Advanced treatment of petrochemical secondary effluent by Fenton: performance and organics removal characteristics

Min Xu, Changyong Wu and Yuexi Zhou

ABSTRACT

The Fenton process was used to treat petrochemical secondary effluent. The effects of initial pH, H₂O₂, and FeSO₄·7H₂O dosages on chemical oxygen demand (COD) removal, the dissolved organic matter (DOM) removal and the transformation and migration of typical organic matters during the treatment process were investigated. The results showed that the optimum conditions were initial pH of 3.0, H₂O₂ (30%) dosage of 0.4 mL/L, and FeSO₄·7H₂O dosage of 1.0 g/L. The highest COD removal efficiency of 61.9% could be achieved for this condition when the average influent COD was 78.5 mg/L. Most of the DOM in the petrochemical wastewater could be removed effectively by Fenton through direct oxidation and coagulation. For example, for trans-1,2-dichlorocyclopentane, results showed that 56.3% of it could be removed by Fenton oxidation, while 13.3% of it could be absorbed by the in situ generated Fenton chemical sludge. The Fenton process is simple and it is suitable for the advanced treatment of petrochemical secondary effluent.

Key words | dissolved organic matter (DOM), Fenton, optimization, petrochemical secondary effluent, transformation

INTRODUCTION

Petrochemical wastewater is generated during the processes of petroleum cracking, refining, and synthesis. The petrochemical wastewater contains many organic pollutants such as volatile phenols, benzene, and benzene derivatives with high toxicity and low biodegradability (Wu et al. 2015). After a biological treatment process, the biochemical oxygen demand to chemical oxygen demand (COD) ratio of petrochemical secondary effluent is often less than 0.05 and it is very difficult to biodegrade (Wu et al. 2016). In order to improve the wastewater quality, advanced treatment is needed to remove the refractory organics from the petrochemical secondary effluent.

Fenton is an effective advanced treatment process. The hydroxyl radical (HO·) can be generated from the reaction between aqueous ferrous ions and hydrogen peroxide (H₂O₂) and it can destroy refractory and toxic organic pollutants in wastewater (Lucas et al. 2007). There are many reports concerning the use of Fenton to treat refractory/toxic wastewater (Dogruel et al. 2009; Wang et al. 2014; He et al. 2015). Fenton performance has been mainly investigated according to the variations of the [Fe²⁺]/[H₂O₂]₀ ratio and initial solution pH (Yoon et al. 2001; Fu et al. 2010). In the Fenton process, strong oxidative HO· is produced and the ferrous ions are oxidized into ferric ions. Since both ferrous and ferric ions are coagulants, the Fenton process can, therefore, have the dual functions of oxidation and coagulation in the treatment process.

A large amount of ferric sludge is produced during the practical application of the Fenton process (Zhu & Logan 2015). The solid sludge, which is potentially hazardous waste due to residual organics adsorbed from treated wastewater, requires proper treatment to reduce the secondary pollution. To minimize the ferric sludge, two approaches have been investigated: the use of heterogeneous catalysts (Phan et al. 2012) and the reuse of the iron-containing sludge (Bolobajev et al. 2014). Although many studies focus on the Fenton performance and minimizing the production of Fenton sludge, the contributions of oxidation and coagulation to the removal of organics remain unclear. Kang et al. (2002) investigated the contribution of oxidation and coagulation to the removal of COD in treated synthetic textile wastewater. It was reported that the decolorization occurs mainly through HO· oxidation.
and the COD removal mainly through the Fenton-based coagulation. However, there are many toxic and refractory organics existing in actual industrial wastewater. The secondary effluent of a petrochemical wastewater mainly contains dissolved organic matters (DOM). The removal ability of DOM is an important index to evaluate the ability of a petrochemical wastewater treatment process (Wu et al. 2016). However, there has been a lack of information about DOM removal by the Fenton process treating the secondary effluent of petrochemical wastewater. The chemical sludge, produced during the Fenton process, is an important medium for the organics removal. However, there are few studies investigating the relationship of DOM removal between the raw wastewater, treated wastewater, and chemical sludge throughout the Fenton process.

