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Graphical abstract
Selective removal of nitroaromatic compounds from wastewater in an integrated zero valent iron (ZVI) reduction and ZVI/H$_2$O$_2$ oxidation process

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Abstract

In this study, an integrated system comprised of zero-valent iron (ZVI) reduction and ZVI-based Fenton oxidation process (ZVI-ZVI/H$_2$O$_2$) was applied for the selective removal of nitroaromatic compounds (NACs) from 2,4-dinitroanisole (DNAN) producing wastewater. For ZVI reduction process, at hydraulic retention time (HRT) of 6 h and natural pH of 7.2, removal efficiencies of 2,4-dinitroanisole (DNAN), 2,4-dinitrophenol (DNP) and 2,4-dinitrochlorobenzene (DNCB) were as high as 81.3±3.6%, 80.6±1.8% and 90.9±3.5%, respectively, demonstrating the excellent performance of ZVI. For ZVI/H$_2$O$_2$ oxidation process, the optimal pH and H$_2$O$_2$ dosage were found to be 3.0 and 100 mmol/L, respectively. Under this optimal condition, NACs and their degradation intermediates could be removed selectively and effectively in the coupled ZVI reduction and ZVI/H$_2$O$_2$ oxidation process, as was indicated by the low UV$_{254}$ value of 0.104±0.003 and the low TOC removal efficiency of 32.4±0.7% in the effluent. Ferrous ions could be generated in situ through the corrosion of the metal iron in both the ZVI reduction process and ZVI/H$_2$O$_2$ oxidation process, giving rise to potent Fenton-type reaction. In addition, the enhanced Fenton reaction with the aid of reaction between Fe$^0$ and Fe$^{3+}$ was probably due to the presence of Fe$^0$ in ZVI/H$_2$O$_2$ oxidation process, which promoted the utilization efficiency of Fenton catalyst, i.e., Fe$^{2+}$. Compared to the sequential ZVI reduction and homogeneous Fenton oxidation process (ZVI-Fe$^{2+}$/H$_2$O$_2$), the low consumption of iron shavings, the reduced H$_2$O$_2$ consumption and the low yield of ferric sludge made the integrated ZVI-ZVI/H$_2$O$_2$ process promising for the treatment of NACs containing wastewater.

Keywords: Nitroaromatic compound; Reduction; Oxidation; Zero valent iron; Fenton
1. Introduction

2,4-Dinitroanisole (DNAN), one of the insensitive munitions (IMs), is considered as a promising substitute for 2,4,6-trinitrotoluene (TNT), as it is a less sensitive melt-cast medium than TNT.\textsuperscript{1,2} With the increasing production of IMs such as DNAN, industrial wastewater will be increasingly released to the environment. The discharge of these wastewaters to the environment poses a health concern since many nitroaromatic compounds (NACs) in it are toxic and mutagenic in nature.\textsuperscript{5-5} During the production of DNAN, raw materials such as 2,4-dinitrochlorobenzene (DNCB) and methanol, final product DNAN, as well as the byproducts such as 2,4-dinitrophenol (DNP), are the major constituents in DNAN producing wastewater. DNAN producing wastewater is always characterized by intense color, high toxicity, concentrated substrate and salt (usually exceeding 3 wt.%), poor decolorization.\textsuperscript{6}

Available conventional processes, including adsorption, solvent extraction, microbial degradation and chemical oxidation, are effective in the remediation of the site contaminated by NACs. The physical-chemical methods, such as adsorption, solvent extraction and chemical oxidation, suffer from such drawbacks as harsh conditions, high cost, formation of toxic byproducts, therefore their applicability was limited to some extent.\textsuperscript{7} In addition, because of the strong electron-withdrawing nature of nitro group on the NACs, DNAN producing wastewater is generally refractory for the biological treatment processes, which is environmental friendly and cost effective.\textsuperscript{8} Therefore, considering the highly toxic and recalcitrant nature of NACs in DNAN producing wastewater, the physical-chemical pretreatment before biological process is essential and highlighted.

