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Wastewater screening method for evaluating applicability of zero-valent iron to industrial wastewater

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ABSTRACT

This study presents a screening protocol to evaluate the applicability of the ZVI pretreatment to various industrial wastewaters of which major constituents are not identified. The screening protocol consisted of a sequential analysis of UV–vis spectrophotometry, high-performance liquid chromatograph (HPLC), and bioassay. The UV–vis and HPLC analyses represented the potential reductive transformation of unknown constituents in wastewater by the ZVI. The UV–vis and HPLC results were quantified using principal component analysis (PCA) and Euclidian distance (ED). The short-term bioassay was used to assess the increased biodegradability of wastewater constituents after ZVI treatment. The screening protocol was applied to seven different types of real industrial wastewaters. After identifying one wastewater as the best candidate for the ZVI treatment, the benefit of ZVI pretreatment was verified through continuous operation of an integrated iron-sequencing batch reactor (SBR) resulting in the increased organic removal efficiency compared to the control. The iron pretreatment was suggested as an economical option to modify some costly physico-chemical processes in the existing wastewater treatment facility. The screening protocol could be used as a robust strategy to estimate the applicability of ZVI pretreatment to a certain wastewater with unknown composition.

1. Introduction

Biological processes are commonly used for domestic and industrial wastewater treatment because it is a relatively simple and cost-effective way to efficiently mineralize organic constituents in industrial discharges. However, treatment of some industrial wastewaters by conventional aerobic biological process is difficult due to the presence of refractory and toxic organic substances. Various pretreatment technologies for enhancing the biodegradability of refractory compounds in wastewater have been reported and these include anaerobic treatment [1,2], Fenton oxidation [3], preozonation [4,5], photocatalytic pretreatment [6], and zero-valent iron [7,8]. The zero-valent iron (ZVI) technology is a proven technology to reductively transform several classes of refractory and toxic substances including explosives [9,10], halogenated organic compounds [11,12], nitroaromatic compounds [13–15], highly toxic chemicals [16,17] and azo-aromatics dyes [18–21]. Treatment of wastewaters containing azo dyes, nitroaromatic compounds, and acrolein with ZVI iron markedly enhanced the rates and extents of mineralization of these refractory compounds in subsequent biological oxidation processes [7,8,16].

The mechanism of a redox reaction involving ZVI can occur through at least three mechanisms, each involving a different type of reducing agent. The first mechanism is direct transfer of electron from ZVI to the adsorbed oxidized pollutants. Balko and Tratnyek [22] showed that the reduction of chlorinated compounds by ZVI was controlled by electron transfer at the iron surface. Another possible reduction mechanism involves ferrous ions, which are the products of anaerobic corrosion of ZVI by water. Even though aqueous Fe^{2+} is not an effective reducing agent, Klausen et al. [23] demonstrated that Fe^{2+} ions adsorbed to mineral surfaces (including ZVI surfaces) were capable of readily reducing nitroaromatic compounds to corresponding anilines. The third mechanism of ZVI reduction involves atomic hydrogen, which is released during anaerobic iron corrosion by water. Based on product analysis, Oh et al. [15] showed that atomic hydrogen was an important reductant for the transformation of dinitrotoluene to diaminotoluene.

Since the ZVI reacts preferably with highly oxidized substances, it is important to confirm the presence of the iron reactive substances in the target wastewater when the ZVI is considered as a pretreatment method. However, the constituents of industrial wastewater are not readily identified and may vary from plant to

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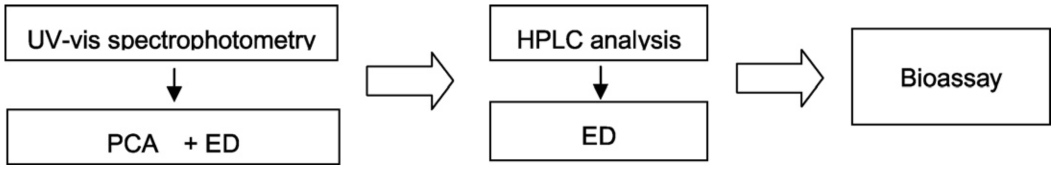

Fig. 1. Schematic of proposed screening protocol for ZVI-treatable wastewater.

plant [24]. Thus, a suitable screening protocol capable of estimating the applicability of ZVI to wastewater with unknown composition is needed. The purpose of this study was to develop a screening protocol using simple and readily available analytical tools to evaluate the ZVI treatment potential of wastewaters without knowing their composition. The enhanced biotreatability of selected wastewater by ZVI pretreatment was verified through the laboratory-scale operation of an integrated ZVI-biological system.