In this study, the petrochemical secondary effluent was treated by Fenton. Process optimization in terms of COD removal was performed using orthogonal experiments through jar tests. More importantly, the characteristics, transformation, and migration of DOM in petrochemical secondary effluent during the treatment process were identified by Fourier transform infrared (FTIR), excitation-emission matrix (EEM), and gas chromatography mass spectrometry (GC-MS) analysis.

MATERIALS AND METHODS

Wastewater

The wastewater was obtained from the secondary settling tank of a petrochemical wastewater treatment plant with anoxic/oxic (A/O) as the core process. The wastewater discharged from the petrochemical wastewater treatment plant is the mixed wastewater (from more than 50 sets of petrochemical production plant). The main qualities of the secondary effluent were: COD 60–120 mg/L, pH 7–8, total organic carbon 21.4–28.3 mg/L. The purity of the chemicals used in the experiment is at least analytical grade.

Fenton treatment experiment

A series of Fenton experiments were performed using jar test apparatus. Five hundred millilitres of wastewater was treated in glass jars (1 L) with different FeSO₄·7H₂O and H₂O₂ (30%) dosages in the range of 0.4–1.2 g/L and 0.1–0.5 mL/L, respectively. pH was varied from 2 to 6 by addition of H₂SO₄ solution (2 N). FeSO₄·7H₂O and H₂O₂ were added into the wastewater and then the experimental procedure consisted of three phases: stirring at 300 rpm for 2 min, stirring at 50 rpm for 20 min, and settling for 30 min. The supernatant obtained after 30 min of settling was used for COD analysis. The optimum reaction conditions were determined with respect to COD removal. Each experiment with the specific dosage was repeated twice and the COD results presented here were the average values. The standard deviation of the results was less than 5%. The settled sludge was used for leaching tests.

Analytical methods

Three-dimensional fluorescence analysis

A toxicity characteristics leaching procedure was carried out to extract the organic compounds from the chemical sludge using a vacuum filter (T-50, Jinteng, China) according to the standard procedure (USEPA 1992). The extraction fluid was 0.2 N acetic acid containing 64.3 mL of 1 N NaOH/L (pH 4.93 ± 0.05). The liquid/solid ratio of 10 was adopted to promote appropriate contact between the sludge and the eluent (François et al. 2006; Parodi et al. 2011). The mixture was agitated on a horizontal shaking system at 50 rpm for 18 h. The extraction was carried out in 250 mL conical flasks at 23 ± 2 °C. Then, the mixture was pressurized in a vacuum filter with a pressure of 200 Mpa. Finally, the filtrate was diluted to 500 mL with the extraction fluid. The samples were used for three-dimensional fluorescence analysis.

The raw wastewater, treated wastewater, and sludge leachate were analyzed by fluorescence EEM spectra (F-7000, Hitachi, Japan). The wastewater samples were filtered through a 0.45 μm cellulose acetate membrane before measurement. The emission and excitation spectra were scanned from 200 to 500 nm with a 10 nm increment with a slit width of 5 nm and scan rate of 12,000 nm/min.

GC-MS analysis

The organic compounds in raw wastewater, treated water, and chemical sludge produced during the treatment were analyzed by GC-MS. The pretreatment methods of different samples are described below.

The organic compounds in solution before and after Fenton treatment were identified by GC-MS (7890/5975 GC-MS, Agilent, USA). Prior to GC-MS measurement, 400 mL samples were extracted with CH₂Cl₂ under acidic (pH < 2) and alkaline (pH > 12) conditions, respectively. Each sample was extracted three times with 10 mL of CH₂Cl₂. The three extracted layers were mixed, dehydrated...
by anhydrous sodium sulfate, and concentrated to 1.0 mL with the aid of nitrogen flow.

The sludge leachate for GC-MS analysis was obtained by Soxhlet extraction (CSEPA 2007). Ten grams of dry sludge samples was mixed with 10 g anhydrous sodium sulfate. The extraction fluid (CH2Cl2 (mL):CH3H2O (mL) = 1:1) of 400 mL was used to extract the mixture in a Soxhlet extractor at 70 °C for 24 h. Then, the leachate was cooled at ambient temperature. The dehydration and concentration procedures were the same as for the previous description.

