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Additional Information

1 **Commercial steel wool used for Zero Valent Iron and as a**

2 **source of dissolved iron in a combined red-ox process for**

3 **pentachlorophenol degradation in tap water**

4

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11

12 **Abstract**

13 Pentachlorophenol solutions in tap water were treated with a combined process of zero

14 valent iron (ZVI) reduction followed by a photo-Fenton oxidation. Commercial steel

15 wool was used as ZVI source, demonstrating its effectivity for pentachlorophenol de-

16 chlorination at acidic pH values. The reductive pathway was monitored by the use of

17 excitation emission matrices, showing the transformation of the initial compound into

18 the fluorescent species 4-chlorophenol and phenol.

19 While the use of tap water represented a drawback in photo-Fenton oxidative reactions

20 (at least half kinetic constants values) an improvement was achieved when the reductive

21 stage was applied in the studied pH range. The transformation of pentachlorophenol into

22 phenol produced an increase in oxidative stage rate of about 8 times. This fact could be

related to the treatment time and hydrogen peroxide consumption of the photo-Fenton process, enhancing the economic viability. Furthermore, the de-chlorination of the pentachlorophenol minimized the possibility of releasing toxic by-products in the photo-Fenton process.

Keywords: steel wool, tap water, ZVI, photo-Fenton, pentachlorophenol

Graphical abstract
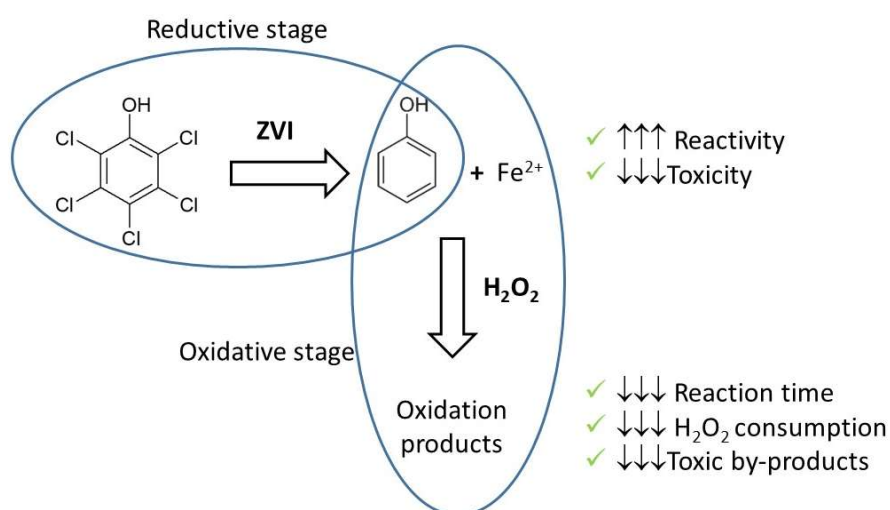
1. Introduction

Advanced oxidation processes (AOPs) are a group of techniques able to produce important changes in chemical composition of pollutants, and eventually, reaching significant mineralization [1]. AOPs have been studied for the treatment of highly polluted effluents [2, 3] and recently, as a tertiary process to deal with low concentrations of recalcitrant pollutants [4,5]. In both cases, the presence of salts has been described as detrimental, because their scavenging effect on the reactive species involved in the AOP results in an important decrease in reaction rates [6]. This negative effect can be overcome by working under stronger oxidation conditions, but this strategy should be disregarded for economic and ecologic reasons, at least when dealing with pollutants at low concentration [4]; in addition, when pollutant/inorganic salts ratio decreases, the reactive species is more likely to find the inorganic ion than the pollutant, thus increasing its scavenging role. For these reasons, the option of coupling a pre-reductive stage seems attractive, especially for those compounds with electron-withdrawing groups (e.g. nitro groups, sulfonates, cyano group) that deactivate electrophilic attack of the reactive species [7]. In this case, the negative effect produced by the presence of salts can be overcome if the pre-reductive stage forms more reactive intermediates vs. oxidative processes.