1.1. Proposed screening protocol

The screening protocol proposed in this study consists of a series of chemometric and respirometric analysis: UV–vis spectrophotometry, high-performance liquid chromatograph (HPLC) and bioassay (Fig. 1). The UV–vis screening method was the first step in the screening procedure. The absorbance of wastewater sample was scanned over a broad range of UV–vis wavelength and the shift in the absorbance after ZVI treatment was correlated to the reductive transformation of compounds by ZVI. The degree of changes in the absorbance was quantified using principal component analysis (PCA) and Euclidian distance (ED). Secondly, the wastewater samples that exhibited a significant shift in the first screening step were selected for the HPLC analysis. The HPLC screening method examined the fate of each unidentified organic peaks after ZVI treatment. The shift in the peak distribution was attributed to the strong reactivity of chemical contaminants in the wastewater with ZVI. The greater changes in the peak distribution (removed and appeared) after ZVI treatment indicated that more organic constituents were reactive with ZVI. Similar to the UV–vis screening method, the degree of the change in HPLC peak distribution was quantified using ED. The final screening step was the short-term respirometric analysis to evaluate the enhanced aerobic biodegradation of the wastewater due to the ZVI reduction of the refractory substances.

2. Materials and methods

2.1. Industrial wastewater

Seven different types of industrial wastewater samples were collected for screening test and their characteristics are summarized in Table 1. These industrial wastewaters were selected as candidates for this screening test based on our survey results; the selected treatment facilities have experienced insufficient biological treatment efficiency at one time or another. In order to prevent reductive transformation of the samples during delivery, wastewater samples (1 L) were collected and stored in a 2-L plastic container with a sufficient head space. Immediately after receiving the wastewater samples, they were filtered with 0.2-μm membrane filters to minimize the potential interference of particles on the rate of iron-reduction reactions and stored for subsequent iron-reduction experiments.

2.2. Batch iron-reduction experiment

Batch reduction experiments were conducted using 15-mL glass vials containing 7.5 mL of wastewater samples and 2.5 g of high purity iron powder (99.5%, <10-μm, Aldrich, WI). The pH of each wastewater sample was adjusted to 4.0 using 1.0 M hydrochloric acid to provide a favorable condition for the rapid ZVI reduction [16,25,26]. Each batch reaction vials was prepared in an anaerobic glove box filled with 95% nitrogen and 5% hydrogen (Coy Laboratory, Grass Lake, MI). The vials were horizontally placed on a rotary shaker and continuously mixed at 160 rpm. All batch reduction experiments were conducted at room temperature (21 ± 1 °C). After 3 h of incubation, the experimental vials were centrifuged and supernatant was vacuum filtered through a 0.2-μm membrane filter for subsequent analysis by a HPLC or a UV–vis spectrophotometer.

2.3. Respirometric bioassay

Aerobic biodegradability of wastewater samples was assessed using a Hach BOD apparatus (Hach BODTrak, Loveland, CO). The apparatus continuously measured change in oxygen partial pressure resulting from aerobic respiration inside a sealed BOD bottle. The system was interfaced with a PC for automatic data acquisition at fixed time intervals. Duplicate 340 mL of diluted wastewater samples were transferred to 600-mL dark BOD bottles. Five milliliters of nitrification inhibitor solution (36 g/L, Hach Formula 2533) and 20 mL of 0.5 M phosphate buffer solution were added along with a capsule of BOD nutrient buffer (Hach). A BOD seed (Hach) was pre-aerated and settled, and 5 mL of supernatant was used to inoculate each sample. Lithium hydroxide powder was placed near the top of the bottle to absorb CO_2 generated from aerobic respiration. The bottles were sealed and placed in a temperature-controlled incubator at 25 °C for 5 days. BOD values of test samples were corrected against cumulative BOD of control bottles due to endogenous respiration.