After preparation of all samples, a 1 μL sample was injected into a GC-MS system equipped with an HP-5MS capillary column. The GC was operated at the initial temperature of 40 °C for 3 min, then increased to 300 °C at the rate of 5 °C/min lasting for 3 min. Helium (99.999%) was used as carrier gas at a flow rate of 1.0 mL/min. The MS conditions were: ion source temperature 230 °C, quadrupole temperature 150 °C, electron ionization 70 eV, scan field 29–350 m/z. Analysis and identification of the organics were based on the NIST 05 mass spectral library database.

**FTIR analysis of sludge**

The blank sample of chemical sludge was obtained by the Fenton treating ultrapure water. The settling sludge, named sample ‘a’, was produced during the process of treating petrochemical secondary effluent by Fenton (Supplementary material, Figure S1, available with the online version of this paper). To obtain the spectra for the blank sample and sample ‘a’, the samples were first dried in an oven at 105 °C for 2–3 d. Then, each dried solid sample (1 mg) was mixed with KBr (100 mg) and ground with an agate ball mill. Finally, the mixture was tableted and used for spectral recording. FTIR spectra were tested by an FTIR spectrophotometer (Equinox 55, Bruker, Germany) with a wavenumber of 4,000–450 cm⁻¹.

**Other analytical methods**

The COD was assayed with a COD analyzer (CTL-12, HATO, China) with standard methods (CSEPA 2002). The pH was measured using a pH meter (FE20, Mettler Toledo, Switzerland).

**RESULTS AND DISCUSSION**

**Performance and reaction optimization**

In the Fenton process, pH, Fe²⁺ concentration, and H₂O₂ dosage are three major operating parameters determining the DOM removal efficiency (Masomboon et al. 2009; Mazzone et al. 2011). Fe²⁺ and H₂O₂ can react with generated HO· and pH is related to the available ratio of Fe²⁺/Fe³⁺ (Deng & Englehardt 2006). The orthogonal test designed for optimizing the Fenton process is shown in Supplementary material, Table S1 (available with the online version of this paper). Effects of pH, Fe²⁺, and H₂O₂ dosage on COD removal are shown in Figure 1. In this study, Fenton reached the highest COD removal of 53.1% at pH 5.0, while the COD removal efficiency decreased to 48.7% with increasing pH from 3.0 to 6.0 (Figure 1(a)). This is because the decomposition of H₂O₂ in the Fenton process is inhibited at pH > 5.0 due to ferric hydroxide precipitation; thus oxidation of organic pollutants is prohibited (Gulkaya et al. 2006; Ahmed et al. 2011). Fenton reagent is used to produce HO· to oxidize organic matter (Equation (1)) (Neyens & Baeyens 2003). The COD removal increased with H₂O₂ dosage until 0.4 mL/L, then it dropped when more H₂O₂ was added. When the Fe²⁺ concentration was up to 1.0 g/L, the COD removal efficiency increased to 52.5%. However, it decreased when the Fe²⁺ concentration was above 1.0 g/L. Usually, excessive H₂O₂ and Fe²⁺ would react with generated HO· (Equations (2) and (3)), resulting in the reduction of oxidation efficiency (Tang & Huang 1997).

\[
\text{H}_2\text{O}_2 + \text{Fe}^{2+} + \text{H}^+ \rightarrow \text{H}_2\text{O} + \text{Fe}^{3+} + \text{HO} \tag{1}
\]

\[
\begin{align*}
\text{H}_2\text{O}_2 + \text{HO} & \rightarrow \text{H}_2\text{O} + \text{O}_2\text{H} \\
& = 2.7 \times 10^7 \text{ M}^{-1}\text{s}^{-1}
\end{align*} \tag{2}
\]

\[
\begin{align*}
\text{Fe}^{2+} + \text{HO} & \rightarrow \text{Fe}^{3+} + \text{OH}^- \\
& = 3 \times 10^8 \text{ M}^{-1}\text{s}^{-1}
\end{align*} \tag{3}
\]

According to the results of the orthogonal test, one combination condition for the highest COD removal efficiency of 61.9% was obtained. The parameters of the condition are: pH of 3.0, H₂O₂ and Fe²⁺ dosage of 0.4 mL/L and 1.0 g/L, respectively.