Zero valent iron (ZVI) can act as reducing agent (standard redox potential of -0.44 V) in the pre-reductive stage; in fact ZVI-based processes are commonly employed for decontamination of water and groundwater [8]. In particular, ZVI has been used to remove different types of pollutants from water such as chlorinated compounds, arsenic, nitrate, dyes or nitro-aromatic compounds [9-11]. It is important to mention that the

presence of dissolved salts enhances ZVI reduction process, since they promote the oxidation of the iron [12].

When ZVI is present in water a large number of reactions can occur, but the following ones play the major role in most cases [13]:

$$Fe^0 + 2H^+ \rightarrow Fe^{2+} + H_2\uparrow \tag{1}$$

$$2Fe^0 + O_2 + H_2O \rightarrow 2Fe^{2+} + 4OH^- \tag{2}$$

According to the reactions above, ferrous salts are released into the solution during the ZVI process. As iron cations are present in solution, Fenton and related processes can be used in the oxidative stage, in particular if hydrogen peroxide is added to the reaction mixture [14].

Fenton process consists in a combination of ferrous salts and hydrogen peroxide at an optimum pH of 2.8, that are able to generate highly reactive species, mainly hydroxyl radicals. Fenton can be accelerated by light (photo-Fenton) and interestingly, sunlight can be used for this purpose [15]. The ability of this process to oxidize a wide range of pollutants under different experimental conditions is well-established [16] and hence, increasing attention has been paid to several aspects related to (photo)-Fenton, such as economics, automatization or modelling [17-19].

The application of Fenton-related processes as tertiary treatment suggests the use of mild conditions (near neutral pH and low iron and hydrogen peroxide concentrations [20]). In this context, a pre-reductive stage can facilitate photo-Fenton oxidation and, in addition to this, corrosion of zero-valent iron (ZVI) could be used as a continuous source of iron salts replacing the amount that could suffer inactivation via formation of iron oxides or hydroxides [21].

81 Separation of the reductive and oxidative stages in different parts of the reactor allow

82 tuning the best conditions for each stage. In particular, this type of set-ups avoids the

83 unnecessary consumption of hydrogen peroxide by reaction with ZVI permits

84 irradiation without light scattering [10]. From an economical and practical point of

85 view, commercial ZVI with high specific surface area (e.g. steel wool) seems a good

86 choice for this purpose. Furthermore, possible negative effects related to nano-iron

87 particles in the environment are also excluded [22].

88 This combined redox process would be meaningful for some applications, such as

89 treatment of effluents containing pollutants reluctant to chemical oxidation and/or with

90 potential to generate non-desired oxidation by-products; putting all together ZVI/photo-

91 Fenton could be a niche application for pollutants difficult to oxidize, present at low

92 concentration, with high amounts of salts in the effluent, when mild oxidizing

93 conditions are required and the release of toxic oxidation by-products cannot be

94 disregarded.

95 With this background, the aim of this work is to study a combined ZVI-Fenton process

96 using tap water. Commercial steel wool has been used as an iron source and a reaction

97 set-up able to separate ZVI-based reduction and photo-Fenton has been employed. As

98 factors influencing the photo-Fenton process are well-known, special emphasis will be

99 paid to the reductive phase. A typical halogenated toxic compound, pentachlorophenol

100 (PCP), has been used as a model pollutant. This compound is widely employed as a

101 pesticide, it is one of the chlorinated compounds less reactive towards oxidative

102 processes [23] and problems associated to its incomplete oxidation have been reported

103 [24].

2. Experimental

2.1. Reagents.

High purity PCP, 2,4-dichlorophenol (2,4-DCP), 4-chlorophenol (4-CP) and phenol were supplied by Sigma-Aldrich. Sulphuric acid (96 %), sodium hydroxide (99 %) ferrous sulphate (99 %), hydrogen peroxide (30 %) and acetonitrile (HPLC grade) were provided by Panreac. The water employed was tap water from Alcoy (Spain) water supply (table 1). The commercial steel wool (iron with 0.1% of carbon) classified as fine grade with a fiber thickness of ca. 0.05 mm was employed as Zero Valent Iron (ZVI). This commercial product is available in long reels of 8 cm width and 0.5 cm thickness.