In our previous study, the combined ZVI reduction process and homogeneous Fenton oxidation process (ZVI-Fe\textsuperscript{2+}/H\textsubscript{2}O\textsubscript{2}) has been developed for the efficient pretreatment of DNAN producing wastewater.\textsuperscript{6} In this combined process, ZVI process was used for the efficient reductive transformation of NACs. The unstable aminoaromatic compounds produced in the ZVI reduction process could be removed easily through the sequential Fe\textsuperscript{2+}/H\textsubscript{2}O\textsubscript{2} oxidation process. In addition, Barreto-Rodrigues et al.\textsuperscript{9} found that TNT could be effectively removed in the
ZVI-Fe$^{2+}$/H$_2$O$_2$ process. ZVI has drawn great attention as an inexpensive, environmentally friendly and strong reducing agent.$^{10,11}$ The reductive transformation of the nitro functional groups by ZVI overcame the hindrance to oxidation in the sequential Fenton process.$^{12-15}$ The high efficiency of ZVI-Fe$^{2+}$/H$_2$O$_2$ process made it a promising choice for the treatment of DNAN producing wastewater. However, the main drawback of homogeneous Fenton process was related to the high consumption of H$_2$O$_2$ and ferrous iron salts. In addition, iron ions should be separated from the treated effluent through precipitation, leading to considerable generation of ferric sludge which required further treatment. Thus, the ZVI-Fe$^{2+}$/H$_2$O$_2$ process become economically prohibitive for DNAN producing wastewater.

In this study, a novel system comprised of ZVI reduction and ZVI-based Fenton oxidation process (ZVI-ZVI/H$_2$O$_2$) was applied for the selective removal of NACs from DNAN producing wastewater. It was noteworthy that ZVI was applied as catalyst in Fenton oxidation process for the replacement of Fe$^{2+}$. The operation condition was optimized and the overall performance of this integrated process was evaluated. Moreover, the possible mechanism for the enhanced NACs removal in the integrated ZVI reduction and ZVI/H$_2$O$_2$ oxidation system was explored preliminary.

2. Material and methods

2.1. Materials

DNAN, DNCB and DNP were provided by Hubei Dongfeng Chemical Co. Ltd. in Hubei Province, China. Iron shavings of 30CrMoSi steel were used in this study. The iron shavings contained iron (>95%), carbon (0.30-0.35%), silica (0.2-0.35%), chromium (1.40-1.70%), manganese (0.40-0.60%), Molybdenum (0.15-0.25%), aluminum (0.60-0.78%), and a few other trace elements. All other chemicals were of the highest purity available and were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China).

2.2 Characteristics of DNAN producing wastewater

Table S1 showed the characteristics of DNAN producing wastewater taken from
Hubei Dongfang Chemical Co. Ltd. The wastewater was characterized by its extremely high COD concentration but relatively low NACs concentration. The high COD was attributed to the high strength of methanol, which could be easily removed through subsequent biological process. However, the NACs, such as DNAN, DNCB and DNP, which were highly toxic and recalcitrant, should be removed prior to the subsequent biological process.

2.3 Experimental equipment

The performance of the integrated ZVI reduction and ZVI-based Fenton oxidation (ZVI-ZVI/H$_2$O$_2$) system was investigated in a lab-scale reactor, as shown in Fig. 1. The reactor was consisted of three parts, i.e., sludge collecting zone, ZVI reduction zone and ZVI/H$_2$O$_2$ oxidation zone, with the total empty bed volume of 5.1 L. The empty bed volumes of ZVI reduction area and ZVI/H$_2$O$_2$ oxidation area were 1.3 L and 1.7 L, respectively. Air diffuser was installed in the sludge collecting area for the washing of the ZVI bed in both ZVI reduction zone and ZVI/H$_2$O$_2$ oxidation zone, so as to keep high activity of ZVI. Both ZVI reduction zone and ZVI/H$_2$O$_2$ oxidation zone were filled respectively with 0.2 kg iron shavings. In order to improve NACs reduction performance in reduction process, the iron shavings used in the reduction area was doped by Cu. 0.2 wt. % of copper was applied to the iron surface by reductive precipitation to form the so-called bimetallic ZVI structures. However, fresh iron shavings were filled in ZVI/H$_2$O$_2$ oxidation area but without the doping of Cu. The operation temperature during the test period was varied between 20 and 25°C.

2.4 Experimental procedure

The DNAN producing wastewater at natural pH was pumped into the bottom of ZVI reduction zone by peristaltic pump. In order to investigate the effectiveness of ZVI process in the treatment of DNAN producing wastewater, DNAN, DNCB, DNP, TOC concentrations, and EC$_{50, 48 \text{ h}(\% \text{, v/v})}$ of the influent and effluent were monitored at hydraulic retention time (HRT) of 4-7 h.

H$_2$O$_2$ and diluted H$_2$SO$_4$ were added into the effluent of the ZVI reduction process
by peristaltic pumps. Then the mixture flowed upwards through the ZVI bed in the ZVI/H$_2$O$_2$ oxidation area at HRT of 8 h. Operation parameters of the ZVI/H$_2$O$_2$ oxidation process, such as pH and H$_2$O$_2$ dosage, were optimized respectively. During pH optimization, the ZVI/H$_2$O$_2$ oxidation process was operated at H$_2$O$_2$ dosage of 100 mmol/L, while pH varied in range of 2.0-6.0. During the optimization of H$_2$O$_2$ dosage, the ZVI/H$_2$O$_2$ oxidation process was operated at pH of 3.0, while H$_2$O$_2$ dosage varied from 60 to 140 mmol/L.