**EEM spectra analysis of DOM of different samples**

**DOM fractions in different samples**

The EEM spectra of the DOM for raw wastewater, treated wastewater, and chemical sludge leachate are shown in Figure 2. In raw wastewater, there are three types of fluorescence peaks. Peak B₁ (Ex/Em = 235/345 nm) is a short-excitation wavelength tryptophan-like peak, which is related to aromatic amino acid and amino-acid residue (Coble et al. 1994).
Peak B₂ (Ex/Em = 280/345 nm) is associated with high-excitation wavelength tryptophan-like materials as soluble microbial products (Xu et al. 2013). Humic-like fluorescence peak C, which is centered at the Ex/Em wavelength pair of ~255/455 nm, is observed in the EEM spectra (Artinger et al. 2000). After Fenton treatment, peaks B₁ and B₂ disappeared in the treated wastewater and the intensity of peak C was weakened. It showed that these DOMs were degraded by Fenton oxidation. The location of peak C was blue-shifted by 40 nm along the emission axis in treated wastewater. Such change implied that molecular size and humification degree of treated wastewater decreased and some aromatic polycondensations emerged during the reaction (Senesi et al. 1999). In addition, humic-like peak C appeared in Fenton sludge leachate, indicating that some macromolecules such as humic-like organics were adsorbed by Fenton sludge.

Fluorescence regional integration (FRI) can reveal the configuration and heterogeneity of DOM. It has been widely used to quantitatively analyze all wavelength-dependent fluorescence intensity data from EEM spectra (He et al. 2011). In the present study, the EEM spectra were divided into five regions based on previous research (Chen et al. 2003). Regions I and II are protein-like fluorescence regions and originate from tyrosine- and tryptophan-like phenolic compounds (Ahmad & Reynolds 1999). Regions III and V represent fulvic acid-like and humic acid-like organic fractions. In addition, fluorescence emitted by soluble microbial by product-like materials commonly appear in region IV. The normalized region-specific EEM volume ($\Phi_{i,n}$) is the volumetric integration under the EEM within each region by normalizing to the projected excitation-emission area of the region. $\Phi_{i,n}$ (au-nm²) values in different composts from FRI analysis are listed in Table 1. $P_{i,n}$ is calculated by the normalized
region-specific EEM volume to the total normalized integral volume. Figure 3 presents the $\Phi_{i,n}$ distribution in each sample.

**Transformation of DOM during the Fenton process**

As shown in Table 1, the continuum of $\Phi_{i,n}$ values illustrates that aromatic protein-like (regions I and II) materials are the major pollutants. Soluble microbial by product-like materials (region IV) are the sub-dominant organic species. A small concentration of the fulvic acid-like and humic acid-like organics is present in DOM in the raw wastewater. The $\Phi_{i,n}$ value for each region dramatically decreased after Fenton treatment. The two high removal percentages of $\Phi_{i,n}$ in Fenton-treated wastewater occurred in regions II

![Figure 2](image-url)  
**Figure 2** | EEM contours of DOM from raw wastewater, treated wastewater, and Fenton sludge leachate.