2.2. Experimental set up

The target solution in reductive processes was pentachlorophenol (1 mg/L) in tap and Mili-Q water. In photo-Fenton, in addition to PCP, 2,4-DCP, 4-CP and phenol were also used as substrates (always with an initial concentration of 1 mg/L). This range of concentrations was chosen in order to allow a reliable monitoring of the kinetics of the process and to assess the effect of operational variables. Furthermore, 1 mg/L is not far from the total amount of emerging pollutants that can be found in the effluents of wastewater treatment plants [4].

The commercial steel wool (1.4 g) was placed into a cylindrical container of 17 mm diameter and 220 mm height located over an open glass reactor with magnetic stirring (Scheme 1). The solution was continuously recirculated from the open reactor to the steel wool at a flow rate of 20 mL/min using a peristaltic pump PR7 (SEKO). The solution was flown through the steel wool by gravity and returned to the open reactor.

129   A pH-meter was placed inside the reactor. Periodically, samples were taken for

130   monitoring the pollutant and dissolved iron concentration.

131   For photo-Fenton reactions, a solar simulator (Oriel Instruments, Model 81160

132   equipped with a 300W xenon lamp) whose emission spectrum closely matches the solar

133   one was employed to irradiate the open glass reactor. The apparatus was equipped with

134   specific glass filters for cutting off the transmission of wavelengths below 300 nm was

135   used. The UVA irradiance (320-400 nm) was 32 W/m^2. This value represents an

136   average irradiance in a sunny country and it has been used as a reference, by many

137   authors, to normalize reaction time supposing a constant sun irradiance (t_{30W}) [16].

138   For each experiment, the reactor was loaded with 250 mL of solution and the pH was

139   adjusted to the desired value by dropwise addition of sulphuric acid or sodium

140   hydroxide; in some experiments only initial pH was adjusted, while in other cases, a

141   constant pH was kept along the process. For photo-Fenton reactions, hydrogen peroxide

142   was added to reach a concentration of 2.5 mg/L; this accounts for ca. twice the

143   stoichiometric amount required to completely oxidize PCP and it was chosen to

144   minimize the scavenging role of the excess of H_2O_2 towards photo-Fenton (17). Iron

145   employed in the oxidative reaction was 5 mg/L, that was in the range of the amount of

146   iron released by ZVI at pH = 5; furthermore, it has been demonstrated that this is a

147   convenient concentration to drive mild photo-Fenton [4]. Samples were periodically

148   collected from the reactor and filtered through 0.45 μm nylon filters (Millipore Millex-

149   HN) before analyses. Eventually, in order to prevent the decomposition of organic

150   components after sampling, samples were immediately diluted (1:3 v/v) with methanol.

151   All experiments have been repeated at least twice.

152

153

2.3. Chemical analysis

155 Pentachlorophenol and its reductive products concentration were determined by high

156 performance liquid chromatography. The apparatus employed was a LaChrom from

157 Merck-Hitachi equipped with autosampler and diode array detector. A reverse phase

158 column LiChrospher® 100 RP-18 (5 μm) was used and a mixture of 1 mM sulfuric acid

159 and acetonitrile (20/80 %) were employed as a mobile phase in a flow rate of 1.0

160 mL/min.

161 The fluorescence Excitation Emission Matrices (EEMs) were recorded with a modular

162 QuantaMaster spectrofluorometer and collected by subsequent scanning emission from

163 300 to 600 nm at 5 nm increments by varying the excitation wavelength from 250 to

164 550 nm at 5 nm increments. Data at lower excitation wavelengths were not recorded

165 because of the excessive background noise, caused by the low intensity of the lamp in

166 the range of 200–250 nm. The spectra were recorded using excitation and emission slit

167 bandwidths of 5 nm. The fluorescence intensities are reported in c.p.s. (counts per

168 second).

169 UV-Vis absorption spectra were recorded on a Helios γ spectrophotometer (Thermo

170 Scientific), using quartz cells of 1.0 cm optical path length.

171 The concentration of iron species in the water was measured according to the o-

172 phenanthroline standardized spectrometric procedure (ISO 6332) [25]. Hydrogen

173 peroxide presence and consumption was checked by the use of colorimetric strips

174 (MQuant Peroxide Test).