Table 1
Characteristics of the industrial wastewaters tested for this study.

Wastewater	Type of industry	TOC (mg/L)	COD (mg/L)	pH
E	Electronics	1520 ± 156	4460 ± 110	7.1
P	Personal care products	2080 ± 292	4650 ± 70	6.4
C1	Chemical ([a]display device coating, battery)	147 ± 7	440 ± 40	8.8
C2	Chemical ([a]personal care products)	136 ± 25	190 ± 7	8.7
C3	Chemical ([a]UV stabilizer)	4084 ± 587	11,500 ± 140	2.1
C4	Mixed chemical + domestic ([a]UV stabilizer, dye)	2633 ± 177	4330 ± 250	9.4
D	Mixed (dye + domestic)	127 ± 11	250 ± 9	7.5

[a] Primary manufacturing products of the chemical industry.

2.4. Integrated iron-bioreactor system

Integrated iron-bioreactor system consisted of an iron-packed column and a biological reactor operated in sequencing batch reactor (SBR) mode. A glass column (50 mL) was filled with a mixture of cast iron granules (Peerless Inc., Detroit, MI) and Ottawa sand (1:1 volume ratio). The iron column was operated in an up-flow mode with a contact time of 1.5 h. The iron column effluent was collected in a sealed glass vessel (4 L), which served as a feed reservoir for SBR. The glass vessel was continuously purged with nitrogen gas to minimize oxidative degradation of organics prior to entering the SBR. Bench-scale SBR units were constructed with rectangular plexiglass reactors with a liquid volume of 2 L. The dissolved oxygen (DO) concentration was maintained above 6 mg/L with pure oxygen supply.

The SBR was operated with a 12-h fill-and-draw cycle that consisted of 1-h feeding period, 10-h aeration/mixing period, followed by 0.5-h settling period, and 0.5 h of supernatant decanting. The hydraulic retention time (HRT) and solids retention time (SRT) of the SBR were 3.5 and 20 days, respectively. The SBR was supplemented with appropriate amounts of NH_4Cl and KH_2PO_4 daily to prevent nutrient deficiency.