<table>
<thead>
<tr>
<th>Projects</th>
<th>$C_1$</th>
<th>$C_2$</th>
<th>$C_3$</th>
<th>$\phi_{i,n}$ removal of $C_2$ (%)</th>
<th>$\phi_{i,n}$ accumulation of $C_3$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Phi_{I,n}$</td>
<td>671,678.57</td>
<td>23,957.35</td>
<td>26,483.86</td>
<td>96.43</td>
<td>3.94</td>
</tr>
<tr>
<td>$\Phi_{II,n}$</td>
<td>4,348,932.00</td>
<td>47,174.84</td>
<td>83,770.78</td>
<td>98.92</td>
<td>1.93</td>
</tr>
<tr>
<td>$\Phi_{III,n}$</td>
<td>540,614.43</td>
<td>18,008.32</td>
<td>27,134.48</td>
<td>96.67</td>
<td>5.02</td>
</tr>
<tr>
<td>$\Phi_{IV,n}$</td>
<td>1,007,758.70</td>
<td>9,406.08</td>
<td>35,412.36</td>
<td>99.07</td>
<td>3.51</td>
</tr>
<tr>
<td>$\Phi_{V,n}$</td>
<td>140,288.20</td>
<td>2,534.61</td>
<td>7,150.47</td>
<td>98.19</td>
<td>5.10</td>
</tr>
<tr>
<td>$\Phi_{T,n}$</td>
<td>6,709,272.00</td>
<td>101,081.20</td>
<td>179,952</td>
<td>98.49</td>
<td>2.68</td>
</tr>
</tbody>
</table>
and IV, but protein-like (region II) organics accumulated relatively less in Fenton sludge leachate. This indicates that the protein-like compounds with a simple structure were degraded directly by Fenton oxidation. The \( P_{I,n} \) of fulvic acid-like and humic acid-like fluorescence region ranges from 8.06% to 15.08% and 2.09% to 3.97% in the raw wastewater and Fenton sludge leachate (Figure 3). Fulvic acid-like and humic acid-like organics (regions III and V) accumulated more highly than the other organics in the Fenton sludge leachate, indicating that macromolecule organics in raw wastewater can be removed preferentially by coagulation during Fenton treatment (Deng & Englehardt 2006). Figure 3 shows that the concentration of aromatic protein-like II (region II) and soluble microbial by product-like materials (region IV) in raw wastewater were higher than the other two samples. More importantly, the \( P_{I,n} \) values of region II and region IV in the treated wastewater significantly decreased, whereas those for fulvic acid-like and humic acid-like pollutants (regions III and V) increased at the phase of Fenton treatment. This indicates that aromatic protein-like and soluble microbial by product-like organics are the principally removed pollutants during Fenton treatment. The \( P_{I,n} \) of aromatic protein-like substance in treated wastewater increased. This is because some macromolecules could be degraded into small microbial products by Fenton oxidation (Liu et al. 2015).

The composition and transformation of DOM can be easily assessed by EEM spectroscopy with FRI analysis. In order to explain the transformation of specific DOM during the Fenton process, this also needs to be combined with GC-MS analysis.

Organic pollutants’ removal characteristics

Volatile organic compounds (VOC) are easily removed by good aeration in an A/O unit. Semi-VOC, originating mainly from petroleum products, cannot easily be degraded and often attach to the particles for a longer time (Fu et al. 2016). Operation of Fenton was performed twice under the optimum condition and all replicates were analyzed by GC-MS. Probability values of higher than 50% were used to identify the compounds. The details of organic compounds that existed in the raw wastewater, treated wastewater, and Fenton sludge leachate samples are summarized in Table 2. As shown in Table 2, the raw wastewater generated 18 peaks. Cycloalkanes, aromatic compounds, and nitriles are the dominant organic matter in raw wastewater. It has been reported that microbial activity was inhibited by these organics (Zhao et al. 2005). The spectra of treated wastewater have three peaks; two of them presented in the raw wastewater disappeared. However, one new peak was formed during the reaction. The peak areas of organic compounds presented here were the average values of all replicates. The percentages of reduction were calculated based on peak areas (Wu et al. 2013). After treatment by Fenton, cycloalkanes were reduced by 88.59%, and only two types of cycloalkanes could be detected in the treated wastewater. C\(_5\)H\(_8\)Cl\(_2\) and C\(_{10}\)H\(_{30}\)O\(_5\)Si\(_5\) were partially removed by Fenton with removal efficiency of 69.57% and 5.58%, respectively. As for nitrile, C\(_8\)H\(_{32}\)N\(_2\) was removed but C\(_8\)H\(_{12}\)N\(_4\) was newly formed in the treated wastewater. The total nitriles were reduced by 85.83%. In addition, aromatic compounds and other organics cannot be detected in the treated wastewater, suggesting that Fenton can remove most of the DOM in the petrochemical secondary effluent. The results are in agreement with FRI analysis, as mentioned above.

