GCU
Glasgow Caledonian
University

University for the Common Good

Reaction kinetics and oxidation product formation in the degradation of acetaminophen by ferrate (VI)

Wang, Hongyu; Liu, Yibing; Jiang, Jia-Qian

1 **Reaction kinetics and oxidation product formation in the degradation of**

2 **acetaminophen by ferrate (VI)**

3 Hongyu Wang[1],*, Yibing Liu[1], Jia-Qian Jiang[2],*

4 [1] School of Civil Engineering and Architecture, Zhejiang University of Technology,

5 Hangzhou 310014, People's Republic of China

6 [2] School of Engineering and Built Environment, Glasgow Caledonian University,

7 Glasgow G4 0BA, Scotland, United Kingdom

8

9

10

11

12

13

14

15

16 *Corresponding authors:

17 Hongyu Wang, Tel.: +86 571 8887 1516; Fax: (+86) 571-88320180.

18 E-mail address: hywang@zjut.edu.cn

19 Jia-Qian Jiang, Tel.: +44(0) 141 331 8850

20 E-mail address: jiaqian.jiang@gcu.ac.uk

21

Abstract

This paper investigates the degradation of acetaminophen (AAP) in aqueous solutions by ferrate (VI), aiming to propose the kinetics, pathways and the oxidation products' formation in the AAP degradation. A series of jar tests were undertaken over ferrate (VI) dosages (molar ratios of ferrate (VI):AAP, 5:1 to 25:1) and pH values (4~11). The effects of co-existing ions (0.2~5 mM) and humic acid (10~50 mg·l^{-1}) on the AAP removal were investigated. Ferrate (VI) can remove 99.6 % AAP (from 1000 µg·l^{-1}) in 60 minutes under study conditions when majority of the AAP reduction occurred in the first 5 minutes. The treatment performance depended on the ferrate(VI) dosage, pH and the type and strength of co-existing ions and humic acid. Raising ferrate (VI) dosage with optimal pH 7 improved the AAP degradation. In the presence of humic acid, the AAP degradation by ferrate (VI) was promoted in a short period (< 30 min) but then inhibited with increasing in humic acid contents. The presence of Al^{3+}, CO_3^{2-} and PO_4^{3-} ions declined but the existence of K^+, Na^+, Mg^{2+} and Ca^{2+} ions can improve the AAP removal. The catalytic function of Al^{3+} on the decomposition of ferrate (VI) in aqueous solution was found.

The kinetics of the reaction between ferrate (VI) and AAP was pseudo first-order for ferrete (VI) and pseudo second-order for AAP. The pseudo rate constant of ferrate (VI) with AAP was 1.4×10^{-5} L^2·mg^{-2}·min^{-1}. Three oxidation products (OPs) were identified and the AAP degradation pathways were proposed.

Keywords: Potassium ferrate (VI); Acetaminophen; Reaction mechanism; Influence factors; Oxidation products

1. Introduction

In recent years, pharmaceutical and personal care products (PPCPs) have been detected in numerous water resources (Boyd et al., 2003; Kim et al., 2009; Liu and Wong, 2013). The potential hazard toward aquatic organisms and public health (Fent et al., 2006; Crane et al., 2006; Witorsch and Thomas, 2010) resulting from increasing PPCPs concentrations, and the incomplete removal of PPCPs has been found in various conventional wastewater treatment plants (Boyd et al., 2003; Khetan and Collins, 2007). As a typical anti-inflammatory and analgesic medication, acetaminophen (AAP) is produced and consumed about 1.45×10^5 tons per year worldwide (Kasprzyk-Horderna et al., 2008). AAP has high solubility up to 12.78 $g \cdot kg^{-1}$ in aqueous solutions at 20 °C, and has been detected frequently in water courses (Granberg and Rasmuson, 1999). More than 65 μg/L of acetaminophen has been detected in surface water and the concentration of acetaminophen might be much higher in pharmaceutical industry wastewater (Roberts and Thomas, 2006). Research has shown that AAP had toxicity on bivalve *Dreissena polymorpha* (Parolini et al., 2013).

Due to the possession of dual functions of oxidation and coagulation, ferrate (VI) has been studied widely and demonstrated to be a very promising chemical for both water and waste water treatment (Jiang and Lloyd, 2002; Lee et al., 2004; Jiang et al., 2006). The elimination of PPCPs by ferrate (VI) has been conducted by many researchers (e.g., Yang et al., 2012; Jiang et al., 2013; Jiang, 2014; Sharma et al., 2015). So far, the degradation of AAP has been reported by anodic oxidation with a

67   boron-doped diamond electrode (Brillas et al., 2005), subsurface flow constructed

68   wetlands (Ranieri et al., 2011), ozonation and H_2O_2/UV system (Andreozzi et al.,

69   2003), Photo-Fenton process (Trovo et al., 2008) and TiO_2 photocatalysis (Yang et al.,

70   2008). However, to the best of our knowledge, the study on the degradation of AAP

71   using ferrate (VI) has not been reported so far.

72   And thus, this study focused on the removal of AAP in aqueous solutions by

73   ferrate (VI). Conditions of the degradation of AAP were investigated with respect to

74   ferrate (VI) dosage, pH value, and the presence of humic acid and various co-existing

75   ions (K^+, Na^+, Mg^{2+}, Ca^{2+}, Al^{3+}, CO_3^{2-}, SO_4^{2-}, PO_4^{3-}). The study also aimed to reveal

76   oxidation products (OPs) and kinetics for the degradation of AAP by ferrate (VI).

77

78   **2. Experimental section**

79   *2.1 Chemicals and reagents*

80   Acetaminophen (AAP) was purchased from aladdin (Shanghai, China); Sodium

81   hydroxide, methanol (LC) and potassium hydroxide (AR) were purchased from

82   Hangzhou Xiaoshan Chemical Reagent Factory (Hangzhou, China); Humic acid (HA)

83   was obtained from Nanjing Chemical Reagent Factory (Nanjing, China). Ferrate (VI)

84   solution of high concentration was synthesized by the electro-chemical way (Wang et

85   al., 2015), and then transferred to solid potassium ferrate (VI) after various

86   purification steps (Li et al., 2005). The ferrate(VI) strength of the resulting dry

87   product was measured by chromite method and direct spectrophotometric method

88   using a wavelength of 505 nm and an absorbance coefficient of 1100 $M^{-1}\cdot cm^{-1}$ (Jiang

89   et al., 2009). The purity of ferrate (VI) was continuously monitored on the daily basis.

90   The other reagents were supplied by Sinopharm Chemical Reagent Co. Ltd.

91   (Shanghai, China). Experimental water was generated by ultra pure water supplier

92   (UPHW1-90T, Sichuan europtronic ultra pure Technology Co. Ltd., China). Stock

93   solutions of AAP were prepared in pure water at 100 $mg\cdot l^{-1}$ for the use of jar test

94   experiments, identification of oxidation products and kinetic analysis.

95   *2.2 Jar test experiment*

96   The oxidation of AAP by ferrate (VI) was studied using a magnetic stirrer (Color

97   squid, IKA (Guangzhou) equipment Co. Ltd, China) with a mixing speed of 600 rpm.

98   Pipette (Shanghai Kangmin inspection equipment Co. Ltd, China) was used for

99   sampling at given reaction time intervals; 1, 2, 5, 10, 20, 40 and 60 min, respectively,

100   and sodium hyposulfite was used as a quencher.

101   In order to examine the formation of AAP oxidation product as well as to assess

102   the degradation performance readily, two initial AAP concentrations, 500 and 1000

103     $\mu g\cdot l^{-1}$ respectively, were used for the study. The selected AAP concentrations were

104   also in line with that used by other researchers (e.g., Yang et al., 2008). The influence

105   of operating conditions were investigated using 100 mL test solutions with initial AAP

106   concentrations of 1000 $\mu g\cdot l^{-1}$ and by adjusting a number of ferrate (VI) dosages, pH

107   values and HA concentrations. Ferrate (VI) was dosed into the test solution as dried

108   powder and the dosage applied was in the molar ratio of ferrate (VI):AAP from 5:1 to

109   25:1. The pH of test solutions was adjusted by 0.01 M hydrochloric acid and 0.01 M

110   sodium hydroxide to pH 4~11. The HA concentration in testing solutions was 10~50

111   mg·l^{-1}.