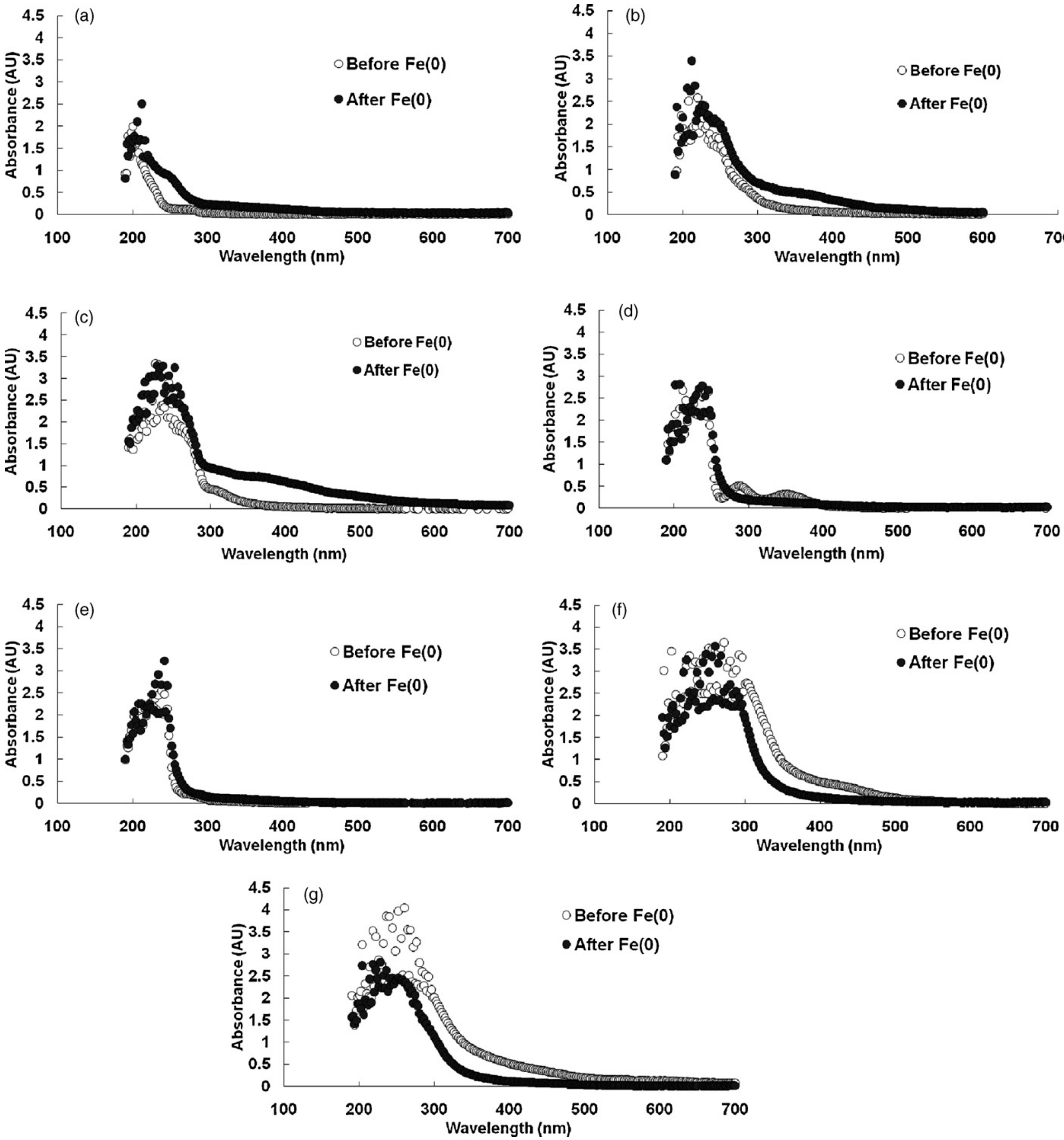

Fig. 2. UV–vis absorption profiles of various wastewaters before and after ZVI treatment: (a) E, (b) D, (c) P, (d) C1, (e) C2, (f) C3, and (g) C4.

2.5. Analytical methods

The sample pH was measured using a bench-top pH meter (Cole-Parmer, USA). Total organic carbon (TOC) was determined using a Rosemount Dohrmann DC-190 TOC analyzer. A UV–vis spectrophotometer (Hewlett Packard 8452, USA) was used to measure the absorbance of wastewaters within UV and visible wavelength ranges (190–720 nm). The HPLC (Agilent series 1100, Germany) equipped with a Diode Array Detector (DAD) was used to determine the distribution of organic constituents at 254 nm of wavelength. The mobile phase was 40% acetonitrile solution and the flow rate was 1.5 mL/min.

2.6. Statistical analysis

Principal component analysis (PCA) was conducted for multivariate analysis of UV–vis scanning data using a ‘princomp’ procedure in SAS 9.1. PCA is a statistical technique for reducing the complexity of high-dimensional data. A high-dimensional raw data matrix is inputted and a summarized data with a fewer dimension is created as an output through the ‘princomp’ procedure. Each dimension created is called as a principal component and represents a linear combination of the original variables. In detail, the PCA is to establish a set of new eigenvectors extracting principal components from multi-variables (raw UV–vis scanning data) and ultimately to plot the extracted principal components with recreated scores onto the reduced dimensional plane (mostly two or three dimension). The efficiency of extraction from raw data is explained by eigenvector coefficient for two major principal components.