2.5. Analytical methods

Before analysis, water samples were passed through a 0.22 µm filter. COD, TOC and acute toxicity were determined according to our previous study. Before COD analysis, samples were heated on the water bath at 80°C for 40 min to eliminate the residual H$_2$O$_2$. DNAN, DNCB, DNP were identified and quantified by HPLC (Waters 2996, Waters Incorporation, USA) through authentic standard and UV-vis light analysis. The HPLC analysis was conducted at room temperature using a Waters RP18 column (5 µm, 4.6 mm×250 mm) and a UV–vis detector. The mobile phase was a mixture of 45% methanol and 55% water pumped at a flow rate of 1.00 mL/min. The analysis was performed at 254 nm, with column temperature at 35°C. Aromatic compounds in the wastewater were evaluated by UV$_{254}$. Dissolved iron concentration was determined by using atomic absorption spectrometry (PinAAcle900T, PerkinElmer, America). The concentration of ferrous ion was measured through o-phenanthroline colorimetric method on an UV/vis spectrophotometer. Indirect determinations of hydroxyl radicals were carried out by quantitating hydroxyl radical reactions with benzoic acid, which produced p-hydroxybenzoic acid. ZVI before and after use in the ZVI bed was characterized through scanning electron microscope (SEM) (JSM-6380, JEOL, Japan), X-ray powder diffraction (XRD) (D8 Advance, Bruker, Germany) and Raman spectroscopy (LabRAM Aramis, HORIBA JOBIN YVON, France). Surface morphology of ZVI was characterized by the SEM and all samples were dried at room temperature. XRD recorded in the 2θ range from 20° to 80° were obtained with a Philips X-Pert diffractometer using Cu Kα radiation. Raman
spectroscopy were recorded by the Raman spectrometer using 0.1 M HClO₄ as electrolyte, a platinum wire as counter electrode, and an Ag/AgCl electrode as the reference electrode.

3. Results and discussion

3.1 Characterization of ZVI reduction process

It is also very important to determine the appropriate HRT because the performance of ZVI reduction process is associated with HRT closely. The efficiency would decrease and the construction cost would increase if HRT is too long. Thus, the effect of HRTs on NACs reduction was investigated to determine an optimal HRT for further research. From Fig. 2, it could be seen that DNP, DNAN and DNCB reduction efficiencies increased with the increase of HRT from 4 h to 7 h. At HRT of 6 h, reduction efficiencies of DNAN, DNP and DNCB were as high as 81.3±3.6%, 80.6±1.8% and 90.9±3.5% respectively. However, no insignificant improvement in terms of NACs reduction was observed with further increase of HRT to 7 h. Therefore, HRT of 6 h for ZVI process was chosen as the optimal parameter for further investigation.

Considering the involvement of hydrogen ions in the ZVI reduction, it was believed that pH plays a significant role in the ZVI reduction process. Obviously, the acidic condition was favorable for ZVI reduction. At lower pH, the passive oxide layer on the iron surface could be eliminated, with the enhanced release of Fe²⁺ and electron, increased reactive sites and lower oxidation-reduction potential (ORP) value, which were all beneficial for NACs reduction. However, ZVI consumption and hardness of ZVI bed could be aggravated at acidic pH values, restricting the life span of the ZVI process. Therefore, it was necessary to explore an effective way to enlarge the pH range on the premise of maintaining high reduction efficiency. It was well known that iron could be oxidized much faster when it was in contact with a less active metal (e.g., Cu, Pd, Ag). The coupled iron and less active metal formed galvanic cells where iron served as the anode and could be preferably oxidized. The Cu-doped iron shavings showed good reactivity over a wide pH range in the NACs reduction process.
Excellent reduction performance of NACs was observed at neutral pH using Cu-doped iron shavings in our previous study.\textsuperscript{16} Thus, considering the reduction efficiency and the consumption of the iron shaving, DNAN producing wastewater was fed into Fe-Cu reduction process at natural pH of 7.2, but without acidification.