112   Test solutions of 200 mL with AAP initial concentration of 500 µg·l^{-1} were used

113   to study the impact of the presence of 0.2~5 mM co-existing ions (K^+, Na^+, Mg^{2+},

114   Ca^{2+}, Al^{3+}, CO_3^{2-}, SO_4^{2-}, PO_4^{3-}) on the AAP degradation performance by ferrate(VI).

115   The AAP solutions were mixed with given amount of NaCl, KCl, MgCl$_2$, CaCl$_2$,

116   Al$_2$(SO$_4$)$_3$, Na$_2$CO$_3$, Na$_2$SO$_4$ and Na$_3$PO$_4$, respectively, to achieve the required ion

117   concentrations. The ferrate (VI) with dosage of the molar ratio of 28:1(ferrate

118   (VI):AAP) was mixed with the test solution and the sampling time was 0, 1, 2, 3, 5, 7

119   and 15 min. All samples in jar test experiments were filtered by 0.45 µm glass

120   membrane filters (Shanghai Xingya purifying material factory, China) before

121   analyzing the residual AAP concentrations. The AAP concentration and removal

122   percentage of each sample were detected by liquid chromatography (LC) (see sub-

123   section 2.5).

124   *2.3 Identification of degradation products*

125   Test solutions of 1000 µg·l^{-1} AAP were prepared in pure water. Ferrate (VI) was

126   added to the solution of AAP with the molar ratio of 40:1. The samples were obtained

127   after determined intervals, 0, 1, 5, 15, 30, 45 and 60 min. Detailed procedures of

128   identification of AAP degradation products can be seen in sub-section 2.5.

129   *2.4 Kinetic analysis*

130   Kinetic analysis of AAP with ferrate (VI) was performed at room temperature

131      $(20\pm2{}^{0}C)$ under pseudo-first-order conditions with ferrate (VI) in excess. The test

132   solutions of AAP were prepared in pure water. A given ferrate (VI) dose of 32.5 mg·l^{-1}

133   was added into test solutions with AAP concentrations of 300, 500, 700, 900 μg·l^{-1}

134   respectively. On the other hand, several ferrate (VI) doses, 13, 19.5, 26, 32.5 mg·l^{-1}

135   respectively, were dosed into the test solutions with a given AAP concentration of

136   1000 μg·l^{-1}. For the given time intervals as stated above, the reacting solutions were

137   quenched with sodium hyposulfite solution.

138   *2.5 Analytical methods*

139   The concentration of chemical oxygen demand (COD) of test solutions before

140   and after ferrate (VI) treatment was measured by potassium dichromate method

141   (APHA et al., 1998).

142   Ion chromatograph (ICS-900, Dionex, US), coupled with an anion column

143   (IonPac AS19, 4×250 mm) and a flow rate of 0.8 mL·min^{-1} of 20 mM KOH solution,

144   was used for the measurement of inorganic ions' concentrations.

145   The measurement of AAP was conducted by an Agilent 1200 LC system

146   (Agilent, US) with diode array detector (DAD). The column utilised for the separation

147   of compounds was a 5 μm, 4.6×150 mm reversed phase Eclipse XDB-C18 column

148   (Agilent, US). The column was kept at 30 ${}^{0}C$ and eluted by 15% methanol and 85%

149   pure water at a flow rate of 0.8 mL·min^{-1}. The injection volume was 10 μl and the

150   DAD detection wavelength for AAP was 257 nm.

151   The oxidation products of AAP treated by ferrate (VI) were analyzed by a GC-

152   MS system (Saturn, USA) equipped with an SE-54 capillary column (Chromse, UK).

153 For each GC-MS injection, samples were pretreated by hydrochloric acid of 1 M to

154 pH<1 and then extracted with chloroform (10 times concentrated). The GC conditions

155 were given as follows: a sample volume of 1 μl injected in the splitless mode at 280

156 ^{0}C and the oven temperature programmed from 50 ^{0}C (5 min) to 250 ^{0}C at 10 ^{0}C min^{-1}

157 followed by a 5 min hold at 250 ^{0}C, and helium used as the carrier gas at a flow rate

158 of 0.8 ml min^{-1}. Mass spectrometer was operated under electron ionization mode at 70

159 eV with mass scan range of 40~500.

160

161 **3. Results and discussion**

162 *3.1. Effect of reaction time and ferrate (VI) dosage*

163

164 Fig. 1. Effect of reaction time and ferrate (VI) dosage on AAP degradation

165   Fig.1 shows the variation of AAP degradation efficiency vs. reaction time and

166 ferrate (VI) dosages. The removal of AAP by ferrate (VI) mainly occurred within the

167 first 5 min reactions, followed by a more gradual further removal over the next 10～

168 55 min. Increasing in the ferrate (VI) dose (as molar ratio of ferrate (VI): AAP) from

169 5:1 to 25:1, the removal efficiency of AAP increased sharply for the given time of 60

170 min; that the AAP removal percentage was 50.5, 76.7, 96.9 and 99.6% for the molar

171 ratio of 5:1, 10:1, 15:1 and 25:1, respectively. On the other hand, for a 10 min

172 reaction and high ferrate(VI) dose (molar ratio of 25:1), approximate 90% AAP was

173 removed. In general, ferrate (VI) could remove AAP readily under these conditions.

174   Additionally, COD concentration of the test solution with 10 mg AAP l^{-1} was 31

175 mg l^{-1} and after ferrate(VI) treatment (ferrate (VI) dose of 0.325 g/L) the COD was

176 reduced to 24 mg l^{-1} which gives 23% COD reduction, representing the optimal COD

177 reduction performance.

178

179 *3.2. Effect of pH*

180   Fig.2 shows the variation of AAP degradation efficiency vs. pH value and

181 reaction time. It can be observed that for a given ferrate(VI) dose (25:1 as molar ratio,

182 ferrate (VI):AAP) and pH 4, AAP removal was about 85% and irrelevant to the

183 reaction time. For other pHs, AAP removal was less than 70% and pH 11 was not

184 favorable to the APP removal especially for short reaction time; only 11.3% AAP was

185 removed for the reaction time of 2 min at pH 11. On the other hand, increasing in

186 reaction time was favorable to the AAP removal for pH 6-9; 60 min reaction gave the

187 greatest AAP removal (99.95%) for pH 7. Moreover for pH 4 and 9, the degradation

188 rate of AAP by ferrate (VI) increased rapidly at the initial reaction period (2 min) but

189 approached to slight variations after 10 min.

190

191 Fig. 2. Effect of different pH values on AAP degradation
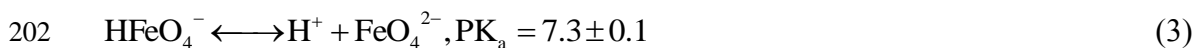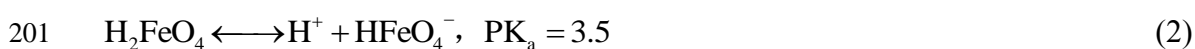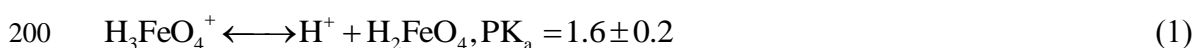
192

193   pH of test solution affects on the oxidation capacity and stability of ferrate (VI).

194 As shown in Fig. 2, degradation rate of AAP by ferrate(VI) at pH 4 was superior to

195   that at pH 11, since ferrate (VI) possesses higher redox potential (2.2 ev) under acidic

196   conditions than that for alkaline conditions. Moreover, ferrate (VI) has been reported

197   to be dissociated to form different species in terms of solution pH as shown in

198   equations 1-3 (Sharma, 2002) and in Fig. S1 of the supplementary material.

199

200    $$H_3FeO_4^+ \longleftrightarrow H^+ + H_2FeO_4, PK_a = 1.6 \pm 0.2 \tag{1}$$

201    $$H_2FeO_4 \longleftrightarrow H^+ + HFeO_4^-, \quad PK_a = 3.5 \tag{2}$$

202    $$HFeO_4^- \longleftrightarrow H^+ + FeO_4^{2-}, PK_a = 7.3 \pm 0.1 \tag{3}$$

203

204   For pH 4 or less, major ferrate (VI) species are $H_3FeO_4^+$, H_2FeO_4 and $HFeO_4^-$,

205   which are readily self-decomposed, resulting in rapid oxidation of APP which has

206   been demonstrated in Fig. 2 where the AAP removal was about 85% and irrelevant to

207   the reaction time. Relatively for pH 7, ferrate (VI) was stable and still had high

208   oxidizing ability and then the best AAP removal performance was achieved for a long

209   reaction duration (60 min).