3. Results and discussion

3.1. UV–vis screening test

Minimal loss of TOC was observed after ZVI treatment indicating that adsorption of organic pollutants to the pure iron powder was insignificant. Iron-reduction process resulted in pH increase of 1–2 pH units in all wastewater samples (data not shown).

Fig. 2 shows the UV–vis absorption profiles for the wastewater samples before and after ZVI treatment. The profile was noticeably shifted after ZVI treatment for all wastewater samples except samples C1 and C2, which were relatively low strength wastewater. Significant shift in absorbance was primarily observed at the UV range especially between 200 and 300 nm regardless of sample. The absorbance at the visible range (400–720 nm) was markedly changed in ‘D’, ‘P’, ‘C3’ and ‘C4’ wastewater indicating that the color was changed or disappeared due to ZVI-mediated transformations.

The change in absorbance before and after ZVI treatment was quantified using PCA. The PCA enabled the reduction of UV–vis absorbance data into a small size data set without impairing the raw data. Two major principal components (PC1 and PC2) were extracted from multi-variables (wavelengths in this study) of each sample and plotted onto the two-dimensional planes of PC1 (x-axis)–PC2 (y-axis). Fig. 3(a) and (b) shows the PCA result for each sample scanned at the UV (190–398 nm) and visible (400–720 nm) range, respectively. Data extraction by PCA was meaningful because the first major principal component (PC1, x-axis) resulted in a relatively high eigenvector coefficient of 72.5% and 92.4% for the UV and visible range absorbance, respectively (Fig. 3(a) and (b)). The absorbance change due to the reduction reaction by ZVI was quantified by computing the Euclidian distance (ED) between the samples before and after ZVI treatment using the following equation:

$$\text{Euclidian distance (ED)} = \sqrt{\frac{\lambda_1}{\lambda_1+\lambda_2}(x_b - x_a)^2 + \frac{\lambda_1}{\lambda_1+\lambda_2}(y_b - y_a)^2} \quad (1)$$

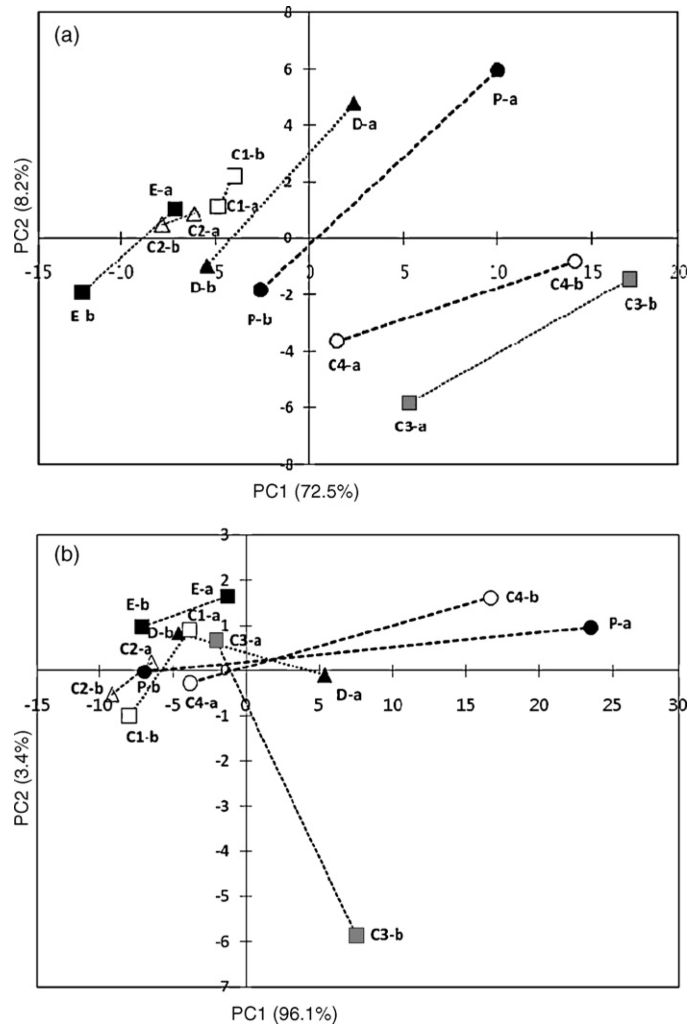

Fig. 3. Plot of PC scores of the wastewaters before (shown as ‘-b’) and after (shown as ‘-a’) ZVI treatment. PCA was conducted for the absorbance data at the (a) UV range and (b) visible range.

