Degradation of oxytetracycline by nano zero valent iron under UV-A irradiation: Chemical mechanism and kinetic

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Abstract. Pharmaceutical wastewater effluents are well known for their difficult elimination by traditional biotreatment methods and their important contribution to environmental pollution due to its fluctuating and recalcitrant nature. OTC is one of the nonbiodegradable antibiotics that makes antibiotic-resistant, so it can make be high risk for environment. NZVI can be a good choice for removal of OTC in aqueous solution. Response surface methodology (RSM) was used to optimize the amounts of NZVI and OTC to be used at pH 3 and under 200 W, UV-A irradiation. The responses were removal percent of absorption at 290 and 348 nm, TOC and COD of OTC. In the optimum condition, Linear model was performed 155 ppm of OTC were removed by 1000 ppm NZVI after 6.5 hours and the removal efficiency of absorption at 290 and 348 nm, TOC and COD were 87, 95, 85 and 89 percent, respectively. In the similar process, there is no organic compound after 14 hours. The parameters ORP, DO and pH were investigated for 6:30 hours to study the type of NZVI reaction in process. In the beginning of reaction, oxidation was the dominant reaction after 3 hours, photocatalytic reaction was remarkable. The mechanism of OTC degradation is proposed by HPLC/ESI-MS and four by products were found. Also the rate constants (first order kinetic chain reaction model) were 0.0099, 0.0021, 0.0010, 0.0049 and 0.0074 min⁻¹, respectively.

Keywords: RSM; ORP; DO; mechanism; kinetic

1. Introduction

The release of pharmaceuticals such as tetracyclines (TCs) into the environment poses a potential risk to human health. Tetracyclines especially oxytetracycline (OTC) as one of the TCs, has been used extensively in human therapy and to livestock as additives to combat diseases. In natural soils, the sorption and transport behaviors of this chemical is similar despite its structural variances (Hua et al. 2011, Crane and Scott 2012 and Huang et al. 2011a). The presence of low levels of antibiotics such as OTC and their transformation products in the environment could facilitate the transfer and spread of antibiotic-resistant determinants among microorganisms, an emerging issue in public health. The levels of TCs in domestic wastewater and the effluent of WWTPs are 0.98–700 µg L⁻¹, which might pose potential environmental risks (Huang et al. 2011b).
Removal of TCs from the aqueous phase can be achieved through different ways such as physical operations such as absorption and photolysis, biological and chemical processes such as ozonation, UV/TiO₂, UV/H₂O₂ and Fenton have been used. In Thailand, the land previously used for shrimp were infected by OTC, soybean seeds as an adsorbent was used for remediation. The amount of OTC in soil was 105 mg/kg Soil, and after 10 days 80% is removed (Boonsaner and Hawker 2010). By photolysis of 40 mg/L OTC at pH = 9 and 500 W, UV irradiation, 13.5% of TOC and 90% of OTC were removed after 240 min (Shaojun et al. 2008). By using phosphoric acid and micro-wave the active surface of activated carbon was proved and at pH = 8.2 absorption of 537 mg/g OTC was promoted to 564 mg/g (Huang et al. 2011b). In activated sludge process with the 3000 mg/L sludge at pH value 7, 2 ppb OTC 74% were removed after 120 min (Huang et al. 2011a). Anaerobic digesters can remove 60% of 10 mg/L OTC in 64 days at 35°C and pH value 7 (Arikan et al. 2006). 100 mg/L OTC concentration during 60 min ozonation at pH =11 and 24 g/hr ozone value, was removed 99%. In 5 to 30 minutes of ozonation, the products were much more toxic than the initial material (Li et al. 2008). The concentration of 1000 mg/L OTC in the photocatalytic process of TiO₂/UV at pH = 7 after 210 min, 88% have been removed (Zhao et al. 2010). In Fenton process, Iron and Hydrogen peroxide in a ratio of 1 to 10, after 120 min 70% of OTC with 100 mg/L initial concentration was removed (Uslu and Balcıoğlu 2009).