210   The second effect of pH on the AAP degradation is attributed to the dissociating

211   products of AAP. The PK_a of AAP was 9.5, and dissociating and/or protonated species

212   could be dominant when pH was 9 (see equation 4). Fig. 2 shows that for pH 9, the

213   AAP removal efficiency was high and it was close to that at pH 7. Hence, the results

214   observed from this study demonstrated that high protonated AAP species were readily

215   degraded by ferrate (VI), which is consistent with that from the reported work where

216   solutions containing phenol and chlorinated phenols were treated by ozone and ferrate

217 (VI) (e.g., Graham et al., 2004).

218

219 $$(4)$$

220
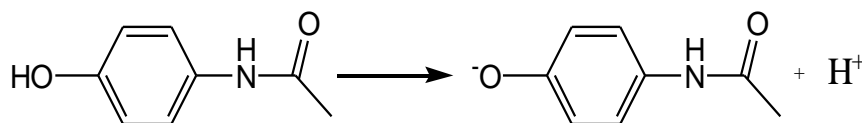
221 *3.3. Kinetics*

222 The rate expression for the reaction of ferrate (VI) with AAP can be expressed as

223 $$r = -d[AAP] \cdot d_T^{-1} = -k \cdot [Ferrate(VI)]^a \cdot [AAP]^b \tag{5}$$

224 where *r* represents the reaction rate of ferrate (VI) with AAP, *k* represents the overall

225 rate constant of ferrate (VI) with AAP, *a* and *b* represent the orders of the reaction,

226 [Ferrate(VI)] and [AAP] represent the concentrations of ferrate (VI) and AAP. The

227 kinetic studies were carried out under pseudo-order conditions with ferrate (VI) in

228 excess. Eq. (5) can be rewritten as

229 $$r = k_1 \cdot [AAP]^b \tag{6}$$

230 Where

231 $$k_1 = k \cdot [Ferrate(VI)]^a \tag{7}$$

232 Eq. (6) can be rewritten as

233 $$\ln r = \ln k_1 + b \ln[AAP] \tag{8}$$

234 Eq. (7) can be rewritten as

235 $$\ln k_1 = \ln k + a \ln[Ferrate(VI)] \tag{9}$$

236

237 Table1. Kinetic parameters of AAP degradation by ferrate (VI)

238

239   Table 1 shows the initial concentrations of AAP, ferrate (VI) dosage, fitting

240   equations and initial reaction rate of AAP. It can be seen that the plot of the reciprocal

241   of AAP concentrations versus reaction time were linear with good coefficient of

242   correlation ($R^2>0.90$) at various concentrations of ferrate (VI), indicating the reaction

243   was second-order with respect to ferrate (VI). Moreover, the plot of the natural

244   logarithm of AAP concentrations versus reaction time were linear with good

245   correlation coefficient ($R^2>0.90$) at various concentrations of AAP, indicating the

246   reaction was first-order with respect to AAP. Although ferrate (VI) was unstable,

247   ferrate (VI) was always in excess in comparison to AAP within the studied reaction

248   time. The value a could be obtained as the slope of ln r versus ln[AAP] with linear

249   fitting and the b is to be determined as the slope of ln k_1 versus ln[Ferrat(VI)] with

250   linear fitting, and this can be seen in Figure 3. Thus, the values of a and b are 1.2

251   ($R^2=0.999$) and 0.38 ($R^2=0.939$), respectively. The apparent third-order rate constant

252   (k) for the reaction was calculated through the intercept in vertical axis. The value of

253   k is 0.000014 $L^2 \cdot mg^{-2} \cdot min^{-1}$. The observed rate law can be written in terms of both

254   ferrate (VI) and AAP as

255    $$r = -d[AAP]d_T^{-1} = -0.000014 \cdot [Ferrate(VI)]^{1.20} \cdot [AAP]^{0.38} \qquad (10)$$

256

257   Fig. 3. Kinetic analysis of AAP degradation by ferrate (VI)

258

259   *3.4. Oxidation products*

260 Based on the measured m/z values and prior literature (Andreozzi et al., 2003;

261 Yang et al., 2009; Moctezuma et al., 2012), the best-fit chemical structures of

262 oxidation products (OPs) were tentatively proposed by considering the molecule

263 pattern of target compounds and the mechanism of ferrate (VI) oxidation; and the

264 probable structures of OPs (AAP-1-3)are presented in Fig. 4. AAP would be attacked

265 by ferrate (VI) which leads to the cleavage of imino group and the transformation of

266 acetyl amino group, forming AAP-1 and AAP-2 respectively. The formation of AAP-3

267 might attribute to further oxidation of intermediate OPs by ferrate (VI). Besides, the

268 NO_3^- was detected in the reaction solution which is consistent with previous studies

269 (Skoumal et al., 2006; Yang et al., 2009), and suggests that the possibility of the

270 broken of C-N bonds.

271

272 Fig. 4. Detection of oxidation products (a – c) and original compound, AAP (d)

273 Fig. 5. Evolution of OPs and nitrate with decreasing of AAP concentration

274

275 Fig.5 shows the evolution of OPs and nitrate during the AAP degradation by

276 ferrate (VI). As it can be observed, AAP-1-2 were formed from the first 1 min

277 reaction, but almost disappeared, together with the AAP, after 60 min reactions. AAP-

278 3 was detected after 15 min and trace nitrate (C_{max}=0.038 mg l^{-1}) was detected in the

279 degradation process. These results also indicate that further oxidation of intermediate

280 OPs by ferrate(VI) occurred.

281 Fig. 6 shows probable pathways of AAP degradation during the treatment by

282   ferrate (VI). The oxidation product, AAP-1, was formed with loss of a C_2H_4NO group

283   from the benzene ring, and the pathway was different with the formation of

284   hydroquinone (Skoumal et al., 2006; Tao et al., 2015) in other AAP degradation.

285   AAP-2 was generated by replacing the hydroxyl group with a quinonyl group and the

286   further loss of a C_2H_3O group from the imino group. In accordance with previous

287   literature (Skoumal et al., 2006; Yang et al., 2008; Moctezuma et al., 2012), AAP-3

288   was also detected, which was a further oxidation product from AAP-1 (phenol).

289   Reference to the prior knowledge (Santos, et al., 2002; Andreozzi et al., 2003; Wang

290   et al., 2014), phenol would be oxidized into para-benzoquinone, which was then

291   converted into maleic acid (AAP-3). The further degradation of AAP-3 could produce

292   oxalic acid and formic acid (Santos, et al., 2002; Skoumal, et al., 2006). Besides, the

293   formation of NO_3^- is due to the deamination of AAP and AAP-2. The attack by

294   ferrate(VI) on the hydroxyl and acetamido groups is consistent with the conclusions

295   made by Zhou and Jiang (2015), that electron-rich moieties were prone to react with

296   ferrate (VI).

297   Fig. 6. Possible pathways of AAP degradation by ferrate (VI)

298

299   *3.5. The presence of humic acid*

300

301   Fig. 7. Effect of different HA dosage on AAP degradation

302

303   The influence of the strength of humic acid (HA) on the removal of AAP by

304   ferrate (VI) treatment was investigated. Fig. 7 shows the changes in residual

305   concentrations of AAP corresponding to HA doses and for the reaction time. As it can

306   be observed, the removal of AAP increased during the intervals between 2 and 10 min

307   after the addition of HA in AAP solutions. However, for 30 and 60 min, the removal

308   efficiency of AAP with HA was less than that of AAP without HA. This suggests that

309   the presence of HA could accelerate the reaction rate of ferrate (VI) and AAP. The

310   observed phenomena might be related to that in the presence of HA, ferrate (VI) could

311   be dissociated to form ferrate (IV) and ferrate (V) which have even greater oxidation

312   capacity (Sharma, 2010) and then assists to the removal of AAP. With increasing in

313   the strength of HA, the removal efficiency of AAP first increased and then decreased,

314   and finally tended to be constant. The high contents of HA could consume more

315   ferrate (VI) in a long reaction time and this might cause the reduction of the removal

316   of PAA for the reaction time of 30 and 60 min.

317

318   *3.6. Effect of coexisting ions*

319   K^+, Na^+, Mg^{2+}, Ca^{2+}, CO_3^{2-}, SO_4^{2-} and PO_4^{3-} ions are common ions in natural

320   water. Aluminum based coagulant is also widely used in water treatment. The effects

321   of above five cations and three anions on the removal percentage of AAP were

322   studied. In the presence of K^+, Na^+, Mg^{2+}, Ca^{2+}, Al^{3+}, CO_3^{2-}, SO_4^{2-}, PO_4^{3-} ions, the

323   AAP removal efficiencies vs. reaction time are shown in Fig. 8(a) for the ion

324   concentrations of 0.2 mM, in Fig. 8(c) for 1 mM and Fig. 8(e) for 5 mM, respectively.