### 3.2 Characterization and optimization of Fenton process

#### 3.2.1 Effect of pH

pH is an important factor affecting the Fenton oxidation process since pH is closely related to catalytic activity, oxidant activity, dominant iron species and the stability of hydrogen peroxide.\textsuperscript{23-26} As shown in Fig. 3a, the residual NACs from the effluent of ZVI reduction process could be further removed at various pH values in ZVI/H\textsubscript{2}O\textsubscript{2} oxidation process, probably due to the reduction by ZVI or the oxidation by Fenton reagent. At pH of 3.0, the removal efficiencies for DNAN, DNP and DNCB in ZVI/H\textsubscript{2}O\textsubscript{2} effluent were as high as 95.8±0.2\%, 100±0.0\% and 99.9±0.1\%, respectively. UV\textsubscript{254} value increased and TOC removal decreased when pH increased from 3.0 to 6.0 (Fig. 3b). The minimal UV\textsubscript{254} value of 0.104±0.003 and the maximum TOC removal efficiency of 32.4±0.7\% were observed at pH of 3.0.

The high removal of DNCB in the effluent of the integrated process could be attributed to the high removal of DNCB in the reduction process, because DNCB reduction occurs more efficiently compared to DNAN and DNP. The high removal of DNP in the effluent of the integrated process could be attributed to the fact that DNP could be more readily removed in the ZVI/H\textsubscript{2}O\textsubscript{2} process. Therefore, the removal of DNAN in the effluent of the integrated process was relatively low. At low pH, ZVI could be easily dissolved, with more Fe\textsuperscript{2+} ions released, resulting in the increased formation of hydroxyl radicals.\textsuperscript{27} However, too low pH would adversely affect the Fenton reaction. When pH was below 3.0, the significant reduction in terms of TOC and UV\textsubscript{254} removal might be attributed to scavenging of hydroxyl radicals with H\textsuperscript{+} ions. At high pH values, more hydrogen peroxide could be decomposed without participation in the oxidation reaction. In addition, as pH further increased, the ferrous ions got converted to ferric ions, which could react with hydroxyl radicals to produce
ferric hydroxide, thereby reducing the availability of ferrous ions in the solution. Therefore, the optimal pH for ZVI/H$_2$O$_2$ oxidation process was around 3.0, which was in agreement with the optimal pH range of 2.5-3.5 reported in the literature.$^{28-32}$

3.2.2 Effect of H$_2$O$_2$ dosage

In Fenton system, H$_2$O$_2$ dosage is an important parameter which can significantly influence the degradation of organic pollutions since H$_2$O$_2$ dosage is directly related to the generation of hydroxyl radicals. Fig. 4 showed the contaminant removal at H$_2$O$_2$ dosage over a range of 60-140 mmol/L at pH 3.0. As H$_2$O$_2$ dosage increased from 60 mmol/L to 100 mmol/L, the removal efficiencies of the three NACs in the effluent of the integrated process increased obviously. At H$_2$O$_2$ dosage of 100 mmol/L, the removal efficiencies of DNAN, DNP and DNCB in the effluent of the integrated process were as high as 95.8±0.2%, 100±0.0% and 99.9±0.1%, respectively. However, further increase of H$_2$O$_2$ dosage resulted in the decrease of NACs removal. At H$_2$O$_2$ dosage of 140 mmol/L, the removal efficiencies of DNAN, DNP and DNCB decreased to 88.8±2.7%, 93.5±2.8% and 95.9±2.9%, respectively. UV$_{254}$ value and TOC removal followed the same trend as NACs removal. As the H$_2$O$_2$ dosage increased from 60 mmol/L to 100 mmol/L, the UV$_{254}$ value decreased and TOC removal increased, and minimum UV$_{254}$ value of 0.104±0.003 and maximum TOC removal efficiency of 32.4±0.7% was achieved at H$_2$O$_2$ dosage of 100 mmol/L. Further increase of H$_2$O$_2$ dosage resulted in the increase of residual UV$_{254}$ and TOC.

From these results, it could be inferred that high H$_2$O$_2$ dosage was beneficial for contaminant removal, however, overhigh H$_2$O$_2$ dosage affected the contaminant removal adversely. Similar phenomenon has been observed in previous studies.$^{33,34}$ This was due to the fact that sufficient hydroxyl radicals could be produced at relatively high H$_2$O$_2$ dosage. However, excessive dosage of H$_2$O$_2$ induced the radical scavenging reaction.$^{35-38}$ According to Eq.(1), excessive dosage of H$_2$O$_2$ resulted in the generation of hydroperoxyl radical HO$_2$•, which was much less reactive than hydroxyl radical HO•. In addition, HO• could be further quenched by HO$_2$•, further resulting to the exhaustion of HO• (Eq.(2)).
\[
\text{HO}^\bullet + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{HO}_2^\bullet \quad \text{Eq. (1)}
\]
\[
\text{HO}_2^\bullet + \text{HO}^\bullet \rightarrow \text{H}_2\text{O} + \text{O}_2 \quad \text{Eq. (2)}
\]

Therefore, \( \text{H}_2\text{O}_2 \) dosage of 100 mmol/L was selected for the treatment of DNAN producing wastewater for the further study.