It is necessary to make a quantitative comparison of transformation and decomposition of specific organics in the three samples. As mentioned above, the Fenton process serves both oxidation and coagulation functions. As for alkanes, C\(_{10}\)H\(_{30}\)O\(_2\)Si\(_5\) and C\(_9\)H\(_{24}\)O\(_4\)Si\(_4\) disappeared after Fenton treatment, while C\(_{12}\)H\(_{16}\)O\(_2\)Si\(_5\) and C\(_{19}\)H\(_{30}\)NO\(_3\)Si\(_3\) appeared in Fenton sludge leachate. The increase in the number of carbon atoms in alkanes demonstrated alkane radicals generated from HO· attack combined with each other to form new alkanes with a larger number of carbon atoms and were adsorbed by Fenton sludge (Wang et al. 2014). The removal efficiency of C\(_2\)H\(_2\)Cl\(_2\) is 69.57%, and it can be detected in Fenton sludge leachate. It accounts for 15.3% of the total amount due to the Fenton coagulation.
Table 2 | Main organic compounds present in the raw wastewater, treated water, and leachate samples by GC-MS analysis

<table>
<thead>
<tr>
<th>S. no.</th>
<th>Organic compounds</th>
<th>Match quality(%)</th>
<th>Molecular formula</th>
<th>Raw wastewater</th>
<th>Fenton effluent</th>
<th>Fenton sludge leachate</th>
<th>Removal (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Cycloalkanes</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>1,3-Dioxolane, 2-(chloromethyl)-</td>
<td>78</td>
<td>C(_2)H(_7)ClO(_2)</td>
<td>1,629,983</td>
<td>–</td>
<td>–</td>
<td>100</td>
</tr>
<tr>
<td>2</td>
<td>Cyclopentane, 1,2-dichloro</td>
<td>91</td>
<td>C(_3)H(_4)Cl(_2)</td>
<td>1,449,203</td>
<td>440,922</td>
<td>192,689</td>
<td>86.7</td>
</tr>
<tr>
<td>3</td>
<td>1,4-Dioxane</td>
<td>53</td>
<td>C(_3)H(_8)O(_2)</td>
<td>476,830</td>
<td>–</td>
<td>–</td>
<td>100</td>
</tr>
<tr>
<td>4</td>
<td>1,3-Cyclohexadiene, 5-ethyl</td>
<td>80</td>
<td>C(_4)H(_12)</td>
<td>419,222</td>
<td>–</td>
<td>–</td>
<td>100</td>
</tr>
<tr>
<td>5</td>
<td>Cyclohexanol, 2-amino-</td>
<td>56</td>
<td>C(_6)H(_13)NO</td>
<td>410,258</td>
<td>–</td>
<td>–</td>
<td>100</td>
</tr>
<tr>
<td>6</td>
<td>Cyclopropane-carboxylic acid, 4-chlorophenyl ester</td>
<td>50</td>
<td>C(_10)H(_9)ClO(_2)</td>
<td>123,438</td>
<td>–</td>
<td>–</td>
<td>100</td>
</tr>
<tr>
<td>7</td>
<td>Cyclopentasiloxane, decamethyl-</td>
<td>83</td>
<td>C(_10)H(_36)O(_5)Si(_5)</td>
<td>95,687</td>
<td>92,259</td>
<td>3.58</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>Cyclohexasiloxane, octamethyl-</td>
<td>64</td>
<td>C(_8)H(_24)O(_4)Si(_4)</td>
<td>68,623</td>
<td>–</td>
<td>–</td>
<td>100</td>
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<tr>
<td>9</td>
<td>Pentasiloxane, dodecamethyl-</td>
<td>69</td>
<td>C(_12)H(_36)O(_4)Si(_5)</td>
<td>–</td>
<td>–</td>
<td>87,835</td>
<td>B(^b)</td>
</tr>
<tr>
<td>10</td>
<td>2-Oxazolidinone, 3-methyl-</td>
<td>77</td>
<td>C(_2)H(_7)NO(_2)</td>
<td>–</td>
<td>–</td>
<td>172,649</td>
<td>B(^b)</td>
</tr>
<tr>
<td>II</td>
<td>Aromatic compounds</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>11</td>
<td>1,3-Benzenedimethanol</td>
<td>53</td>