325　As it can be seen, K^+, Na^+, Mg^{2+}, Ca^{2+} and SO_4^{2-} ions can enhance the AAP removal,

326　however, Al^{3+}, CO_3^{2-} and PO_4^{3-} ions had the opposite effect. The higher the

327　concentration of Mg^{2+}, the greater the removal rate of AAP. The performance of K^+,

328　Na^+, Ca^{2+} and SO_4^{2-} mainly remained constant with the increasing concentration from

329　0.2 to 5 mM.

330

331　Table 2. Kinetic parameters of the AAP degradation in the presence of eight co-
332　existing ions

333

334　　　Fig. 8(b), Fig. 8(d) and Fig. 8(f) show the linear fitting curve of the reciprocal of

335　ferrate (VI) concentration and reaction time in the presence of the above ions. Table 2

336　shows the pseudo reaction rate constant (K_{obs}) and correlation coefficient of the linear

337　fitting curves for Fig. 8(b), Fig. 8(d) and Fig. 8(f). The good correlation coefficients

338　($R^2>0.90$, except Al^{3+}) indicate that the reactions were pseudo second-order with

339　respect to ferrate (VI), which is consistent with that shown in the previous section.

340　When raising the ions' concentration from 0.2 to 5 mM, the K_{obs} of CO_3^{2-} and PO_4^{3-}

341　ions decreased, from 4×10^{-4} to 6.8×10^{-5} min^{-1} and 5×10^{-4} to 2.2×10^{-5} min^{-1},

342　respectively, but the K_{obs} of Mg^{2+} increased, from 3.8×10^{-3} to 8.4×10^{-3} min^{-1} . The

343　resulting rate constants are theoretically evident to the observed effect of co-existing

344　ions on the AAP removal by ferrate(VI); that CO_3^{2-} and PO_4^{3-} ions inhabited while

345　Mg^{2+} ions were beneficial to the reaction between AAP and ferrate(VI).

346　　　In the presence of metal cations, deprotonation of acid-base functional groups in

347　AAP molecules can be accelerated due to the metal-AAP binding and this might also

348   reduce the AAP pK_a value (Jeffrey et al., 2006). In this work, the addition of K^+, Na^+,

349   Mg^{2+}, Ca^{2+} could enhance the deprotonation of AAP and then to accelerate the

350   removal rate. Besides, hydrogen ion could be generated through the hydrolysis

351   reaction of magnesium ion in aqueous solution. The accumulation of hydrogen ions

352   helped the increase of oxidation potential of ferrate (VI) (Jiang, 2014). It may be the

353   reason that the addition of Mg^{2+} has a greater removal rate of AAP than Ca^{2+}.

354   In the presence of Al^{3+}, CO_3^{2-} and PO_4^{3-} ions and when the concentration of each

355   ion increased from 0.2 to 5 mM, the removal of AAP decreased from 66.7 to 22.4%

356   for Al^{3+}, 74.2 to 36.5% for CO_3^{2-}, and 79.9 to 13.1% for PO_4^{3-}, respectively. The

357   hydrolysis of CO_3^{2-} and PO_4^{3-} in the aqueous solution could raise the alkalinity and

358   then decreases the oxidation potential of ferrate (VI) and causes the reduction of AAP

359   removal efficiency. This phenomenon was even clearly to observe when

360   concentrations of phosphate and carbonate ions were greater.

361

362   Table 3. Effect of aluminum ions on ferrate (VI) concentration

363

364   In this work, the decomposition of ferrate (VI) caused by aluminium ions was

365   found (Table 3). As can be seen when 500 µl of aluminium ions solution was added,

366   the ferrate (VI) concentration decreased by 79%. This might be related to the

367   hydrolysis of Al^{3+} to produce hydrogen ions into solution, (Eq. 11), which then

368   accelerates the decomposition of ferrate (VI) and could lower the AAP removal

369   efficiency.

370
$$Al^{3+} + 3H_2O = Al(OH)_3 + 3H^+$$
(11)
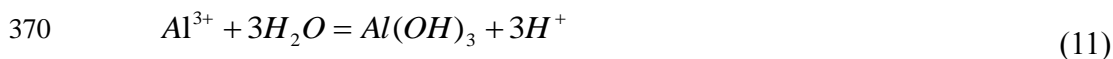
371

372 Fig. 8. Effect of different ions on AAP degradation

373

4. Conclusions

375   The treatment of AAP in aqueous solutions by ferrate (VI) was investigated.

376 Results demonstrated that AAP can be removed effectively under the experimental

377 conditions. More ferrate (VI) dosage and a neutral solution environment could bring a

378 better performance on the AAP degradation. Besides, the pseudo rate constant of

379 ferrate (VI) with AAP is 0.000014 $l^2 \cdot mg^{-2} \cdot min^{-1}$. Three oxidation products (OPs) were

380 identified. The attack on hydroxyl and acetamido groups of the AAP by ferrate (VI)

381 was proposed to be the main pathway of the AAP degradation scheme. Moreover, in

382 the presence of HA, a short time interval (< 30 min) would favour to but longer

383 reaction time (30-60 min) decreased the degradation of AAP. The presence of K^+,

384 Na^+, Mg^{2+} and Ca^{2+} ions in aqueous solutions can improve the AAP removal

385 efficiency by ferrate(VI), and the most promoting effect of Mg^{2+} was observed. The

386 presence of Al^{3+}, CO_3^{2-} and PO_4^{3-} would decline the AAP degradation performance

387 significantly. The catalytic function of Al^{3+} to the ferrate (VI) decomposition in

388 aqueous solution was found in this work, which explains the negative effect of Al^{3+} on

389 the AAP reduction by ferrate (VI).

390

398 **Supplementary material**

399   Supplementary material associated with this article can be found in the online

400 version.

401

402 **References**

403 Andreozzi, R., Caprio, V., Marotta, R., Vogna, D., 2003. Paracetamol oxidation from

404   aqueous solutions by means of ozonation and H_2O_2/UV system. Water Research

405   37, 993-1004.

406 APHA-AWWA-WEF, 1998. Standard methods for the examination of water and

407   wastewater, 20th ed. Washington, DC.

408 Boyd, G.R., Reemtsma, H., Grimm, D.A., Mitra, S., 2003. Pharmaceuticals and

409   personal care products (PPCPs) in surface and treated waters of Louisiana, USA

410   and Ontario, Canada. Sci. Total Environ. 311, 135-149.

411   Brillas, E., Sires, I., Arias, C., Cabot, P.L., Centellas, F., Rodriguez, R.M., Garrido,

412   J.A., 2005. Mineralization of paracetamol in aqueous medium by anodic oxidation

413   with a boron-doped diamond electrode. Chemosphere 58, 399-406.

414   Crane, M., Watts, C., Boucard, T., 2006. Chronic aquatic environmental risks from

415   exposure to human pharmaceuticals. Sci. Total Environ. 367, 23-41.

416   Fent, K., Weston, A.A., Caminada, D., 2006. Ecotoxicology of human

417   pharmaceuticals. Aquat. Toxicol. 76, 122-159.

418   Granberg, R.A., Rasmuson, A.C., 1999. Solubility of paracetamol in pure solvents. J.

419   Chem. Eng. Data 44, 1391-1395.

420   Graham, N., Jiang, C.C., Li, X.Z., Jiang, J.Q., Ma, J., 2004. The influence of pH on

421   the degradation of phenol and chlorophenols by potassium ferrate. Chemosphere

422   56, 949–956.

423   Huang, H., Sommerfeld, D., Dunn, B.C., Eyring, E.M., Lloyd, C.R., 2001. Ferrate(VI)

424   oxidation of aqueous phenol: Kinetics and mechanism. J. Phys. Chem. A 105,

425   3536-3541.

426   Jeffrey J. Werner, William A. Arnold, McNeill, K., 2006. Water Hardness as a

427   Photochemical Parameter: Tetracycline Photolysis as a Function of Calcium

428   Concentration, Magnesium Concentration, and pH[+]. Environ. Sci. Technol. 40,

429   7236-7241.

430   Jia, H.D., Yang, X.L., Yang, Y., Gao, Y.F., 1999. Direct spectrophotometric

431   determination of ferrate(VI). Chin. J. Anal. Chem. 27, 617-617.

432   Jiang, J.Q., Lloyd, B., 2002. Progress in the development and use of ferrate(VI) salt as

433   an oxidant and coagulant for water and wastewater treatment. Water Research 36,

434   1397-1408.

