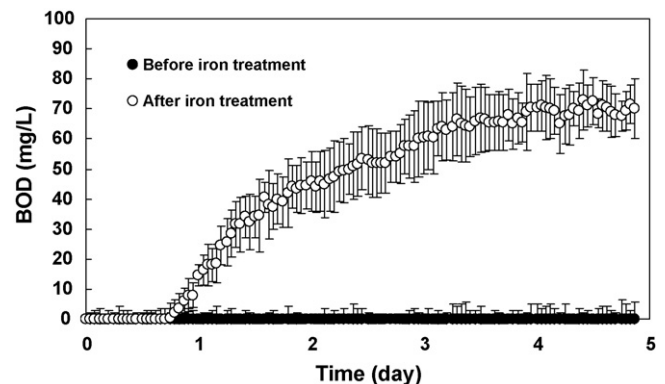


Fig. 8. Biological oxidation of iodine-laden LCD-related industrial wastewater before and after iron treatment.

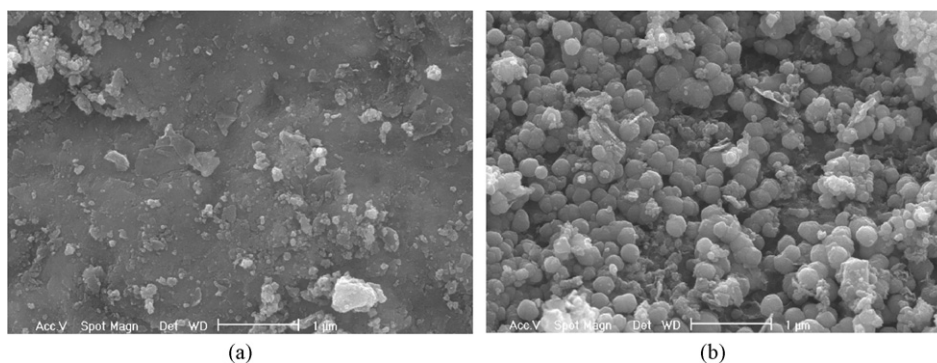


Fig. 9. SEM image of iron (50,000 \times): (a) before and (b) after iodine reduction.

five different concentrations of iodine (including control) on the biological oxidation of synthetic wastewater. The biooxidation was represented as the BOD normalized to initial COD. The rate and extent of biodegradation was substantially inhibited by increase in iodine dosages as the presence of iodine delayed the onset of oxygen consumption in the batch reactors. At 55 mg/L iodine dosage, measurable oxygen consumption was not observed during the 3-day incubation period. On the other hand, the delay in oxygen consumption was not observed in the batch reactors containing iron-treated samples (Fig. 4). Microbial activity in all reactors with iron pretreatment was comparable to that of control reactors (no iodine addition) even at the highest iodine concentration of 55 mg/L. This result suggests that the iron treatment converted toxic iodine to non-toxic products.

The cumulative BOD/COD₀ curves were analyzed by Gompertz three-parameter model and the obtained parameters are shown in Table 1. The Gompertz model was mainly used for fitting the microbial growth [21], and recently the soluble inert COD fractions in leachate from landfill [23] and the biogas production such as hydrogen and methane from anaerobic biological processes [24,25]. The Gompertz equation was successfully fitted to the sigmoidal curve of biological oxygen consumption data with high R^2 (Table 1). The calculated values of maximum BOD/COD₀ (B_{max}) and lag phase (λ) were similar to the observed data, especially for the results from iodine toxic experimental set. The lag phase time determined from this study did not fit a conventional and modified BOD exertion curve equations [26].

Length of lag phase determined by either calculation or observation was proportional to increased iodine dosage (Table 1). Lag phase is often observed in BOD curves when biological inhibitors are present with unacclimated seed cultures [26,27]. Lag phase is sometimes explained with limitation in seed quantities [28], which is more plausible for the lag phase resulting from iodine dose. Since higher dosage of iodine may inactivate more cells in the batch reactor, the unaffected microbial populations would require a longer period to recover and exhibit the measurable oxygen demand. To illustrate the effect of iron treatment on the biological oxidation of iodine-containing wastewater, the final COD removal efficiencies of control and iron-treated iodine batch reactor were compared for each iodine dose (Fig. 5). The extent of COD removal decreased as the iodine dosage increased in the control reactors; on the other hand, similar levels of COD removal efficiencies were maintained in the iron-treated systems for all iodine doses. This result confirms our hypothesis that zero-valent iron converts iodine to products that are less toxic to microorganisms and thus enhance the biological treatment of iodine-containing wastewaters.