It has been suggested that highly reactive nano scale zero valent iron (NZVI) could be applied in groundwater remediation and other environmental applications. For example, NZVI can effectively transform many environmental contaminants (Hua et al. 2011). Chlorinated solvents, organochlorine pesticides, polychlorinated biphenyls, organic dyes, inorganic pollutants, heavy metals, antibiotics have been removed by NZVI. The mechanism of removal was oxidation and reduction in most cases (Kassae et al. 2011, Nowack and Bucheli 2007, Shan et al. 2008 and Ghauch et al. 2009). The oxides and Hydroxide Iron Oxide (FeOOH) have also been used in photocatalytic processes to removal pollutant molecules, for example the 20 mg/L bisphenyl by 200 mg/L α- Fe₃O₄ and 8 W, UV radiation at pH value of 7, 60 min of the 24% was removed after 60 min (Li et al. 2007). 10 mg/L by Reactive Black 5 dye with 500 mg/L FeOOH and 300 W, UV radiation at pH = 7 was reacted and during 480 min 45% of dye was removed (Hsueh et al. 2006). 10 mg/L estradiol (hormone therapy) was also destroyed completely with 500 mg/L FeOOH, 5 mg/L H₂O₂, 15W UV power and pH value of 7, during 1320 min (Rodriguez et al. 2003). The 30 mg/L hexachlorocyclo hexan a by 400 mg/L by Fe₃O₄, UV value 300W at pH = 6 and 60% removal was achieved in a period of 720 min (Fu et al. 2005). 20 mg/L humic acid with 400 mg/L Fe₃O₄, 5mM H₂O₂, UV power value 300W and pH = 7 was reacted completely at 180 min and 100% removal was obtained (Nie et al. 2010).

The core-shell structure has important implications for the chemical properties of nZVI. The defective and disordered nature of the oxide shell renders it potentially more reactive than a simple passive oxide layer formed on bulk iron materials. The relative composition of the oxide and the metal in nZVI is also markedly different from that of bulk ZVI. These considerations make the core-shell structure a highly important aspect to consider when studying the reactivity of nZVI for various remediation processes. The presence of two nano-constituents in the core-shell structure may impart combinational properties for contaminant removal: the metallic iron acts as the electron source and exerts a reducing character, while the oxide shell facilitates sorption of contaminants via electrostatic interactions and surface complexation, and at the same time, permits electron passage from the metal core (Yan et al. 2010).

In several investigation of the oxidation properties of Iron nano particles for degradation of various pollutants used during the removal process, Iron two or three oxides is produced. The
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oxide layer on the surface of nano Iron particles causes it passive. So, the oxidation reaction is stopped. In most of these studies removal of contaminants did not completely, and in some cases toxic byproducts are also produced. No new applications for passive nano Iron oxide have also been suggested (Shan et al. 2008, Ghauch et al. 2009, Li et al. 2007 and Hsueh et al. 2006). But in this study, photocatalytic properties of Iron oxide have been employed during the process of oxidation properties of Iron nano particles to remove the OTC. The removal of OTC was completely and no toxic byproducts were produced. The ORP and DO changes and the mechanism of OTC degradation proved photocatalytic reaction. The kinetic model of process was also studied.

2. Materials and experimental methods

2.1 Materials

In this study the materials were oxytetracycline from Sigma Aldrich with a purity of 99 %, Iron particles in the particle size of 20-80 nm with a purity of 90% from Research Institute of Petroleum Industry. Hydrochloric acid and sodium hydroxide were made by Merck method.

2.2 Experimental methods

2.2.1 Initial concentration of MTBE

In present study oxytetracycline, molecular formula C_{22}H_{24}N_{2}O_{9}.2H_{2}O, molecular weight 496 g/mol, soluble in water, pH equal to 6.5 and the absorption wavelengths of 290 and 348 nm was used (Fig. 1). Two peaks are corresponding to the aromatic system and carbonyl functional groups (C = O) (Pavia 1987).

In this study, the 500 ml aqueous solution of OTC was drawn into the quartz tank with length 60 cm and the inner diameter 5.5 cm, the pH set by sodium hydroxide and hydrochloric acid. The solution is stirred by a glass shaft that attached to the mechanical stirrer with speed 300 rpm. Ten UV-A lamps with power value 20 W are fixed vertically, around the reactor in 7 cm distance. The external plastic tank includes lamps and quartz tank, is covered by Aluminum plates for reduce of loss of energy (Fig. 2).