435   Jiang, J.Q., Wang, S., Panagoulopoulos, A., 2006. The exploration of potassium

436   ferrate(VI) as a disinfectant/coagulant in water and wastewater treatment.

437   Chemosphere 63, 212-219.

438   Jiang, J.Q., 2007. Research progress in the use of ferrate(VI) for the environmental

439   remediation. J. Hazard. Mater. 146, 617-623.

440   Jiang, J.Q., Stanford, C., Alsheyab, M., 2009. The online generation and application

441   of ferrate(VI) for sewage treatment—A pilot scale trial. Sep. Purif. Technol. 68,

442   227-231.

443   Jiang, J.Q., Zhou, Z.W., Patibandla, S., Shu, X.H., 2013. Pharmaceutical removal

444   from wastewater by ferrate(VI) and preliminary effluent toxicity assessments by

445   the zebrafish embryo model. Microchem J. 110, 239-245.

446   Jiang, J. Q., 2014. Advances in the development and application of ferrate(VI) for

447   water and wastewater treatment. Journal of Chemical Technology & Biotechnology

448   89, 165-177.

449   Khetan, S.K., Collins, T.J., 2007. Human pharmaceuticals in the aquatic environment:

450   A challenge to green chemistry. Chem. Rev. 107, 2319-2364.

451   Kasprzyk-Hordern, B., Dinsdale, R.M., Guwy, A.J., 2008. The occurrence of

452   pharmaceuticals, personal care products, endocrine disruptors and illicit drugs in

453   surface water in South Wales, UK. Water Research 42, 3498-3518.

454   Kim, J.W., Jang, H.S., Kim, J.G., Ishibashi, H., Hirano, M., Nasu, K., Ichikawa, N.,

455   Takao, Y., Shinohara, R., Arizono, K., 2009. Occurrence of Pharmaceutical and

456   Personal Care Products (PPCPs) in Surface Water from Mankyung River, South

457   Korea. J. Health Sci. 55, 249-258.

458   Lee, Y., Cho, M., Kim, J.Y., Yoon, J., 2004. Chemistry of ferrate (Fe(VI)) in aqueous

459   solution and its applications as a green chemical. Journal of Industrial and

460   Engineering Chemistry 10, 161-171.

461   Li, C., Li, X.Z., Graham, N., 2005. A study of the preparation and reactivity of

462   potassium ferrate. Chemosphere 61, 537-543.

463   Liu, J.L., Wong, M.H., 2013. Pharmaceuticals and personal care products (PPCPs): A

464   review on environmental contamination in China. Environ. Int. 59, 208-224.

465   Moctezuma, E., Leyva, E., Aguilar, C.A., Luna, R.A., Montalvo, C., 2012.

466   Photocatalytic degradation of paracetamol: Intermediates and total reaction

467   mechanism. J. Hazard. Mater. 243, 130-138.

468   Parolini, M., Pedriali, A., Binelli, A., 2013. Application of a Biomarker Response

469   Index for Ranking the Toxicity of Five Pharmaceutical and Personal Care Products

470   (PPCPs) to the Bivalve Dreissena polymorpha. Arch. Environ. Contam. Toxicol.

471   64, 439-447.

472   Roberts, P.H., Thomas, K.V., 2006. The occurrence of selected pharmaceuticals in

473   wastewater effluent and surface waters of the lower Tyne catchment. Sci. Total

474   Environ. 356, 143-153.

475   Ranieri, E., Verlicchi, P., Young, T.M., 2011. Paracetamol removal in subsurface flow

476   constructed wetlands. Journal of Hydrology 404, 130-135.

477   Sharma, V.K., 2002. Potassium ferrate(VI): an environmentally friendly oxidant. Adv.

478   Environ. Res. 6, 143-156.

479   Sharma, V.K., 2010. Oxidation of inorganic compounds by ferrate(VI) and ferrate(V):

480   one-electron and two-electron transfer steps. Environ. Sci. Technol. 44, 5148-5152.

481   Sharma,V.K., Zboril, R., Varma, R.S., 2015. Ferrates: greener oxidants with

482   multimodal action in water treatment technologies, Accounts of Chem. Res. 48

483   182-191.

484   Santos, A., Yustos, P., Quintanilla, A., Rodríguez, S., García-Ochoa, F., 2002. Route

485   of the catalytic oxidation of phenol in aqueous phase. Applied Catalysis B:

486   Environmental 39, 97-113.

487   Skoumal, M., Cabot, P.L., Centellas, F., Arias, C., Rodríguez, R.M., Garrido, J.A.,

488   Brillas, E., 2006. Mineralization of paracetamol by ozonation catalyzed with Fe^{2+},

489   Cu^{2+} and UVA light. Applied Catalysis B: Environmental 66, 228-240.

490   Tao, H., Liang, X., Zhang, Q., Chang, C.T., 2015. Enhanced photoactivity of

491   graphene/titanium dioxide nanotubes for removal of Acetaminophen. Applied

492   Surface Science 324, 258-264.

493   Trovo, A.G., Santos Melo, S.A., Pupo Nogueira, R.F., 2008. Photodegradation of the

494   pharmaceuticals amoxicillin, bezafibrate and paracetamol by the photo-Fenton

495   process - Application to sewage treatment plant effluent. Journal of Photochemistry

496   and Photobiology a-Chemistry 198, 215-220.

497   Wang, H. Y., Liu, Y. B., Zeng, F. C., Song, S., 2015. Electrochemical Synthesis of

498   Ferrate (VI) by Regular Anodic Replacement. Int. J. Electrochem. Sci. 10, 7966-

499   7976.

500   Wang, J., Fu, W., He, X., Yang, S., Zhu, W., 2014. Catalytic wet air oxidation of

501   phenol with functionalized carbon materials as catalysts: Reaction mechanism and

502   pathway. Journal of Environmental Sciences 26, 1741-1749.

503   Witorsch, R.J., Thomas, J.A., 2010. Personal care products and endocrine disruption:

504   A critical review of the literature. Crit. Rev. Toxicol. 40, 1-30.

505   Yang, L., Yu, L.E., Ray, M.B., 2008. Degradation of paracetamol in aqueous solutions

506   by TiO2 photocatalysis. Water Research 42, 3480-3488.

507   Yang, L., Yu, L.E., Ray, M.B., 2008. Degradation of paracetamol in aqueous solutions

508   by TiO2 photocatalysis. Water Res. 42, 3480-3488.

509   Yang, B., Ying, G.G., Zhao, J.L., Liu, S., Zhou, L.J., Chen, F., 2012. Removal of

510   selected endocrine disrupting chemicals (EDCs) and pharmaceuticals and personal

511   care products (PPCPs) during ferrate(VI) treatment of secondary wastewater

512   effluents. Water Research 46, 2194-2204.

513   Zhou, Z., Jiang, J. Q., 2015. Reaction kinetics and oxidation products formation in the

514   degradation of ciprofloxacin and ibuprofen by ferrate(VI). Chemosphere 119,

515   Supplement, S95-S100.

516 **Figure captions**

517 **Fig. 1.** Effect of reaction time and ferrate (VI) dosage on AAP degradation

518 **Fig. 2.** Effect of different pH values on AAP degradation

519 **Fig. 3.** Kinetics analysis of AAP degradation by ferrate (VI)