where λ_1 and λ_2 are the eigenvector coefficients for PC1 and PC2; x_b the PC score for PC1 before ZVI treatment; x_a the PC score for PC1 after ZVI treatment; y_b the PC score for PC2 before ZVI treatment; y_a is the PC score for PC2 after ZVI treatment.

Table 2 summarizes the ED results of UV–vis screening data for the wastewater samples tested in this study. The higher value of ED indicates the greater shift in absorbance. The highest ED values were observed for the samples C4 and P were for both UV and visible ranges. The top five ranked wastewaters (E, D, P, C3 and C4) were selected for the next screening test and the two bottom ranked wastewater, C1 and C2 were excluded from the subsequent tests.

Table 2
ED value for each wastewater obtained from UV–vis screening method.

Wastewater	UV range	Visible range
E	4.4	5.6
P	11.2	29.4
C1	1.0	3.9
C2	1.5	2.6
C3	10.4	9.2
C4	11.3	19.8
D	7.0	9.7

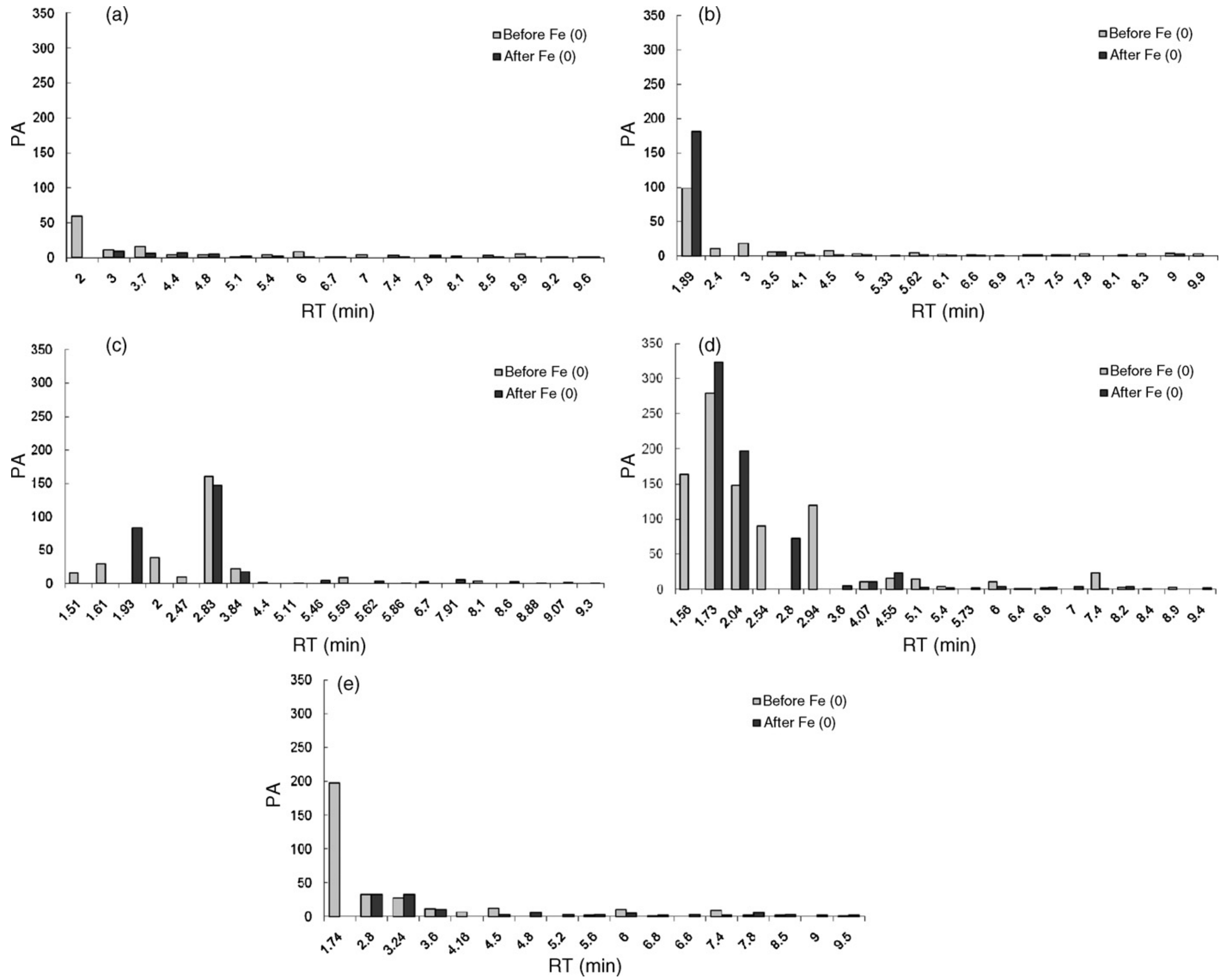

Fig. 4. Peak distribution of the various wastewaters before and after iron treatment in HPLC analysis. Wastewater: (a) E, (b) D, (c) P, (d) C3, and (e) C4.

3.2. HPLC screening test

Based on the UV–vis scanning results, the wavelength of 254 nm was selected for the HPLC analysis of five selected wastewater samples. Detected peak areas from HPLC analysis of five wastewaters before and after ZVI treatment are shown in Fig. 4. The peak distribution appeared to shift