175

3. Results and discussion

3.1. Effect of pH in pentachlorophenol reductive degradation

A first set of experiments was carried in tap water at different initial pH values in order to study the effect of this parameter on the reduction of PCP by ZVI. The pH was adjusted before the reaction to 3, 5 and 7. Pollutant concentration, dissolved iron (released by ZVI) and pH were monitored along the process and results are shown in Figure 1. At pH 7, no significant decrease in PCP concentration was observed, at pH = 5 some degradation of PCP was observed (20% removal after 90 min) and at pH = 3, higher removal was reached (50% after 1 hour), but again in this case, a decrease in the reaction rate was observed beyond this point. The amount of iron released into the solution followed a similar trend: it was very low at pH = 7 and increased with decreasing pH values; in some cases, a decrease in dissolved iron was observed (e.g. at pH = 5) that can be attributed to the iron (III) precipitation. The pH variation is different in all cases: while at initial pH = 7, variation is lower than a unit, reaching values close to 8, followed by a slight decrease at the end of the process; similar behavior is observed for the experiment with initial pH = 5, where an increase of less than 2 pH unit was observed (never reaching pH = 7), again followed by a slight decrease. In the case of pH = 3, the pH increase was higher at the beginning of the reaction (ca. 3.5 units, to reach values around 6.5) and then remained constant.

These results seem to indicate that PCP removal is favored by acidic pH and it is stopped once solution approaches neutral values, iron release also occurs faster at acidic medium and the decrease observed at the end of the process, might be due to the precipitation of iron hydroxides; the pH increase might be related to H^+ reduction to form H_2 and the final slight decrease can be due to the precipitation of iron hydroxide.

9

201   Finally, it seems that all three processes are closely related: ZVI oxidation requires H^+

202   reduction and PCP removal is coupled with these processes: this is in agreement with

203   H_2 acting as reducing agent for PCP, although other processes should not be ruled out,

204   because of the complexity of the system. Also interestingly, the amount of iron released

205   in the solution (above 5 mg/L) is in the range of the concentrations employed for photo-

206   Fenton, what might favor coupling of ZVI and photo-Fenton processes without further

207   iron addition.

208

209   To gain further insight into de effect of pH, three experiments were carried out

210   maintaining the pH constant during all reaction time by small additions of sulfuric acid

211   at the values of 3, 4 and 5. Interestingly, keeping constant the pH value allowed

212   obtaining important degradation percentages, which were not stopped (Figure 2). Best

213   results were obtained at the most acidic value, 3, with more than 90% removal in two

214   hours of reaction. At this pH, the iron released into the solution was more than 40 mg/L.

215   When the pH was maintained at 4, the reaction was only slightly slower and the amount

216   of iron in solution also decreased to 20 mg/L. Finally, when the reaction was carried out

217   at pH = 5, the final degradation was ca. 85 % and the dissolved iron reached a

218   maximum of 12 mg/L and then slightly decreased, most probably because of

219   precipitation at this pH. However, the amount of iron dissolved in the solution was high

220   enough to perform a photo-Fenton process. Putting all this together, although best

221   results were reached at pH = 3, the process can be extended up to pH = 5. A key

222   parameter for the good performance of this approach is the high iron/pollutant ratio that

223   can be applied, as ZVI is immobilized as a wool.

224

225

3.2. Mechanistic studies using excitation-emission matrices

Once the degradation of PCP was achieved and the pH working range assessed, a series of experiments were planned in order to elucidate the mechanism involved in PCP removal, as PCP decrease can be due to different processes. For this reason, it is important to demonstrate that a reductive reaction of de-halogenation was predominating.

The mechanistic route for PCP de-halogenation have been described in depth for several systems [26, 27]. It involves the consecutive chlorine removal from PCP to produce phenol through the formation of tetrachlorophenol, trichlorophenol, dichlorophenol and chlorophenol. In some cases, the formation of chlorine anion has been employed for monitoring the de-chlorination of organic compounds. In our case, the use of tap water with important amounts of chlorine (27 mg/L), the initial low concentration of pentachlorophenol (1 mg/L) and the low expected concentration of by-products made the use of excitation emission matrices (EEMs) an adequate choice, as it has been demonstrated as a good technique to detect major trends in the composition of organic matter through a treatment [28]. With this objective in mind, EEMs were recorded for PCP, 2,4-DCP, 4-CP and phenol solutions in tap water. As presented in figure 3, PCP and 2,4-DCP showed no fluorescence, while 4-CP showed an important emission spectrum in the zone of 300 to 340 nm when excited in the 250 to 290 nm domain. Finally, the phenol solution presented a strong emission in the range of 300 to 340 when excited between 250 to 330 nm and 500 to 550 nm.