3.3 Generation of hydroxyl radicals and release of iron ions in ZVI/\( \text{H}_2\text{O}_2 \) process

The success of Fenton process depends on the formation of hydroxyl radicals, because hydroxyl radical generation has crucial role during the removal of contaminant in wastewater. The generation of ferrous ions in the bulk liquid promoted the generation of hydroxyl radicals through typical Fenton reaction. As Fig. 5a shown, the yield of hydroxyl radicals increased as \( \text{H}_2\text{O}_2 \) dosage increased from 60 mmol/L to 80 mmol/L at pH 3.0. However, further increase of \( \text{H}_2\text{O}_2 \) dosage resulted in a sharp decrease of hydroxyl radical concentration as the excess \( \text{H}_2\text{O}_2 \) could be the scavenger of \( \text{HO}^\bullet \). According to Fig. 5b, the concentration of total dissolved iron ions increased simultaneously with the increase of \( \text{H}_2\text{O}_2 \) dosage, probably due to the increased ZVI corrosion at the presence of \( \text{H}_2\text{O}_2 \). However, the concentration ratio of \( \text{Fe}^{2+} \) to \( \text{Fe}^{3+} \) reached maximum at \( \text{H}_2\text{O}_2 \) dosage of 100 mmol/L. As \( \text{H}_2\text{O}_2 \) dosage increased from 60 mmol/L to 100 mmol/L, the concentration ratio of \( \text{Fe}^{2+}/\text{Fe}^{3+} \) increased concomitantly. However, with the further increase of \( \text{H}_2\text{O}_2 \) dosage from 100 mmol/L to 140 mmol/L, the concentration ratio of \( \text{Fe}^{2+}/\text{Fe}^{3+} \) decreased obviously, probably due to the increased transformation of \( \text{Fe}^{2+} \) to \( \text{Fe}^{3+} \) at relatively high \( \text{H}_2\text{O}_2 \) dosage.\(^{39}\) In addition, ORP would increase when excess \( \text{H}_2\text{O}_2 \) was applied, which had negative effect on the transformation of \( \text{Fe}^{3+} \) to \( \text{Fe}^{2+} \).\(^{40}\)

3.4 Characterization of ZVI surface

Fig. S1 showed the SEM images of the ZVI shavings before and after use in the ZVI bed. Fresh ZVI appeared to be smooth (Fig. S1a), while stripes occurred on the surface of ZVI after reduction process, which was due to the slight corrosion happened to ZVI (Fig. S1b). The surface of ZVI after reduction process mainly maintained smooth and clean, indicating that no obvious iron oxides or intermediates...
was adsorbed to ZVI surface. However, serious corrosion was observed on the ZVI shavings after ZVI/H$_2$O$_2$ oxidation process, which was probably due to the acidic environment and existence of H$_2$O$_2$ in the ZVI/H$_2$O$_2$ area (Fig. S1c). The leaching of Fe$^{2+}$ and Fe$^{3+}$ from surface of ZVI and the reaction between Fe$^{0}$ and Fe$^{3+}$ aggravated the consumption of ZVI. In addition, the corrosion during ZVI/H$_2$O$_2$ process would lead not only to the formation of ferrous ions, but also to the generation of iron oxides on the ZVI surface.

The presence of iron oxides on the surface of ZVI after reduction and ZVI/H$_2$O$_2$ process were further confirmed by the following XRD patterns and Raman spectra, as shown in Fig. 6. The peaks at 44.75° and 65.2° represented the characteristic peaks of Fe$^{0}$ (Fig. 6a). After ZVI/H$_2$O$_2$ oxidation process, although the characteristic peaks of Fe$^{0}$ were still present, the appearance of new weak signals at 35.639° assigned to Fe$_3$O$_4$ demonstrated the formation of iron oxide. However, the presence of other iron oxide phases could not be detected by XRD.