after the ZVI treatment in all wastewaters as the areas of some peaks decreased while some increased. In addition, some peaks disappeared and some new peaks appeared after ZVI treatment, especially in the samples P, C3 and C4. These results suggested that the constituents in P, C3 and C4 were more susceptible to ZVI reduction reactions. Similar to UV–vis screening, multivariate analysis was performed on the peak area data and ED values were calculated for each wastewater sample: E (61.3), D (86.6), P (100.8), C3 (244.8) and C4 (198.8). Since ED values for the samples C3 and C4 were substantially higher than those of the other three samples, they were considered to be more reactive to ZVI and thus they were selected as candidates for the subsequent biodegradation assay.

3.3. Short-term bioassay

Respirometric analysis was conducted to determine the effect of ZVI treatment on aerobic biodegrdability of two selected wastewaters (C3 and C4). Fig. 5 shows that the biodegradable fraction of the C3 and C4 wastewater increased after iron treatment. The biooxidation was represented by BOD data normalized to initial COD values. The biodegradable fraction in C4 increased from 45% to 60% after ZVI treatment; on the other hand, even though an enhancement in

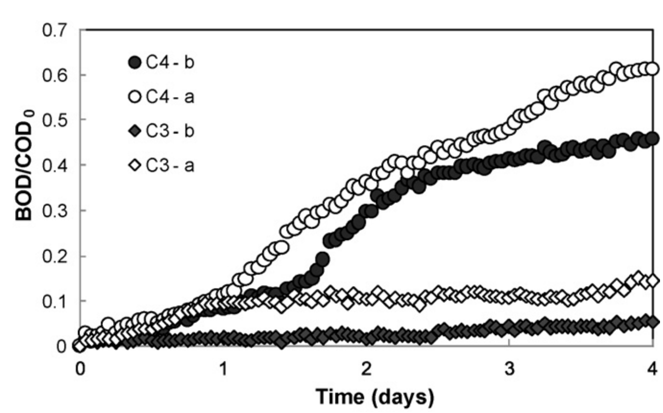

Fig. 5. Biodegradation of the C3 and C4 wastewaters before and after ZVI treatment in short-term bioassay.