![Fig. 1 Structure and absorption spectrum of the OTC](image-url)
In order to find appropriate pH and irradiation power, some initial experiments were carried out by samples of OTC concentrations, 100 ppm, pH of 2, 3, 4, 5, 6, 7, 8, 9 and 11 nano particles Iron 1000 ppm, and the value power of radiation 60, 200 and 240 W in 10 hours. For RSM design the range of concentration of OTC and NZVI were 10 to 300 and 10 to 1000 respectively. Also time of reaction was fixed 1 to 10 hours. pH and UV power were 3 and 200W respectively. The ORP, pH and DO parameters and also mechanism and kinetic model of OTC degradation were studied in optimal condition of reaction.

All experiments were repeated three times at 22-24°C, The measurement methods were based from the book of standard methods of testing water and wastewater (Greenberg et al. 2005). It should be noted that the relative standard deviation (RSD) were less than 2.33 percent, reflecting the high reproducibility of the data. The process for determining appropriate levels of energy consumption for each concentration tested remove the ppm (mg/L) emissions were calculated according to Eq. (1) (Anousha et al. 2009).

\[
\text{Energy Consumption/C} = W.t(\frac{C_{in} - C_{out}}{C_{in}})
\]

In this equation, \( W \) is power consumption (kW), \( t \) the time of irradiation (hr), Energy Consumption/C power to remove any contaminants ppm (milligrams per kilo - watt hours per liter), \( C_{in} \) and \( C_{out} \) are initial and final concentration of sample (ppm). The instruments that used in various stages of testing include a spectrophotometer (DR4000, Hach) for determination of absorbance, COD and TOC, XRD (Philips) for determination of oxide layer, \( \text{pH} \) meter (Metrohm), DO and ORP meter (HQ30d, HACH) CO\textsubscript{2} Analyzer (EXTECH, CO250), HPLC/ESI-MS (Agilent 6410-QQQ) for detecting by products, digital scale Kern model PLS360-3.
3. Results and discussions

3.1 pH effect

At pH = 2, all the Iron particles were dissolved and no reaction happened. As shown in Fig. 3, at pH = 3, hydroxyl and amine functional groups of OTC were removed (Hua et al. 2011) and the high removal efficiency in both wavelengths was observed and the output was achieved at pH = 6.5. As shown in Fig. 4 the output pH is not changed in neutral and alkaline pH, so dissociation of OTC was less than acidic pH. The samples were prepared at alkaline and neutral pH (Fig. 5(a)) had complex of Iron with OTC (Hua et al. 2011) which has a darker color than the first solution and particles of Iron was dissolved completely (non-reusable).

By adding 1 mL concentrated hydrochloridric acid after 12 hours the complex was coagulated and precipitated (Fig. 5(b)). The volume of residue was 10%.

Note that the removal efficiency at pH = 3 was 95%, and pH in both the 290 and 348 nm peak have been changed. The Iron oxide particles, the deposition of insoluble residues and their separation, centrifuge with 3000 rpm at 10 min. was applicable. So pH = 3 was chosen as optimum.

![Fig. 3 Effect of pH on the removal of OTC](image)

![Fig. 4 Changes in the input and output of pH](image)
3.2 UV Irradiation effect

According to the Fig. 6, the power emitted at 200 and 240 watts at acidic pH=3, concentration of 100 mg/L OTC and 1000 mg/L rail for 10 hours, the highest removal efficiency at the wavelengths 290 and 348 nm, COD and TOC was 87, 95, 89 and 85 percent, respectively. 60 and 140 watts of radiant power absorbed at wavelengths 290 and 348 removal efficiency was less than 80% to 95% with increasing radiation intensity has been great. While the TOC and COD removal efficiency increased with increasing irradiation with gentler slopes. This indicates that a more effective role in UV damage than the OTC molecule reaction byproducts was removed. With regard to the relationship of energy to remove 1 mg/L OTC equal to 8.82 W at any time, in order to reduce the cost of electricity, radiation could be emitted as the 200 W was considered optimal.
3.3 **Response surface methodology**

Response surface methodology (RSM) has been used to determination of optimal conditions for the removal of OTC by iron nano particles. In Table 1, the variable concentrations of parameters OTC, the nano iron particles and time of reaction have been shown with the levels ($\pm 1$) and concentration range ($\pm \alpha$). By the results of previous experiments, the value of pH must be 3 and the radiation power because of minimum energy consumption should be 200 W. In Table 2, 20 runs have been designed and four responses removal percents of OTC in wavelengths 290 and 348 nm TOC and COD should be obtained.