Once the reference compounds were recorded, the EEM of samples taken at different degradation levels were also measured (Figure 4). The initial sample showed no significant emission, as expected for PCP. As PCP removal occurred, signals appeared with emission between 300 to 340 nm when excited between 250 to 350 nm, which can

251 be attributed to phenol formation. Nevertheless the presence of the other fluorescent

252 compound, 4-CP cannot be completely discarded, since emitting and exciting zones are

253 partially overlapped with phenol. Finally, EEM obtained when PCP was submitted to

254 photo-Fenton showed no significant emission. Thus, EEM is an important piece of

255 evidence to support PCP reduction to phenol.

256

257 *3.3. The role of salts in reductive/oxidative treatment*

258 The presence of salts in tap water have been reported as favourable for iron corrosion

259 and consequently for reductive reactions when applying ZVI [10, 12]. Contrary to this,

260 the scavenging effect of dissolved salts results in a decrease of the oxidation kinetics

261 [29]. In order to determine the extent of this effect in our system, reduction of PCP was

262 carried out in Mili-Q water to compare with the results obtained in section 3.1 with tap

263 water. Again this case, pH was kept constant at values of 3, 4 and 5.

264 Figure 5a shows the pseudo-first order kinetic constant for PCP removal in tap and

265 Mili-Q water at the different working pH. In all cases, kinetic constants were higher

266 when the reaction was driven in tap water confirming the positive role of the presence

267 of salts. Nevertheless important PCP reduction was also observed in Milli Q water; this

268 could be partly attributed to the addition of electrolytes (e.g. sulphuric acid) to modify

269 the pH values. In fact, differences between both aqueous matrixes were less relevant at

270 $pH = 3$, where more sulphuric acid was present. The final amount of dissolved iron was

271 also monitored (Figure 5b), and in line with the previous results higher amounts of iron

272 were released in tap water.

273 In order to check the effect of salts on the oxidative stage, a series of experiments were

274 dedicated to study the photo-Fenton oxidation of PCP, 2,4-DCP, 4-CP and phenol. The

275 degradation of each pollutant was studied in separate experiments (1 mg/L), and the

12

276   series were run with Mili-Q and tap water (Figure 6) at the three studied pH values. As

277   indicated in the introduction, the presence of electron withdrawing groups results in a

278   more reluctant behaviour towards oxidation. In fact, the following order of reactivity

279   was found: phenol > 4-CP > 2,4-DCP > PCP. This proves that de-chlorination in the

280   reductive stage of PCP to form phenol is meaningful in view of applying photo-Fenton.

281   Regarding pH, the expected behaviour was found, being the reaction systematically

282   faster at pH = 3; although at pH = 5 reaction was clearly slower, significant removal

283   was observed, indicating that application of photo-Fenton at this medium should not be

284   ruled out when dealing with pollutants at low concentration. Finally, the scavenging

285   role of salts was clear in this case, as rate constants were lower in the experiments with

286   tap water, being this effect more significant at pH = 5, most probably due to the lower

287   availability of reactive species. This makes more interesting the ZVI/photo-Fenton

288   coupling, as the oxidation of phenol in tap water is faster than of PCP even when this

289   pollutant is dissolved in Milli-Q water.