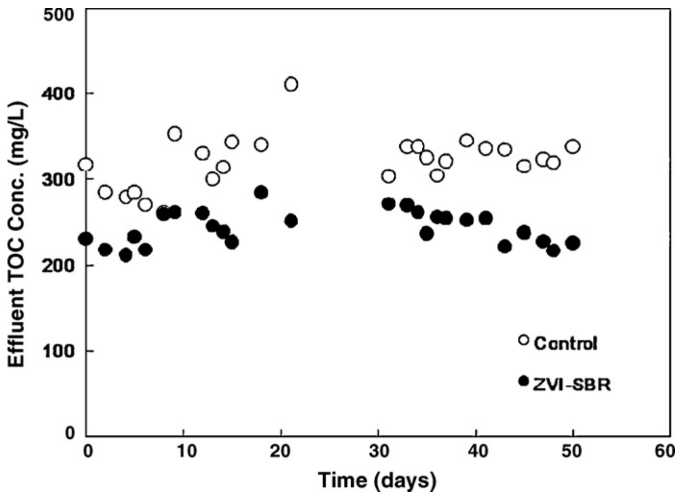

Fig. 6. Effluent TOC concentrations in the control and ZVI-SBR for treatment of C4 wastewater. The average influent TOC concentration was 910 mg/L in this experiment.

biodegradability was evident with ZVI treatment of sample C3, the biooxidation of C3 remained low. The bioassay data suggests that a large portion of recalcitrance compounds in the C4 wastewater was converted to biodegradable substances by ZVI treatment. Based on the bioassay tests, the C4 wastewater was determined as the most suitable wastewater for ZVI pretreatment.

3.4. Verification of screening protocol with integrated iron-SBR system

The integrated iron-SBR system was operated for 50 days with the C4 wastewater to investigate the effect of iron pretreatment on organic removal. Due to severe foaming in the aeration basins, pure oxygen aeration with low gas flow rate was used to maintain dissolved oxygen concentrations of >6.0 mg/L. TOC concentrations in system effluents were consistently lower in the integrated ZVI-SBR system than the control system throughout the 50-day experimental period (Fig. 6). Average effluent TOC concentration during the last 20 days of reactor operation was 330 mg/L for the control SBR system and 240 mg/L for the integrated ZVI-SBR system. This improved organic removal in the ZVI-SBR system is most likely due to reductive transformation of refractory organic constituents by ZVI to more biodegradable compounds.

The existing C4 facility currently treats the wastewater with a pure oxygen activated sludge followed by granular activated carbon (GAC) sorption as a post-treatment. The GAC process not only is expensive but also generates contaminant-laden spent carbon, a hazardous waste that needs to be regenerated or disposed properly. This study demonstrated that the ZVI technology can efficiently and economically transform refractory constituents in wastewater to compounds that are more amenable to biological treatment processes.

4. Conclusion

A screening protocol was developed for selecting a wastewater for the applicability of ZVI treatment. Seven different types of industrial wastewaters were selected as candidates without sufficient information on their compositions. The screening protocol consisted of a sequential analysis of UV–vis spectrophotometry, HPLC, and bioassay. UV–vis screening was able to readily identify the wastewaters with low reactivity toward ZVI and minimal changes in absorbance were eliminated from the subsequent treatability tests. The HPLC screening step allowed the selection of two chemical wastewaters (C3 and C4) as the potential candidates for ZVI pretreatment based on the substantial shift in peak profiles. Respirometric analysis demonstrated that the wastewater C4 was the most favorable candidate for ZVI application with a significant enhancement of biodegradability. Lab-scale operation of SBR coupled with the iron pretreatment significantly increased removal of recalcitrant organics from the selected wastewater (C4) demonstrating that the screening protocol developed in this reported study was reliable in selecting the appropriate wastewater for ZVI treatment without having the detailed composition data. In general, it is difficult and costly to identify most of wastewater constituents and thus limit the widespread applications of ZVI technology to wastewaters. The screening protocol reported in this study will be able to overcome this limitation with using quick and readily available analytical tools. The screening strategy may be used for not only selecting the potential wastewaters for ZVI pretreatment but also determining the best applicable treatment technologies for a certain wastewater.

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