Therefore, Raman spectroscopy analysis was carried out for further investigation, as shown in Fig. 6b. The Raman spectra exhibited strong bands at 218 cm$^{-1}$, 282 cm$^{-1}$, 385 cm$^{-1}$, 670 cm$^{-1}$, and 1320 cm$^{-1}$. On the basis of literature,$^{41,42}$ the strong and narrow bands at 219 cm$^{-1}$, 283 cm$^{-1}$ and 385 cm$^{-1}$ corresponded to hematite ($\alpha$-Fe$_2$O$_3$), and the broad band around 1317 cm$^{-1}$ was attributed to the second order scattering of $\alpha$-Fe$_2$O$_3$. Previous Raman spectroscopic investigations of magnetite (Fe$_3$O$_4$) have identified a characteristic band at around 670 cm$^{-1}$. Therefore, another strong and broad band at around 670 cm$^{-1}$ in Fig. 6b clearly showed the presence of Fe$_3$O$_4$ on the ZVI shavings after ZVI/H$_2$O$_2$ oxidation process, which was consistent with the result of XRD. Raman spectra of ZVI sample after reduction process showed typical hematite ($\alpha$-Fe$_2$O$_3$) peak, which was relatively weak. However, no intensive signal could be observed for the fresh ZVI, implying that there were no oxides or other impurities on the ZVI surface before use. In addition, an obvious absorbance band was observed at around 1566 cm$^{-1}$ for the ZVI shavings after ZVI/H$_2$O$_2$ oxidation process. A relatively weak absorbance band was observed at around 1595 cm$^{-1}$ for the ZVI shavings after ZVI reduction process. Based on the known assignments, these
two bands were assigned to stretch vibrations of C=C double bond. The presence of these two bands was probably due to the adsorption of the NACs and their reduction intermediates on the ZVI surface.

3.5 Mechanism for the enhanced contaminants removal in the integrated system

Based on the results mentioned above, a possible mechanism for enhanced NACs removal in the integrated ZVI-ZVI/H\textsubscript{2}O\textsubscript{2} process was proposed, as indicated in Fig. 7. The detailed mechanism could be described as follows.

(1) The reductive transformation of the nitro functional groups by ZVI overcame the hindrance to oxidation in the sequential Fenton process. The reduction products, i.e., aminoaromatic compounds (Ar-NH\textsubscript{2}) such as DAP, DAAN and DACB, were more susceptible to oxidation by Fenton agent than NACs themselves. Although evidence for the mineralization of aminoaromatic compounds in Fenton process could not be provided, removal of aminoaromatic compounds through polymerization and subsequent capture in the floc was a logical pathway.

\[
\begin{align*}
\text{Fe}^0 + \text{DNP} & \rightarrow \text{Fe}^{2+} + \text{DAP} \quad \text{Eq.(3)} \\
\text{Fe}^0 + \text{DNAN} & \rightarrow \text{Fe}^{2+} + \text{DAAN} \quad \text{Eq.(4)} \\
\text{Fe}^0 + \text{DNCB} & \rightarrow \text{Fe}^{2+} + \text{DACB} \quad \text{Eq.(5)} \\
\text{OH}^• + \text{Ar-NH}_2 & \rightarrow \text{CO}_2 + \text{H}_2\text{O} \quad \text{Eq.(6)} \\
\text{OH}^• + \text{Ar-NH}_2 & \rightarrow \text{polymer} \quad \text{Eq.(7)}
\end{align*}
\]

(2) In situ generation of ferrous ions in both ZVI reduction process and ZVI/H\textsubscript{2}O\textsubscript{2} oxidation process provides Fenton reaction with highly active catalyst.

\[
\begin{align*}
\text{Fe}^0 + 2\text{H}^+ & \rightarrow \text{Fe}^{2+} + \text{H}_2 \quad \text{Eq.(8)} \\
\text{Fe}^0 + \text{H}_2\text{O}_2 + 2\text{H}^+ & \rightarrow \text{Fe}^{2+} + 2\text{H}_2\text{O} \quad \text{Eq.(9)}
\end{align*}
\]

(3) Effective cycle of Fe\textsuperscript{3+} ions to Fe\textsuperscript{2+} ions provides Fenton reaction with highly efficient catalyst, reducing the dosage of ferrous ions thus reducing the generation of ferric sludge.\textsuperscript{45-47}

\[
\begin{align*}
\text{Fe}^{2+} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe}^{3+} + \text{OH}^- + \text{HO}^• \quad \text{Eq.(10)} \\
2\text{Fe}^{3+} + \text{Fe}^0 & \rightarrow 3\text{Fe}^{2+} \quad \text{Eq.(11)}
\end{align*}
\]

(4) The formation of iron oxides on the metallic ZVI surface could be another
alternative and efficient Fenton catalyst.\textsuperscript{48,49}

3.6 Performance of integrated ZVI-ZVI/H\textsubscript{2}O\textsubscript{2} process

As was described previously, for ZVI process, HRT of 6 h was adopted. For ZVI/H\textsubscript{2}O\textsubscript{2} process, pH of 3.0 and H\textsubscript{2}O\textsubscript{2} dosage of 100 mmol/L were favorable for the organic removal. Under these optimal conditions, the integrated ZVI-ZVI/H\textsubscript{2}O\textsubscript{2} process was operated for the pretreatment of DNAN producing wastewater. The performance of integrated ZVI-ZVI/H\textsubscript{2}O\textsubscript{2} process under optimal conditions was described in Table 1, in terms of NACs removal, TOC removal, UV\textsubscript{254} decrease and acute toxicity reduction.