520 **Fig. 4.** Detection of oxidation products (a – c) and original compound, AAP (d)
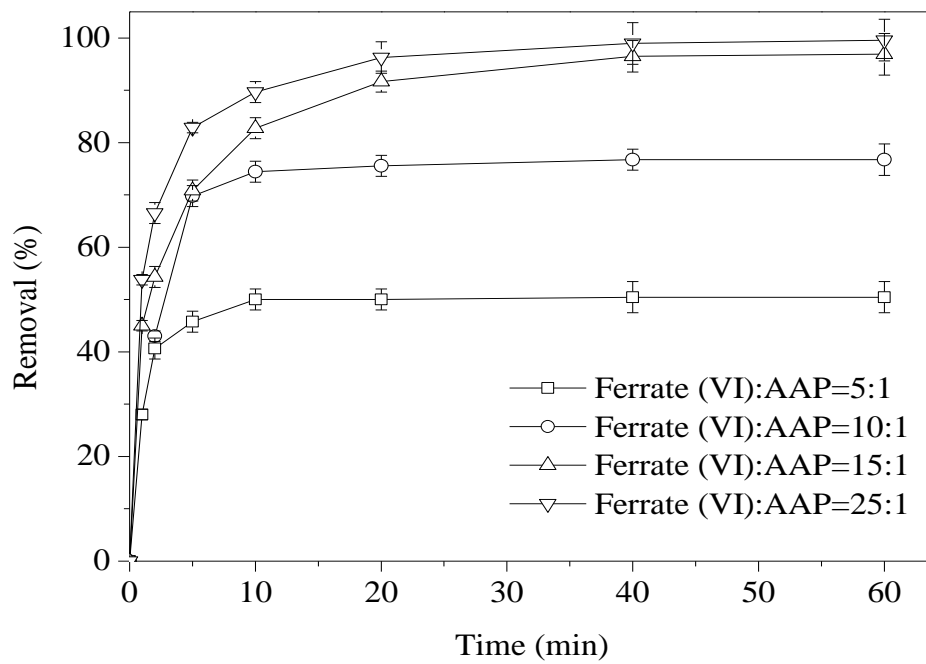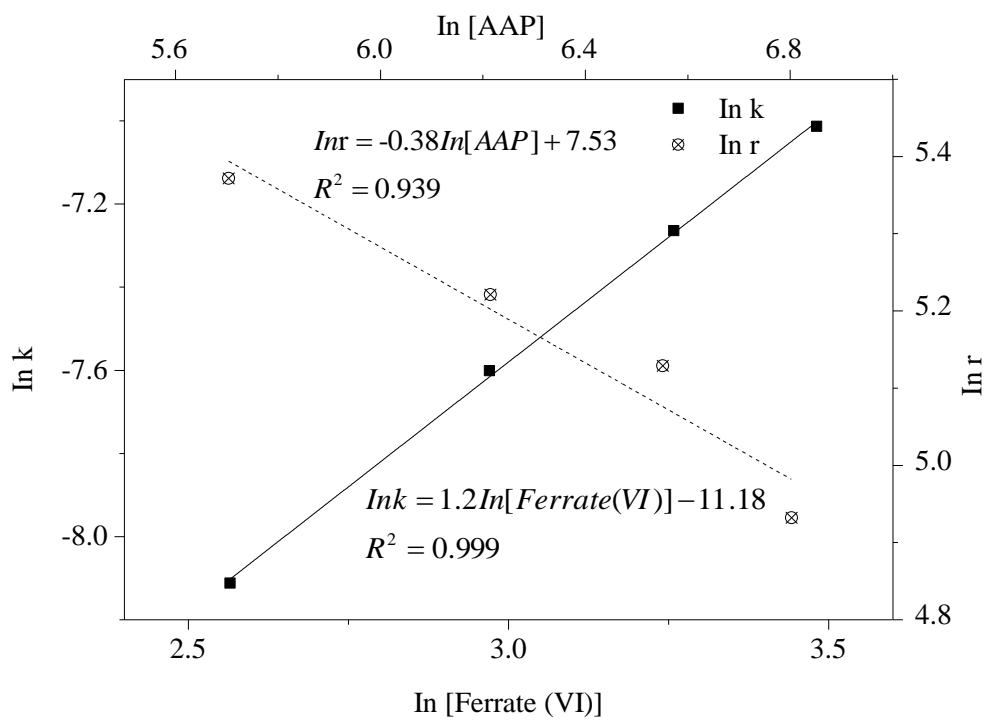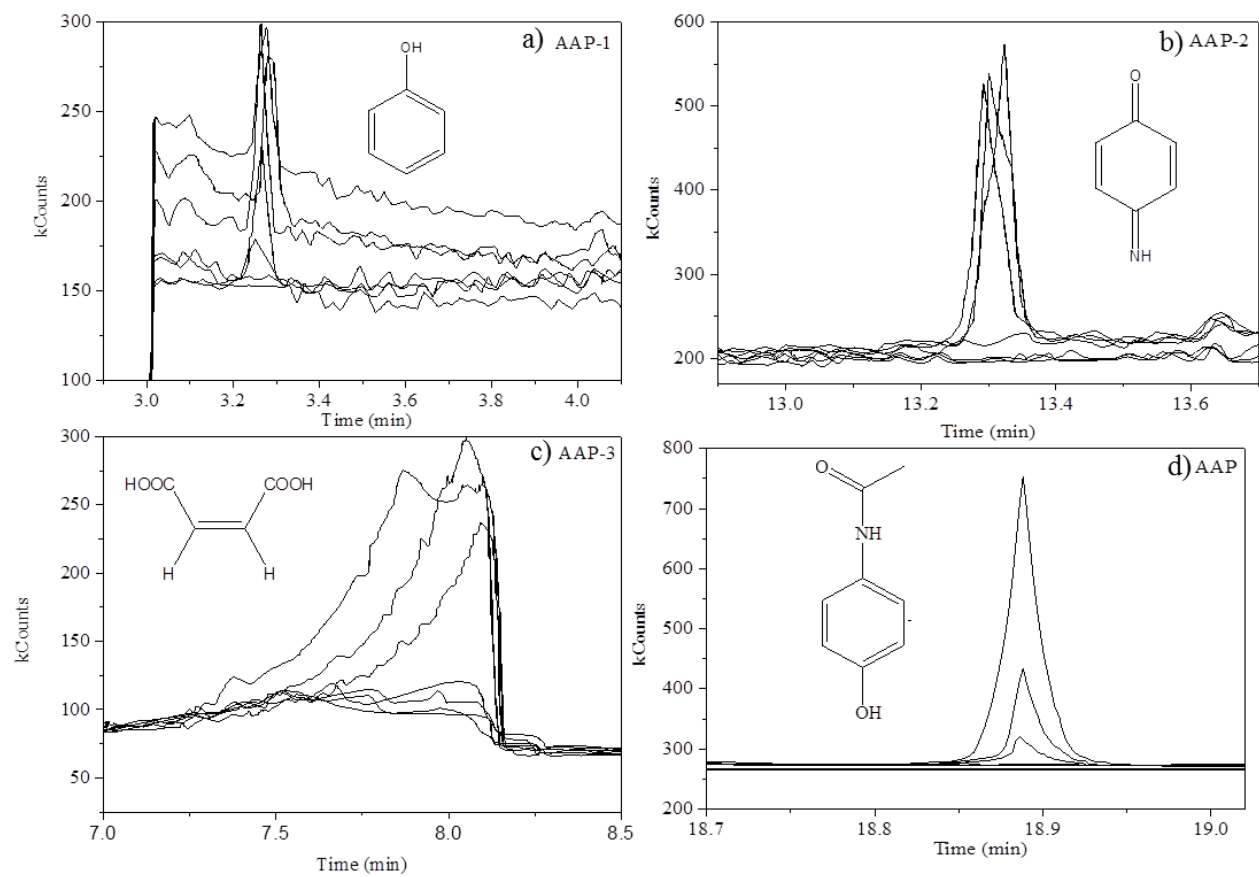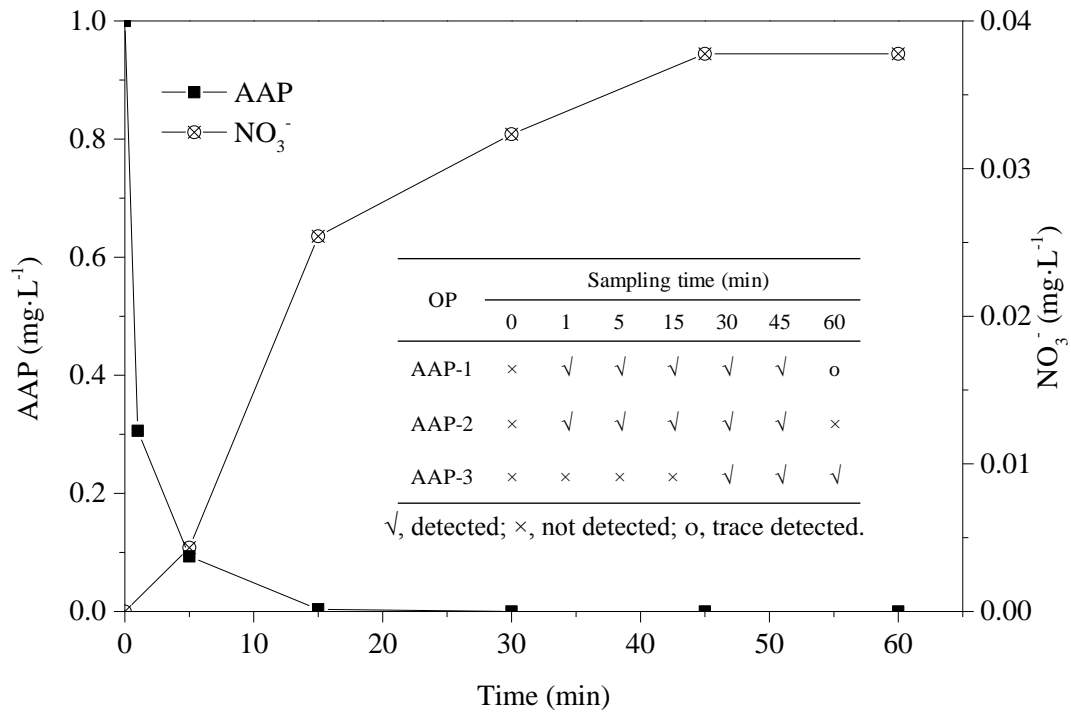
521 **Fig. 5.** Evolution of OPs and nitrate with decreasing of AAP concentration