290

291   *3.4. Environmental considerations*

292   The presence of chlorinated compounds in water have deserved the attention from

293   researchers during the last 30 years due to its high toxicity. The T.E.S.T software

294   (Toxicity Estimation Software Tool) developed by the Environmental Protection

295   Agency (EPA) reports the following values of toxicity for all the chlorinated phenols

296   expressed as *Daphnia magna* LC50 (48 h) mg/L: PCP (0.73); 2,3,5,6-TetraCP (0.57);

297   2,4,6-TCP (6.32); 2,4-DCP (2.6); 4-CP (4.82). Finally, the toxicity of phenol expressed

298   as *Daphnia magna* LC50 (48 h) mg/L is 13.29. Therefore, the reduction of PCP to

299   phenol decreases the toxicity in ca. 20 times. This fact, together with the increase of

300   reactivity towards oxidation in 8 times, should be enough to justify a cheap pre-

13

301 reductive stage before the photo-Fenton process. But in addition to this, the direct

302 oxidation without pre-treatment has been described as dangerous if complete oxidation

303 cannot be achieved, as some toxic condensation products have been identified [24, 30].

304 Finally, the use of steel wool as ZVI has also an environmental benefit since problems

305 associated to the toxicity of nano-ZVI have been also published [22]

306

307

4. Conclusions

A procedure combining reductive and oxidative stages demonstrated to be meaningful for the treatment of PCP, a toxic and low reactive compound against oxidation with photo-Fenton. This combined process seems to be convenient in systems in which the oxidative treatment (photo-Fenton) is not favored, namely compounds difficult to oxidize, present at low concentration, with high amounts of salts in the effluent, when mild oxidizing conditions are required and/or when the release of toxic oxidation by-products cannot be disregarded.

Although the reduction was faster at pH = 3, it could be extended until pH = 5 with no significant loss of efficiency and the presence of salts (e.g tap water) did not represent a drawback for the ZVI process. The major product formed in the process, namely phenol, is more easily oxidized via photo-Fenton than PCP and the iron released during the reduction can be employed in the oxidative step.

The use of commercial steel wool as reducing agent can improve the economic feasibility of the process making this alternative reductive-oxidative treatment interesting, as it allows designing the experimental set-ups that separate the oxidative and reductive stages. In fact, a possibility to be studied in future work is the application of the alternative reductive and oxidative stages in short reaction times by adding controlled amounts of hydrogen peroxide.

Finally, EEM has been confirmed as a good alternative to more sophisticated chromatographic methods. When fine analysis of the complex mixture is not required, the use of EEM allows following major trends in organic matter composition.

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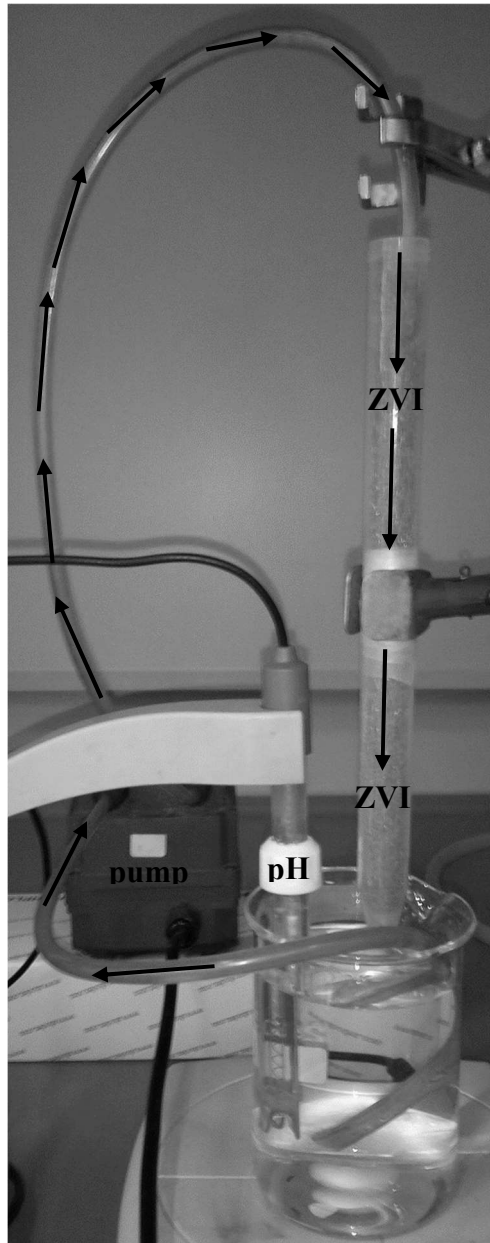
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400   Scheme 1: Experimental set up employed in the reductive process