<table>
<thead>
<tr>
<th>Table 1 Independent variables and their levels in the experimental design</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Factors</strong></td>
</tr>
<tr>
<td>OTC Concentration</td>
</tr>
<tr>
<td>NZVI Concentration</td>
</tr>
<tr>
<td>Time</td>
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</table>

<table>
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<tr>
<th>Table 2 Experimental design and results of the central composite design</th>
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</thead>
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<tr>
<td><strong>Runs</strong></td>
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<tr>
<td>OTC (mg/L)</td>
</tr>
<tr>
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</tr>
<tr>
<td>2</td>
</tr>
<tr>
<td>3</td>
</tr>
<tr>
<td>4</td>
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<td>19</td>
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<tr>
<td>20</td>
</tr>
</tbody>
</table>
Table 3 shows Analysis of variance (ANOVA) provided consistent results for all four responses, P values of the data were less than 0.05 (Prob > F-Values), so linear model with a confidence level more than 95 percent was suitable. The correlation coefficient ($R^2$) for each of the four responses absorption in 290 nm and 348 nm, TOC and COD were 0.90, 0.90, 0.89 and 0.88 respectively and the correlation coefficient adjusted (Adj. $R^2$) were 0.88, 0.88, 0.87 and 0.86 respectively, which was due to the large difference in coefficient model was acceptable. A perfect fit for all four levels of the $P$-Values that indicate poor adaptation of the model to the data. The responses were fitted with linear Eqs. (2)-(5).

Removal efficiency at 290 nm
\[ \text{Removal efficiency at 290 nm} = -10.84013 - 0.19194 \times \text{OTC} + 0.073797 \times \text{NZVI} + 8.15871 \times \text{Time} \] (2)

Removal efficiency at 348 nm
\[ \text{Removal efficiency at 348 nm} = -10.49732 - 0.20734 \times \text{OTC} + 0.079881 \times \text{NZVI} + 8.74458 \times \text{Time} \] (3)

Removal efficiency of TOC
\[ \text{Removal efficiency of TOC} = -7.28781 - 0.19993 \times \text{OTC} + 0.071716 \times \text{NZVI} + 7.82908 \times \text{Time} \] (4)

Removal efficiency of COD
\[ \text{Removal efficiency of COD} = -5.02747 - 0.21838 \times \text{TC} + 0.076624 \times \text{NZVI} + 8.12388 \times \text{Time} \] (5)

<table>
<thead>
<tr>
<th>Responses (% Removal)</th>
<th>Source</th>
<th>Sum of squares</th>
<th>Degree of freedom</th>
<th>Mean square</th>
<th>$F$-Value</th>
<th>$P$-Value</th>
</tr>
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<tbody>
<tr>
<td>Adsorption in 290 nm</td>
<td>Model</td>
<td>16691.32</td>
<td>3</td>
<td>5563.77</td>
<td>48.39</td>
<td>&lt; 0.0001</td>
</tr>
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<td></td>
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<td>16</td>
<td>114.98</td>
<td>-</td>
<td>-</td>
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<tr>
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<td>Lake of fit</td>
<td>1839.63</td>
<td>11</td>
<td>167.24</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Pure error</td>
<td>0.00</td>
<td>5</td>
<td>0.00</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Adsorption in 348 nm</td>
<td>Model</td>
<td>19390.06</td>
<td>3</td>
<td>6463.35</td>
<td>48.48</td>
<td>&lt; 0.0001</td>
</tr>
<tr>
<td></td>
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<td>2133.14</td>
<td>16</td>
<td>133.32</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Lake of fit</td>
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<td>11</td>
<td>193.92</td>
<td>-</td>
<td>-</td>
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<td>5</td>
<td>0.00</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>TOC</td>
<td>Model</td>
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<td>3</td>
<td>5378.57</td>
<td>42.35</td>
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<tr>
<td></td>
<td>Residual</td>
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<td>16</td>
<td>127.02</td>
<td>-</td>
<td>-</td>
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<tr>
<td></td>
<td>Lake of fit</td>
<td>2032.28</td>
<td>11</td>
<td>184.75</td>
<td>-</td>
<td>-</td>
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<td></td>
<td>Pure error</td>
<td>0.00</td>
<td>5</td>
<td>0.00</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>COD</td>
<td>Model</td>
<td>18240.46</td>
<td>3</td>
<td>6080.15</td>
<td>38.97</td>
<td>&lt; 0.0001</td>
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<td>16</td>
<td>156.03</td>
<td>-</td>
<td>-</td>
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<tr>
<td></td>
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<td>11</td>
<td>226.96</td>
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</tr>
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<td>Pure error</td>
<td>0.00</td>
<td>5</td>
<td>0.00</td>
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</tr>
</tbody>
</table>
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The Eqs. (2)-(5) have been shown that by increasing the NZVI concentration and decreasing OTC concentration, the removal efficiency will increase. Also removal of functional groups is easier than aromatic rings and by increasing the time of reaction, the photocatalytic reaction is more efficient than oxidation reaction, so degradation of OTC will be more. In Fig. 7 optimizing the process for removal efficiency (%) 80 to 100 of all responses during 6.5 hours, the yellow zone is the optimized condition. The validation of the model by two experiments have been done, both show confidence level more than 95 percent.