522 **Fig. 6.** Possible pathways of AAP degradation by ferrate (VI)

523 **Fig. 7.** Effect of different HA dosage on AAP degradation

524 **Fig. 8.** Effect of different ions on AAP degradation

525

526

527   Fig. 1. Effect of reaction time and ferrate (VI) dosage on AAP degradation
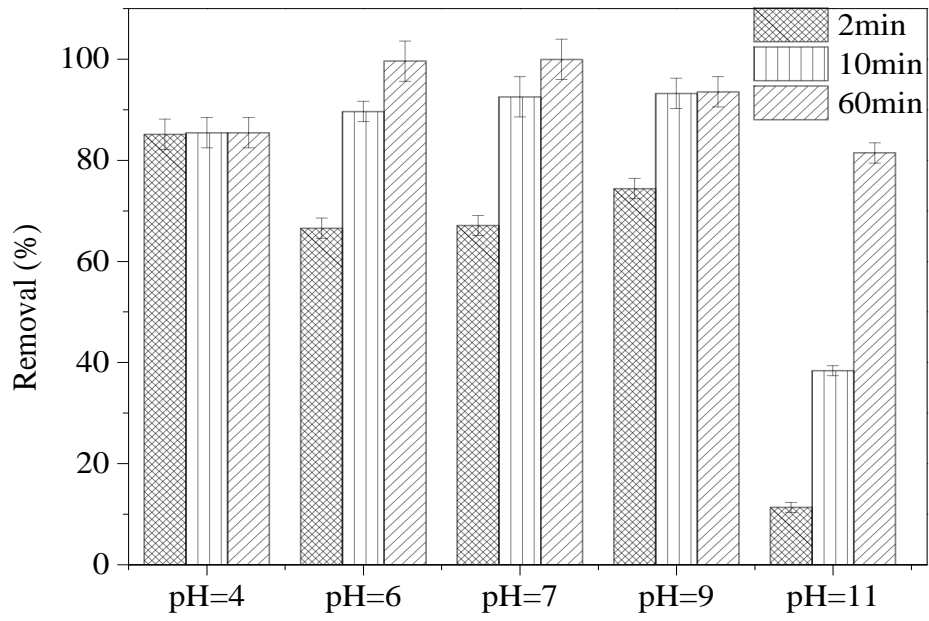
528

529   Fig. 2. Effect of different pH values on AAP degradation

530

In r = -0.38In[AAP] + 7.53
$R^2 = 0.939$

In k = 1.2In[Ferrate(VI)] − 11.18
$R^2 = 0.999$

531

532   Fig. 3. Kinetics analysis of AAP degradation by ferrate (VI)

533

534

535   Fig. 4. Detection of oxidation products (a – c) and original compound, AAP (d)
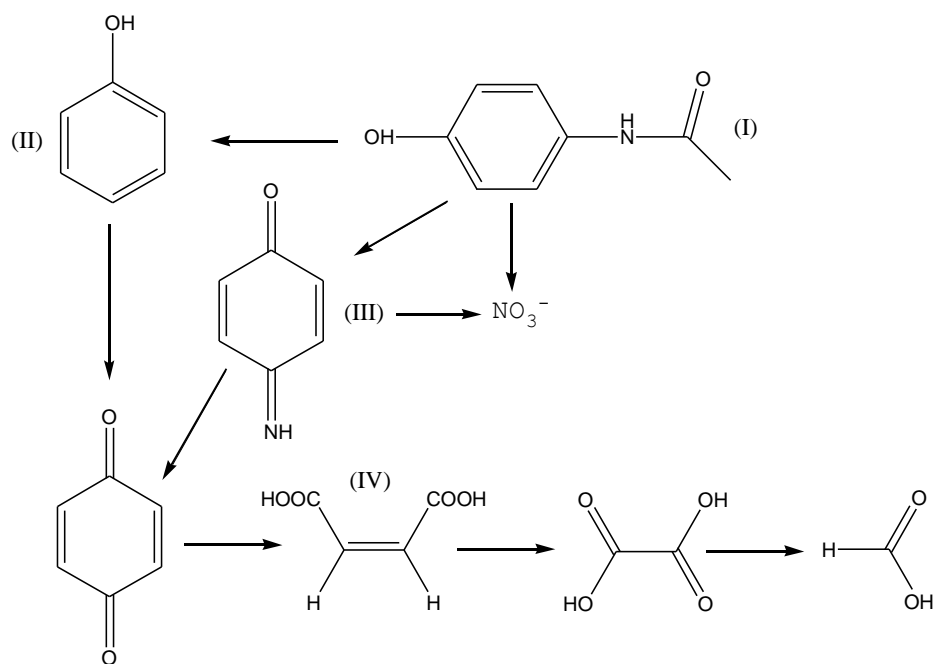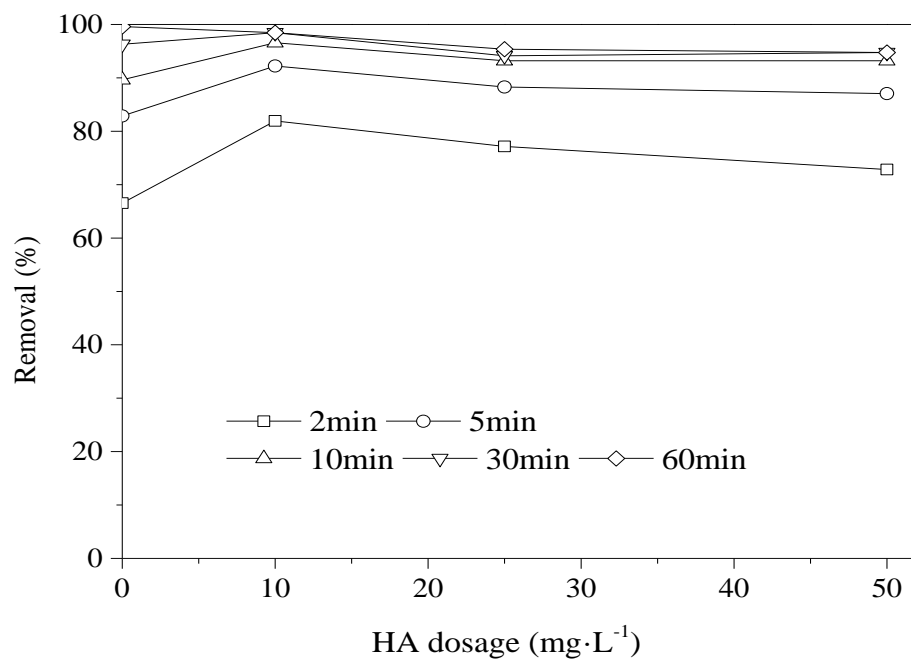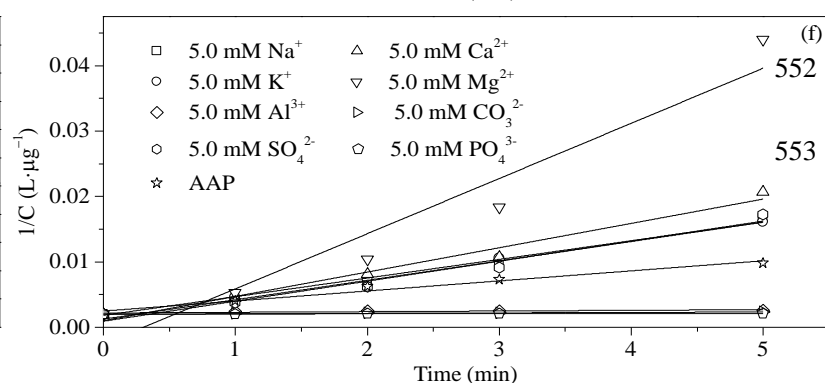
536

OP	Sampling time (min)						
	0	1	5	15	30	45	60
AAP-1	×	√	√	√	√	√	o
AAP-2	×	√	√	√	√	√	×
AAP-3	×	×	×	×	√	√	√

√, detected; ×, not detected; o, trace detected.