Although TOC removal was not high (32.4±0.7%), the integrated process exhibited excellent performance in terms of NACs removal from DNAN producing wastewater. DNAN, DNCB and DNP could be almost completely removed eventually, indicating the high selectivity of this integrated system in terms of NACs removal. UV\textsubscript{254} values, which indicated the concentration of total aromatic compounds, decreased from 0.808±0.129 to 0.104±0.003, indicating excellent pretreatment performance of the integrated process. The EC\textsubscript{50, 48 h (v/v)} values of the influent was only 0.67%, which indicated that the DNAN producing wastewater was highly toxic and was much resistant to mineralization by biological process. After pretreatment by ZVI process, the toxicity was slightly lowered as revealed by the increase of EC\textsubscript{50, 48 h (v/v)} from 0.67% to 1.14%, probably due to the incomplete conversion of DNAN, DNCB and DNP. However, EC\textsubscript{50, 48 h (v/v)} increased to 13.5% after ZVI/H\textsubscript{2}O\textsubscript{2} oxidation process. The reduction of the acute toxicity demonstrated the effectiveness of this integrated process in terms of detoxification when treating DNAN producing wastewater. The evolution of UV-vis (Fig. S2) and HPLC (Fig. S3) spectra also confirmed that aromatic compounds could be removed effectively in this integrated system.

The performance of the sequential ZVI-Fe\textsuperscript{2+}/H\textsubscript{2}O\textsubscript{2} process and the integrated ZVI-ZVI/H\textsubscript{2}O\textsubscript{2} process was compared, as was indicated in Table 2. NACs removal in both systems was highly efficient, as was indicated by high NACs removal efficiencies and low residual UV\textsubscript{254} values. However, the UV\textsubscript{254} value in the effluent
of the integrated ZVI-ZVI/H$_2$O$_2$ process was lower than that of the sequential ZVI-Fe$^{2+}$/H$_2$O$_2$ process, indicating the excellent removal performance for total aromatic compounds in the integrated ZVI-ZVI/H$_2$O$_2$ process. H$_2$O$_2$ dosage required in the integrated ZVI-ZVI/H$_2$O$_2$ process was 100 mol/L, which was about half of the sequential ZVI-Fe$^{2+}$/H$_2$O$_2$ process. The treatment of ferric sludge generated in traditional Fenton process was rather costly and tough, limiting the wide use of traditional Fenton process. However, only 3.5±0.9 g ferric sludge per liter wastewater was generated in the integrated ZVI-ZVI/H$_2$O$_2$ process, which was about a quarter of the sequential ZVI-Fe$^{2+}$/H$_2$O$_2$ process. Considering the reduced H$_2$O$_2$ dosage, less ferric sludge generated and avoidance of additional iron salts, the integrated ZVI-ZVI/H$_2$O$_2$ process was much more economical than the sequential ZVI-Fe$^{2+}$/H$_2$O$_2$ process in treating NACs containing wastewater.

4. Conclusions

The purpose of this study was to evaluate the effectiveness of the integrated ZVI reduction and ZVI/H$_2$O$_2$ oxidation process (ZVI-ZVI/H$_2$O$_2$) for the pretreatment of DNAN producing wastewater. The following conclusions were derived:

(1) Almost complete removal of nitroaromatic compounds and their degradation byproducts could be achieved in the integrated ZVI-ZVI/H$_2$O$_2$ process. Reductive transformation of the nitro functional groups by ZVI overcame the hindrance to subsequent Fenton oxidation.

(2) Fenton reaction was provided with highly active catalyst, due to the in situ generation of ferrous ions in both ZVI reduction process and ZVI/H$_2$O$_2$ oxidation process, and the effective cycle of ferric ions to ferrous ions due to the presence of Fe$^0$.