3.4 Photocatalytic efficiency

Degradation of OTC was used to evaluate the photocatalytic reactivity of the catalysts. The initial concentration of the OTC was 155 mg/l and the dosage of NZVI, was kept at 1000 mg/l. The pH was 3 and irradiation was carried out at 200 W UV-A (a run of the optimized condition). After 6.5 hr the oxide layer over the NZVI was analyzed by XRD, FeOOH was detected and the photocatalytic mechanism is explained by Eqs. (6)-(9) (Nie et al. 2010).

\[
\text{FeOOH} + h\nu \rightarrow e^- + h^+ \tag{6}
\]

\[
\text{H}_2\text{O} + h^+ \rightarrow \text{OH}^* + \text{H}^+ \tag{7}
\]

\[
\text{O}_2 + e^- \rightarrow \text{O}_2^{-*} \tag{8}
\]

\[
\text{O}_2^{-*} + 2\text{H}^+ \rightarrow 2\text{OH}^* \tag{9}
\]

Fig. 7 Optimized condition in 6.5 hr
Also the oxidation reduction potential (ORP), DO and pH were determined to find the photocatalytic reaction time. Fig. 8 shows the DO and ORP in system dropped from 6.48 mg/L and 465.64 mV to 1.08 and –378.88 mV respectively. During this reaction, iron oxidized and OTC reduced (Eqs. (10)-(14)) (Chen et al. 2012).

\[
2\text{Fe}^0 + 4\text{H}^+ + \text{O}_2 \rightarrow 2\text{Fe}^{2+} + 2\text{H}_2\text{O} \tag{10}
\]

\[
2\text{Fe}^{2+} + 2\text{H}_2\text{O} \rightarrow 2\text{Fe}^{3+} + \text{H}_2 + 2\text{OH}^- \tag{11}
\]

\[
\text{Fe}^{3+} + 3\text{OH}^- \rightarrow \text{Fe(OH)}_3 \tag{12}
\]

\[
\text{Fe}^{3+} + 2\text{H}_2\text{O} \rightarrow \text{FeOOH} + 3\text{H}^+ \tag{13}
\]

\[
\text{Fe(OH)}_3 + 3\text{H}^+ \rightarrow \text{FeOOH} + \text{H}_2\text{O} \tag{14}
\]

During next 3 hours, the DO and ORP were raised to 2.92 mg/L and 456.00 mV respectively, this time iron was reduced and the byproducts of OTC were oxidized. The pH increased from 3 to 7 because of separation hydroxyl groups (Eqs. (15)-(16)) (Crane et al. 2012).

\[
\text{FeOOH} + 3\text{H}^+ + e^- \rightarrow \text{Fe}^{2+} + 2\text{H}_2\text{O} \tag{15}
\]

\[
\text{O}_2 + 2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^- \tag{16}
\]

3.5 Mechanism of degradation

By destroying the OTC molecule during the reaction, some major by products have been detected by HPLC/MS and CO2 Analyzer (Fig. 9). \(P_1\) (C22H23N2O5) and \(P_2\) (C10H26) were produced.
Degradation of oxytetracycline by nano zero valent iron under UV-A irradiation during oxidation of NZVI and $P_3$ (C$_3$H$_8$O$_3$), $P_4$ (C$_3$H$_6$O$_3$) and $P_5$ (CO$_2$) were produced in photocatalytic reaction.