<td>C(_8)H(_10)O(_2)</td>
<td>312,270</td>
<td>–</td>
<td>–</td>
<td>100</td>
</tr>
<tr>
<td>12</td>
<td>Benzene, 1,2,3-trichloro-4-methoxy-</td>
<td>50</td>
<td>C(_6)H(_5)Cl(_3)O</td>
<td>205,488</td>
<td>–</td>
<td>–</td>
<td>100</td>
</tr>
<tr>
<td>13</td>
<td>1,3,5-Triazine-2,4-diamine, 6-chloro-N,N'-bis(1-methylthyl)-</td>
<td>78</td>
<td>C(_8)H(_16)ClN(_5)</td>
<td>62,825</td>
<td>–</td>
<td>–</td>
<td>100</td>
</tr>
<tr>
<td>III</td>
<td>Phthalates</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>Dibutyl phthalate</td>
<td>50</td>
<td>C(<em>{10})H(</em>{22})O(_4)</td>
<td>–</td>
<td>–</td>
<td>395,522</td>
<td>B(^b)</td>
</tr>
<tr>
<td>15</td>
<td>1,2-Benzenedicarboxylic acid, bis(2-methylpropyl) ester</td>
<td>83</td>
<td>C(<em>{10})H(</em>{22})O(_4)</td>
<td>–</td>
<td>–</td>
<td>37,214</td>
<td>B(^b)</td>
</tr>
<tr>
<td>IV</td>
<td>Nitriles</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>Tetramethylbutane-dinitrile</td>
<td>90</td>
<td>C(_8)H(_12)N(_2)</td>
<td>1,669,709</td>
<td>–</td>
<td>–</td>
<td>100</td>
</tr>
<tr>
<td>17</td>
<td>2,2'-Azobis(2-methylpropionitrile)</td>
<td>83</td>
<td>C(_8)H(_12)N(_4)</td>
<td>–</td>
<td>–</td>
<td>236,556</td>
<td>A(^a)</td>
</tr>
<tr>
<td>V</td>
<td>Others</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>5-Formyl-6-methyl-4,5-dihydropryan</td>
<td>86</td>
<td>C(_8)H(_12)O(_2)</td>
<td>1,306,160</td>
<td>–</td>
<td>–</td>
<td>100</td>
</tr>
<tr>
<td>19</td>
<td>2,4-Hexadienoic acid, ethyl ester</td>
<td>58</td>
<td>C(_8)H(_12)O(_2)</td>
<td>644,276</td>
<td>–</td>
<td>–</td>
<td>100</td>
</tr>
<tr>
<td>20</td>
<td>2-Pteridinamine, N,N-dimethyl-4-(trifluoromethyl)-</td>
<td>53</td>
<td>C(_8)H(_8)F(_3)N(_5)</td>
<td>369,876</td>
<td>–</td>
<td>–</td>
<td>100</td>
</tr>
<tr>
<td>21</td>
<td>1-Propanol, 3-methoxy-2-(methoxymethyl)-2-methyl</td>
<td>62</td>
<td>C(_3)H(_6)O(_3)</td>
<td>158,199</td>
<td>–</td>
<td>–</td>
<td>100</td>
</tr>
<tr>
<td>22</td>
<td>3-Hydroxy-2,6,6-trimethyl-hept-4-enoic-acid</td>
<td>65</td>
<td>C(_{10})H(_12)O(_3)</td>
<td>151,583</td>
<td>–</td>
<td>–</td>
<td>100</td>
</tr>
<tr>
<td>23</td>
<td>Hydrazine, 1-methyl-1-(2-propenyl)-</td>
<td>59</td>
<td>C(_8)H(_10)N(_2)</td>
<td>72,444</td>
<td>–</td>
<td>–</td>
<td>100</td>
</tr>
<tr>
<td>24</td>
<td>Propanoic acid, 2-methyl-</td>
<td>58</td>
<td>C(_3)H(_2)O(_2)</td>
<td>–</td>
<td>–</td>
<td>1,164,994</td>
<td>B(^b)</td>
</tr>
<tr>
<td>25</td>
<td>Ethane, 1,1,2-trichloro-2-fluoro-</td>
<td>57</td>
<td>C(_2)H(_2)ClF</td>
<td>–</td>
<td>–</td>
<td>168,756</td>
<td>B(^b)</td>
</tr>
<tr>
<td>26</td>
<td>N-Methyladrenaline, tri-TMS</td>
<td>65</td>
<td>C(_{10})H(_39)NO(_3)Si(_3)</td>
<td>–</td>
<td>–</td>
<td>142,109</td>
<td>B(^b)</td>
</tr>
<tr>
<td>27</td>
<td>Sulfurous acid, 2-propyl tridecyl ester</td>
<td>72</td>
<td>C(_{18})H(_32)O(_3)S</td>
<td>–</td>
<td>–</td>
<td>122,694</td>
<td>B(^b)</td>
</tr>
<tr>
<td>28</td>
<td>Oxalic acid, decyl propyl ester</td>
<td>51</td>
<td>C(_{13})H(_25)O(_4)</td>
<td>–</td>
<td>–</td>
<td>28,409</td>
<td>B(^b)</td>
</tr>
</tbody>
</table>