(3) The reduced H$_2$O$_2$ dosage, less ferric sludge generated and avoidance of additional iron salts made the integrated ZVI-ZVI/H$_2$O$_2$ process more economical than the sequential ZVI-Fe$^{2+}$/H$_2$O$_2$ process in treating NACs containing wastewater.
Acknowledgements

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References


**Figure captions**

**Fig.1** Experiment installation used in this study

**Fig.2** Effect of HRT on DNP, DNAN and DNCB removal in ZVI reduction process

**Fig.3** Effect of pH on NACs removal (a), \textit{UV}_{254} and TOC removal (b) in ZVI/H_{2}O_{2} oxidation process

**Fig.4** Effect of H_{2}O_{2} dosage on NACs removal (a), \textit{UV}_{254} and TOC removal (b) in ZVI/H_{2}O_{2} oxidation process

**Fig.5** Generation of hydroxyl radicals and release of iron ions in ZVI/H_{2}O_{2} process

**Fig.6** XRD patterns (a) and Raman spectroscopy (b) of fresh ZVI, used ZVI after reduction and oxidation process

**Fig.7** Mechanism for the enhanced contaminants removal in the integrated ZVI-ZVI/H_{2}O_{2} system
Fig. 2

Reduction efficiencies of NACs (%)

HRT (h)

DNP
DNAN
DNCB
Fig. 3

(a) Removal efficiencies of NACs (%)

(b) TOC removal efficiency (%)

- DNP
- DNAN
- DNCB

- UV \text{\textsubscript{254}}

pH

Removal efficiencies of NACs (%)

0.0

2 3 4 5 6

80 -

70 -

90 -

100 -

UV \text{\textsubscript{254}}

20

22

24

26

28

30

32

34

TOC Removal

- TOC

pH

2 3 4 5 6

0.0

0.1

0.2

0.3

0.4

0.5

- TOC removal efficiency (%)

- UV \text{\textsubscript{254}}
Fig. 5

Hydroxyl radicals generation (mmol/L) vs. H$_2$O$_2$ dosage (mmol/L) (a)

Concentrations of Fe$^{2+}$ and total iron ions (mg/L) vs. H$_2$O$_2$ dosage (mmol/L) (b)
Fig. 6

(a) X-ray diffraction patterns of fresh ZVI, ZVI after reduction, and ZVI after oxidation. The peaks at 2θ = 35.639° correspond to the (012) diffraction plane of iron.

(b) Raman spectra of fresh ZVI and ZVI after reduction and oxidation. The Raman shifts at 282 cm⁻¹, 385 cm⁻¹, and 1566 cm⁻¹ are indicative of specific vibrational modes in the samples.
Fig. 7

ZVI Reduction Process

ZVI/H₂O₂ Oxidation Process
**Table 1 Performance of integrated ZVI-ZVI/H$_2$O$_2$ process**

<table>
<thead>
<tr>
<th></th>
<th>TOC (mg/L)</th>
<th>DNP (mg/L)</th>
<th>DNAN (mg/L)</th>
<th>DNCB (mg/L)</th>
<th>UV$_{254}$</th>
<th>EC$_{50}$ (h/v)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Influent</td>
<td>7151±329</td>
<td>110.4±4.2</td>
<td>123.1±3.8</td>
<td>249.3±6.9</td>
<td>0.808±0.129</td>
<td>0.67%</td>
</tr>
<tr>
<td>Eff$_{ZVI}$</td>
<td>6300±289</td>
<td>22.8±1.1</td>
<td>23.7±1.3</td>
<td>25.0±4.9</td>
<td>0.502±0.252</td>
<td>1.14%</td>
</tr>
<tr>
<td>Eff$_{ZVI/H_2O_2}$</td>
<td>5077±234</td>
<td>-</td>
<td>5±0.2</td>
<td>0.4±0.1</td>
<td>0.104±0.003</td>
<td>13.50%</td>
</tr>
</tbody>
</table>

- undetectable

*25 times diluted*
Table 2 Comparison of ZVI-Fe\textsuperscript{2+}/H\textsubscript{2}O\textsubscript{2} process and ZVI-ZVI/H\textsubscript{2}O\textsubscript{2} process

<table>
<thead>
<tr>
<th></th>
<th>DNP removal (%)</th>
<th>DNAN removal (%)</th>
<th>DNCB removal (%)</th>
<th>Effluent UV\textsubscript{254} \textsuperscript{a}</th>
<th>H\textsubscript{2}O\textsubscript{2} dosage (mmol/L)</th>
<th>Sludge yield (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZVI-Fe\textsuperscript{2+}/H\textsubscript{2}O\textsubscript{2}</td>
<td>100±0.0%</td>
<td>100±0.0%</td>
<td>100±0.0%</td>
<td>0.182±0.011</td>
<td>216</td>
<td>13.6±1.3</td>
</tr>
<tr>
<td>ZVI-ZVI/H\textsubscript{2}O\textsubscript{2}</td>
<td>100±0.0%</td>
<td>95.8±0.2%</td>
<td>99.9±0.1%</td>
<td>0.104±0.003</td>
<td>100</td>
<td>3.5±0.9</td>
</tr>
</tbody>
</table>

\textsuperscript{a} 25 times diluted