The mechanisms of producing P1 to P5 explain by two processes. Fig. 10 shows the removal of functional groups from rings of OTC during oxidation of NZVI (Morgan et al. 2012).

![Fig. 9 By products of OTC degradation](image_url)
In photocatalytic reaction (Fig. 11) the hydroxyl radicals destroy the byproducts by Eqs. (17)-(20). $R_1$, $R_2$ and $R_3$ are carbon chains or rings

\[
R-H + ^\cdot\text{OH} \rightarrow H_2O + ^\cdot R 
\]  

(17)

\[
^\cdot R + O_2 \rightarrow RO_2 
\]  

(18)

\[
R + ^\cdot R \rightarrow R-R 
\]  

(19)

\[
R + ^\cdot\text{OH} \rightarrow R-OH 
\]  

(20)

3.6 Kinetic study

Fig. 12 shows the concentration changes of OTC and it's byproducts during the reaction. Production of $P_1$ and $P_2$ were started in the 15 min of reaction, after 460 and 580 min their concentration became 5 ppm respectively. $P_3$ and $P_4$ were produced in the 150 min of reaction and...
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after 740 and 790 min their concentration became 5 ppm respectively. The Carbon dioxide produced after 160 min of reaction.

The kinetic constant of OTC and it's by products removals calculate were first order chain reactions that have shown by Eqs. (21)-(26). The Central numerical determination was used to solve the equations (House 2007).

\[
\frac{d[\text{OTC}]}{dt} = -K_1[\text{OTC}] \\
\frac{d[P_1]}{dt} = -K_1[\text{OTC}] - K_2[P_1] \\
\frac{d[P_2]}{dt} = -K_2[P_1] - K_3[P_2] \\
\frac{d[P_3]}{dt} = -K_3[P_2] - K_4[P_3] \\
\frac{d[P_4]}{dt} = -K_4[P_3] - K_5[P_4] \\
\frac{d[P_5]}{dt} = -K_5[P_4]
\]

\(P_1\) and \(P_2\) were produced when all the functional groups (hydroxyl and carbonyl) removed completely from OTC structure, \(K_1\) and \(K_2\) depend on Production of \(P_1\) and \(P_2\) were calculated 0.0099 and 0.0021 min\(^{-1}\) respectively. \(K_2\) is less than \(K_1\), because the carbonyl group has stronger bond rather than amines and hydroxyl groups. \(P_3\) and \(P_4\) are the photocatalytic production. \(K_3\) is the most less kinetically constant of converting \(P_2\) to \(P_3\) (0.0010 min\(^{-1}\)), because the rings of \(P_2\) had to break, so it took much time (Yuan et al. 2011). Converting \(P_3\) to \(P_4\) was done by kinetic constant \(K_4\) (0.0049 min\(^{-1}\)). \(K_4\) is faster than \(K_3\), because the structure of \(P_4\) is simple than \(P_3\). \(K_5\) (0.0074 min\(^{-1}\)) is the kinetic constant of converting \(P_4\) to CO\(_2\).
4. Conclusions

The removal of OTC as a hard biodegradable compound by Nano zero valent Iron particles as a suitable remediation subject, was happened at pH 3. The optimal UV-A irradiation was obtained 200 W, because the more removal yield (90%) and the less consumption energy (8.82 W/hr for removal of 1 ppm OTC) was obtained.

The layer oxide over the NZVI particles was detected as FeOOH. This chemical compound has photocatalytic properties to produce hydroxyl radicals. The ORP, DO and pH changes and structure of by products, during the reaction have confirmed that. After 3 hours of removal reaction the photocatalytic reaction by FeOOH was highlighted.

In this process there were no toxic byproducts but in photolysis (Shaojun et al. 2008), Ozonation (Li et al. 2008 and Uslu and Balcioglu 2009) and UV/TiO₂ (Zhao et al. 2010), the by products were toxic. The biological treatments for OTC removing were not very successful, because of the toxicity of OTC for microorganism and low yield of removing by them (Huang et al. 2011a and Arikan et al. 2006).

The rate of removal reaction in this process was faster than photolysis and UV/TiO₂ reactions. In photolysis and UV/TiO₂ reactions, just hydroxyl and amines groups of OTC were removed by 0.0075 and 0.0018 min⁻¹ respectively (Shaojun et al. 2008 and Zhao et al. 2010).

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