\(^a\)A stands for compounds that only appeared in Fenton effluent.

\(^b\)B stands for compounds that existed in Fenton sludge.
Thus, 56.3% of C₅H₅Cl₂ could be removed by Fenton oxidation. Furthermore, some new intermediates were produced. For instance, several organics were probably converted into C₁₆H₃₂O₄, C₁₆H₃₄O₃S, and C₁₅H₂₈O₄ and this is consistent with the general decrease of pH in the Fenton treatment. C₆H₁₃NO and C₉H₈F₃N₅ were completely degraded by Fenton treatment, while C₂H₇NO₂ and C₂H₂Cl₃F were generated as by products in the Fenton process. The results of GC-MS are mainly consistent with the results of FTIR analysis (as shown in Supplementary material, Table S2, available with the online version of this paper). Such by products are hazardous pollutants presenting in Fenton sludge. Therefore, great attention should be paid to exact levels of the hazardous pollutants and the treatment of Fenton sludge. For example, the reuse of iron-containing sludge as an iron source in the oxidation part of the Fenton-based treatment has attracted much attention in the last few years (Bolobajev et al. 2014).

CONCLUSIONS

In this study, Fenton was applied to treat petrochemical secondary effluent. Parameters affecting the COD removal were investigated. At the optimum conditions (pH 3.0, H₂O₂ and Fe²⁺ dosage of 0.4 mL/L and 1.0 g/L, respectively), the COD removal efficiency was as high as 61.9%. Aromatic protein-like and soluble microbial by product-like organics of DOM were removed by 98.92% and 99.07%. They are the main removed pollutants in Fenton treatment. The percentage of fulvic acid-like and humic acid-like fluorescence region increased 15.08% and 3.97% between the raw wastewater and Fenton sludge leachate. These macromolecule organics in raw wastewater were removed preferentially by coagulation. The removal efficiencies of cycloalkanes, nitriles, aromatic compounds and phthalates were 85.83%–100%. The Fenton process has the dual functions of oxidation and coagulation. For example, 56.27% of C₅H₅Cl₂ was removed by Fenton oxidation and 13.5% of it was adsorbed by Fenton sludge. Hazardous pollutants were detected as by products in Fenton sludge, and the minimization of sludge should be further investigated.

ACKNOWLEDGEMENTS

The work is financially supported by the China special S&T project on treatment and control of water pollution (2012ZX07201-005) and the National Natural Science Foundation of China (51208484).

REFERENCES


CSEPA 2007 Identification for extraction toxicity. China National GB Standards. GB 5085.3.


He, X. S., Xi, B. D., Wei, Z. M., Jiang, Y. H., Yang, Y., An, D., Cao, J. L. & Liu, H. L. 2011 Fluorescence excitation-emission matrix spectroscopy with regional integration analysis for characterizing composition and transformation of dissolved


Maezono, T., Tokumura, M., Sekine, M. & Kawase, Y. 2011 Hydroxyl radical concentration profile in photo-Fenton oxidation process: generation and consumption of hydroxyl radicals during the discoloration of azo-dye Orange II. Chemosphere 82, 1422–1430.


First received 2 June 2016; accepted in revised form 12 December 2016. Available online 2 January 2017