3.3. Integrated ZVI-biological treatment system

Iodine-containing synthetic wastewater was constantly fed to an integrated ZVI-biological system to verify the effectiveness of iron technology for detoxification of iodine. In addition to the integrated system, a bioreactor system without iron pretreatment was operated in parallel to assess the effect of iodine on reactor performance. A control system treating wastewater without iodine was also operated. Fig. 6 compares COD removal efficiencies of three biological systems. During the first 14 days of operation, all three systems achieved about 90% COD removal efficiencies. At day 14, 30 mg/L of iodine was added to the iodine-fed systems. The COD removal efficiency of iodine-fed system decreased to about 80% after 30 days of operation, suggesting that the continuous exposure to 30 mg/L of iodine had detrimental effects on the microbial activity. On the other hand, COD removal efficiencies of integrated ZVI-biological system remained constant around 90%. The same level of COD removal was maintained in the control system, suggesting that the iron pretreatment of iodine-laden wastewater was able to remove the inhibitory effects of iodine.

Decrease in COD removal efficiency at 30 mg/L of iodine was closely correlated with the decreased concentration of biomass. Fig. 7 shows mixed liquor suspended solids (MLSSs) concentrations during the 30-day experimental period. The MLSS concentrations in all three reactors steadily decreased and reached a steady-state level of about 1500 mg/L in 14 days. Once the steady-state MLSS concentrations were achieved in all reactors, 30 mg/L of iodine was added to the iodine-fed systems and this addition of iodine resulted in gradual decrease of MLSS concentration to 350 mg/L in 15 days, clearly demonstrating the biocidal impact of iodine. Experiments with bench-scale activate sludge systems were terminated at 31 days of operation because it was not possible to maintain the MCRT in the iodine-fed system.

3.4. Verification of concept with real iodine-containing wastewater

Application of iron technology to treat iodine-laden wastewater was demonstrated with real LCD manufacturing wastewater in the same manner as the respirometric bioassay described previously. The wastewater was collected from a wastewater treatment facility at a LCD polarizing film manufacturer in Ochang, Korea and transported to our laboratory in Newark, Delaware. According to the information provided by the facility personnel, iodine concentrations in the raw wastewater range from 10 to 30 mg/L. However, since the transport of wastewater sample from the plant to our lab typically took 2–3 days, iodine in the sample disappeared during the transport. As a result, iodine was spiked at 10 mg/L prior to

conducting the laboratory experiment. Effect of iron pretreatment on detoxification of iodine in the real industrial wastewater was markedly significant (Fig. 8). No oxygen consumption was observed with the iodine-dosed wastewater sample for the 5-day incubation period, while the biodegradation of the wastewater was highly enhanced after iron treatment. This is most likely due to reduction of iodine toxicity. The surface morphology of both the iron before and after iodine reduction is shown in Fig. 9. The surface of the iron was mostly covered with iron oxide aggregate after iodine reduction revealing that the iron was significantly oxidized.

The existing treatment facilities in Korea currently use a granular activated carbon filter to remove toxic iodine from the influent wastewater prior to biological treatment process. Fenton oxidation systems are often present in these facilities as post-treatment to chemically oxidize the residual organics in the effluents, in case of biological system failure due to iodine breakthrough in carbon filter. From this result, iron pretreatment may be suggested as an alternative option to activated carbon for eliminating the iodine toxicity and enhancing the performance of subsequent biological treatment of the LCD manufacturing wastewater.

4. Conclusion

Zero-valent iron pretreatment was found to be effective in controlling inhibitory effects of iodine-laden wastewater in both batch culture and CSTR experiment. Iodine was completely and rapidly reduced by ZVI and the majority of the iodine was converted to iodide ion. In batch bioassay tests, inhibitory effects of iodine on microbial activity was represented by a lag phase in oxygen consumption as the duration of lag phase was closely correlated with the iodine dosage. On the other hand, the bioassay reactors receiving ZVI-pretreated iodine wastewater did not have any lag phase for all iodine doses, suggesting that the reduction products of iron were non-toxic to the biological wastewater treatment system. An integrated ZVI-activated sludge system was effective in treating iodine-laden wastewater and, based on this finding, an integrated ZVI-activated sludge system may be potential option for the treatment of wastewater containing inhibitory levels of iodine.