A

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B

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C
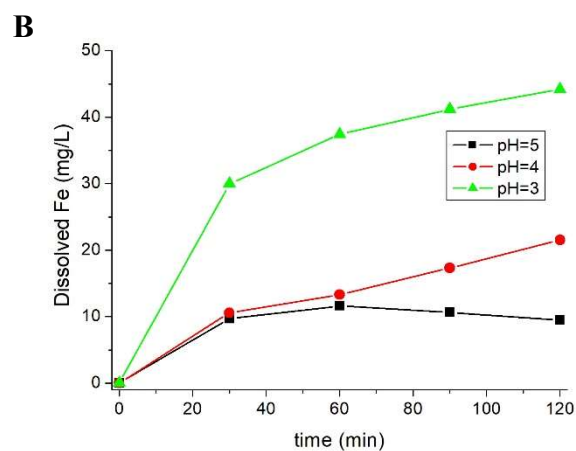

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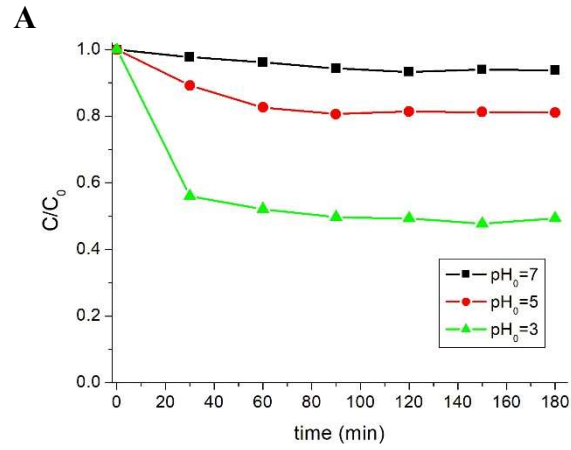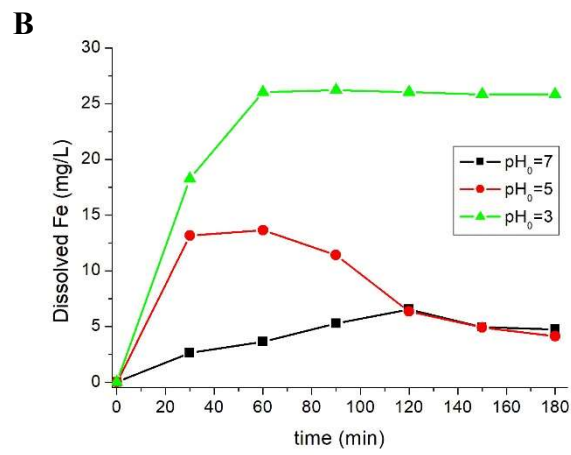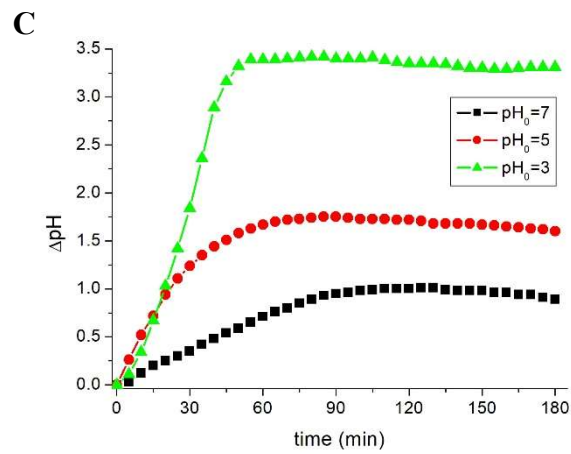
Figure 1: PCP (1 mg/L) removal by ZVI under different pH conditions: Variation of