537

538   Fig. 5. Evolution of OPs and nitrate with decreasing of AAP concentration

539

540

541   Fig. 6. Possible pathways of AAP degradation by ferrate (VI)

542

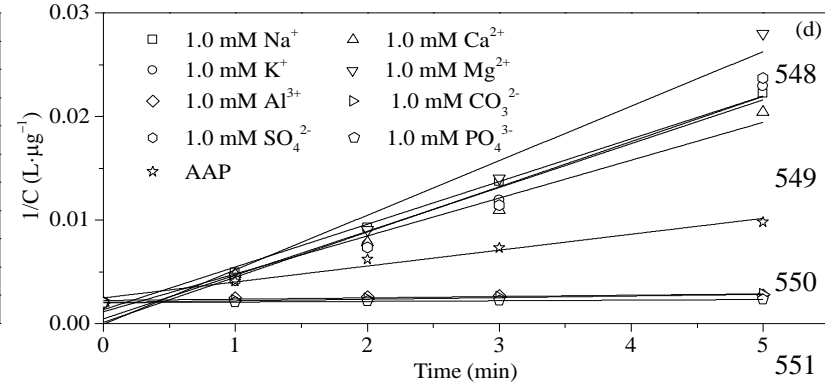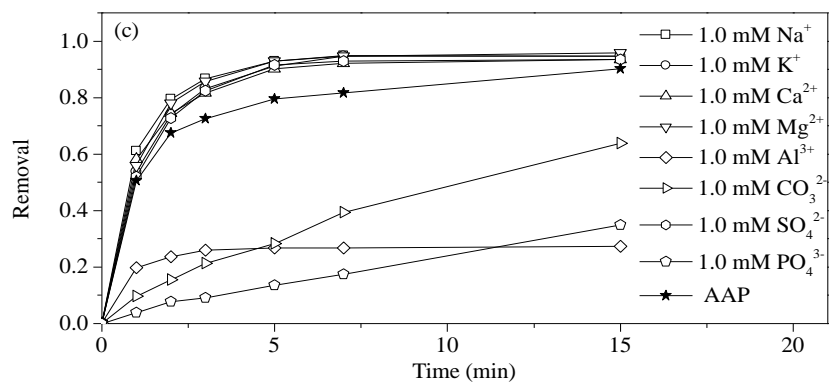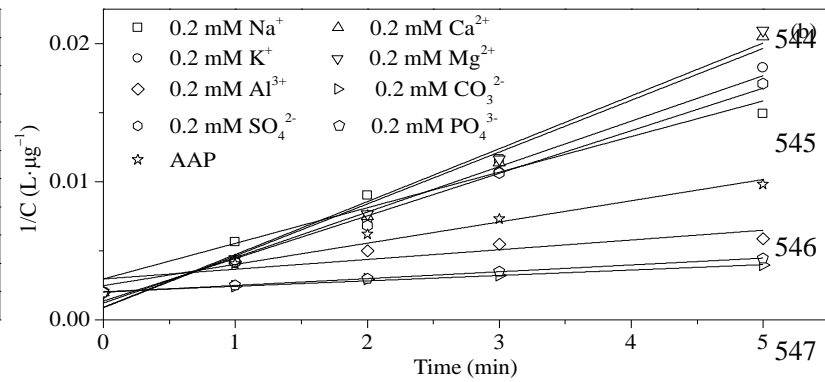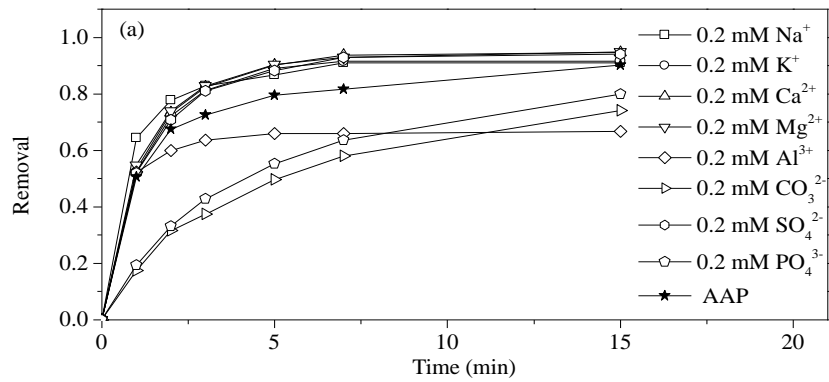543   Fig. 7. Effect of different HA dosage on AAP degradation
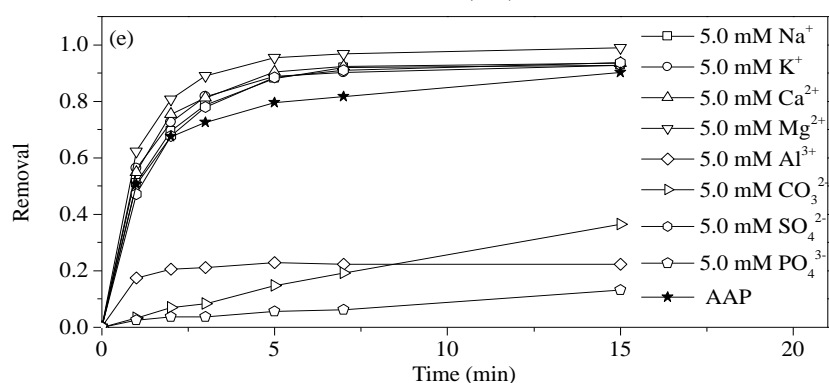
Fig. 8. Effect of different ions on AAP degradation

554   Table 1

555   Kinetic parameters of AAP degradation by ferrate (VI)

$D_{Ferate\ (VI)}$ (mg·L^{-1})	C_{IAAP} (µg·L^{-1})	Fitting equation	K_{obs}(min^{-1})	R^2	R_{IR} (µg·L^{-1}·min^{-1})
13	1000	1/C=0.0003X+0.0012	0.0003	0.9093	208.3
19.5	1000	1/C=0.0005X+0.0012	0.0005	0.9946	347.2
26	1000	1/C=0.0007X+0.0013	0.0007	0.9943	414.2
32.5	1000	1/C=0.0009X+0.0012	0.0009	0.9961	625.0
32.5	900	ln C=-0.2647X+6.2611	0.2647	0.9088	138.6
32.5	700	ln C=-0.3920X+6.0656	0.3920	0.9596	168.9
32.5	500	ln C=-0.5504X+5.8182	0.5504	0.9694	185.1
32.5	300	ln C=-0.8308X+5.5569	0.8308	0.9665	215.2

556    $D_{Ferate\ (VI)}$:Ferate (VI) dosage

557   C_{IAAP}:Initial concentration of AAP

558   K_{obs}:The pseudo reaction rate constant

559   R_{IR}:Initial reaction rate

560 Table 2

561 Kinetic parameters of the AAP degradation in the presence of 8 dissolved ions

Parameter	D_{ions} (mM)	Na^+	K^+	Ca^{2+}	Mg^{2+}	Al^{3+}	CO_3^{2-}	SO_4^{2-}	PO_4^{3-}
K_{obs} (min^{-1})	0.2	0.0026	0.0033	0.0038	0.0038	0.0007	0.0004	0.0031	0.0005
R^2		0.9661	0.9905	0.9837	0.9842	0.7765	0.9944	0.9925	0.9999
K_{obs} (min^{-1})	1	0.0041	0.0042	0.0037	0.0053	0.0001	0.0002	0.0044	6.1×10^{-5}
R^2		0.9963	0.9729	0.9829	0.9700	0.6713	0.9893	0.9583	0.9789
K_{obs} (min^{-1})	5	0.0030	0.0029	0.0037	0.0084	0.0001	6.8×10^{-5}	0.0031	2.2×10^{-5}
R^2		0.9852	0.9989	0.9787	0.9340	0.6352	0.9887	0.9728	0.9012

562 D_{ion}:The ions dose

563 K_{obs}:The pseudo reaction rate constant

564

Table 3

Effect of aluminum ions on ferrate (VI) concentration

$V_{aluminum}$ (µL)	0	10	100	200	300	400	500
$C_{Ferrate\ (VI)}$ (mM)	13.2	12.8	11.5	8.9	6.6	4.3	2.8

$V_{aluminum}$:The volume of aluminum ions
$C_{Ferrate\ (VI)}$:The concentration of ferrate (VI)