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References

- [1] U.S. Geological Survey (USGS) Website of Mineral Resources Program in USGS, November 2007, <http://minerals.usgs.gov/minerals/pubs/commodity/iodine/> (assessed December 2007).
- [2] W. Gottardi, Iodine and iodine compounds, in: S.S. Block (Ed.), *Disinfection, Sterilization, and Preservation*, fourth ed., Lea & Febiger, Philadelphia, PA, 1991, pp. 152–166.
- [3] N. Kida, Y. Mochizuki, F. Taguchi, An effective iodide formulation for killing *Bacillus* and *Geobacillus* spores over a wide temperature range, *J. Appl. Microbiol.* 97 (2004) 402–409.
- [4] S.L. Chang, Modern concept of disinfection, *J. San. Eng. Div. Proc. ASCE* 97 (1971) 689.
- [5] W.C. Kruse, Halogen action on bacteria, viruses and protozoa, in: *Proceedings of the ASCE National Special Conference on Disinfection*, Amherst, MA, 1970, pp. 113–137.
- [6] K. Apostolov, The effects of iodine on the biological activities of myxoviruses, *J. Hyg.* 84 (1980) 381–388.
- [7] Occupational Safety & Health Administration (OSHA) Website of OSHA, November 2004, http://www.osha.gov/dts/chemicalsampling/data/CH_247201.html (assessed December 2007).
- [8] A. Drews, T. Klahm, B. Renk, M. Saygili, G. Baumgarten, M. Kraume, Cleaning of iodine CIP waters from X-ray contrast media production using nanofiltration: process design and modeling, *Chem. Eng. Technol.* 26 (2003) 1137–1142.
- [9] Z. Jiang, Y. Liu, X. Sun, F. Tian, F. Sun, C. Liang, W. You, C. Han, C. Li, Activated carbons chemically modified by concentrated H₂SO₄ for the adsorption of the pollutants from wastewater and the dibenzothiophene from fuel oils, *Langmuir* 19 (2003) 731–736.
- [10] X. Liu, X. Quan, L. Bo, S. Chen, Y. Zhao, Simultaneous pentachlorophenol decomposition and granular activated carbon regeneration assisted by microwave irradiation, *Carbon* 42 (2004) 415–422.
- [11] M.J. Martin, A. Artola, M.D. Balaguer, M. Rigola, Towards waste minimization in WWTP: activated carbon from biological sludge and its application in liquid phase adsorption, *J. Chem. Technol. Biotechnol.* 77 (2002) 825–833.
- [12] A. Agrawal, P.G. Tratnyek, Reduction of nitro aromatic compounds by zero-valent iron metal, *Environ. Sci. Technol.* 30 (1996) 153–160.
- [13] T.L. Johnson, M.M. Scherer, P.G. Tratnyek, Kinetics of halogenated organic compound degradation by iron metal, *Environ. Sci. Technol.* 30 (1996) 2634–2640.
- [14] J. Cao, L. Wei, Q. Huang, L. Wang, S. Han, Reducing degradation of azo dye by zero-valent iron in aqueous solution, *Chemosphere* 38 (1999) 565–571.
- [15] R. Kober, E. Welter, M. Ebert, A. Dahmke, Removal of arsenic from groundwater by zerovalent iron and the role of sulfide, *Environ. Sci. Technol.* 39 (2005) 8038–8044.
- [16] S.Y. Oh, J.W. Lee, D.K. Cha, P.C. Chiu, Reduction of acrolein by elemental iron: kinetics, pH effect, and detoxification, *Environ. Sci. Technol.* 40 (2006) 2765–2770.
- [17] D.R. Burris, T.J. Campbell, V.S. Manoranjan, Sorption of trichloroethylene and tetrachloroethylene in a batch reactive metallic iron–water system, *Environ. Sci. Technol.* 29 (1995) 2850–2855.
- [18] R.M. Allen-King, R.M. Halket, D.R. Burris, Reductive transformation and sorption of *cis*- and *trans*-1,2-dichloroethene in a metallic iron–water system, *Environ. Toxicol. Chem.* 16 (1997) 424–429.
- [19] J.R. Perey, P.C. Chiu, C.P. Huang, D.K. Cha, Zero-valent iron pretreatment for enhancing the biodegradability of azo dyes, *Water Environ. Res.* 74 (2002) 221–225.
- [20] S.Y. Oh, D.K. Cha, B.J. Kim, P.C. Chiu, Effect of adsorption on the transformation of TNT and RDX with elemental iron, *Environ. Toxicol. Chem.* 21 (2002) 1384–1389.
- [21] M.H. Zwietering, I. Jongenburger, F.M. Rombouts, K. van't Riet, Modeling of the bacterial growth curve, *Appl. Environ. Microbiol.* 56 (1990) 1875–1881.
- [22] APHA, *Standard Methods for the Examination of Water and Wastewater*, 19th ed., American Public Health Association, Washington, DC, 1995.
- [23] B. Ozkaya, A. Demir, M.S. Bilgili, Soluble substrate concentrations in leachate from field scale MSW test cells, *J. Hazard. Mater. A* 134 (2006) 19–26.
- [24] J.J. Lay, Y.Y. Li, T. Noike, Mathematical model for methane production from a landfill bioreactor, *J. Environ. Eng., ASCE* 124 (1998) 730–736.
- [25] C.C. Chen, C.Y. Lin, M.C. Lin, Acid–base enrichment enhances anaerobic hydrogen production process, *Appl. Microbiol. Biotechnol.* 58 (2002) 224–228.
- [26] Q. He, K. Yao, D. Sun, B. Shi, Biodegradability of tannin-containing wastewater from leather industry, *Biodegradation* 18 (2007) 465–472.
- [27] A. Fialová, E. Boschke, T. Bley, Rapid monitoring of the biodegradation of phenol-like compounds by the yeast *Candida maltosa* using BOD measurements, *Int. Biodeter. Biodegr.* 54 (2004) 69–76.
- [28] J.C. Young, L.S. Clesceri, S.M. Kamhawy, Changes in the biochemical oxygen demand procedure in the 21st edition of standard methods for the examination of water and wastewater, *Water Environ. Res.* 77 (2005) 404–410.