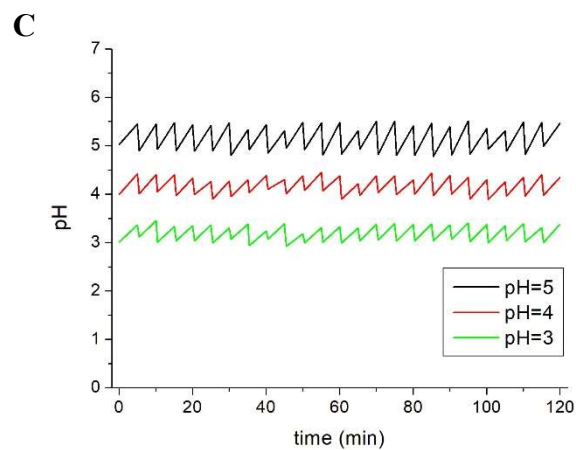some parameters vs time: relative concentration (A), dissolved iron (B) and pH (C).
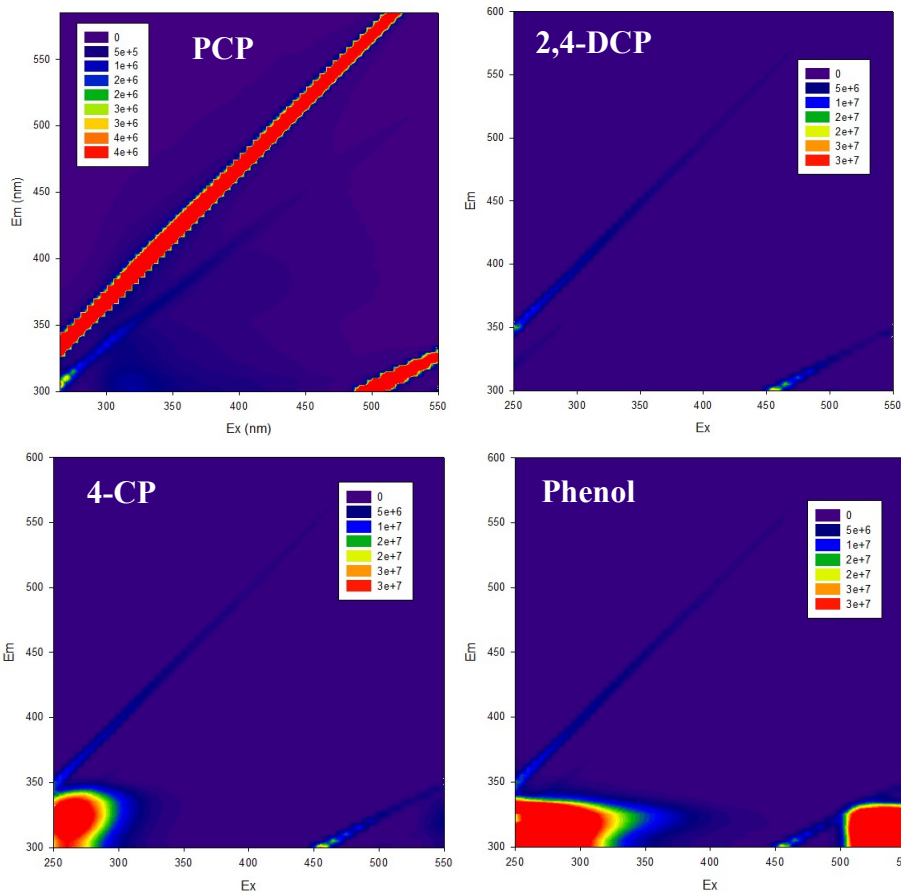
406

A

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B

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C
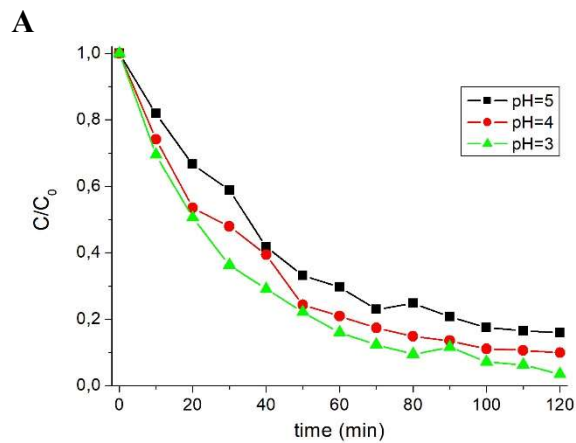
409

410   Figure 2: Evolution of pollutant removal (A), dissolved iron (B) and pH oscillation (C)
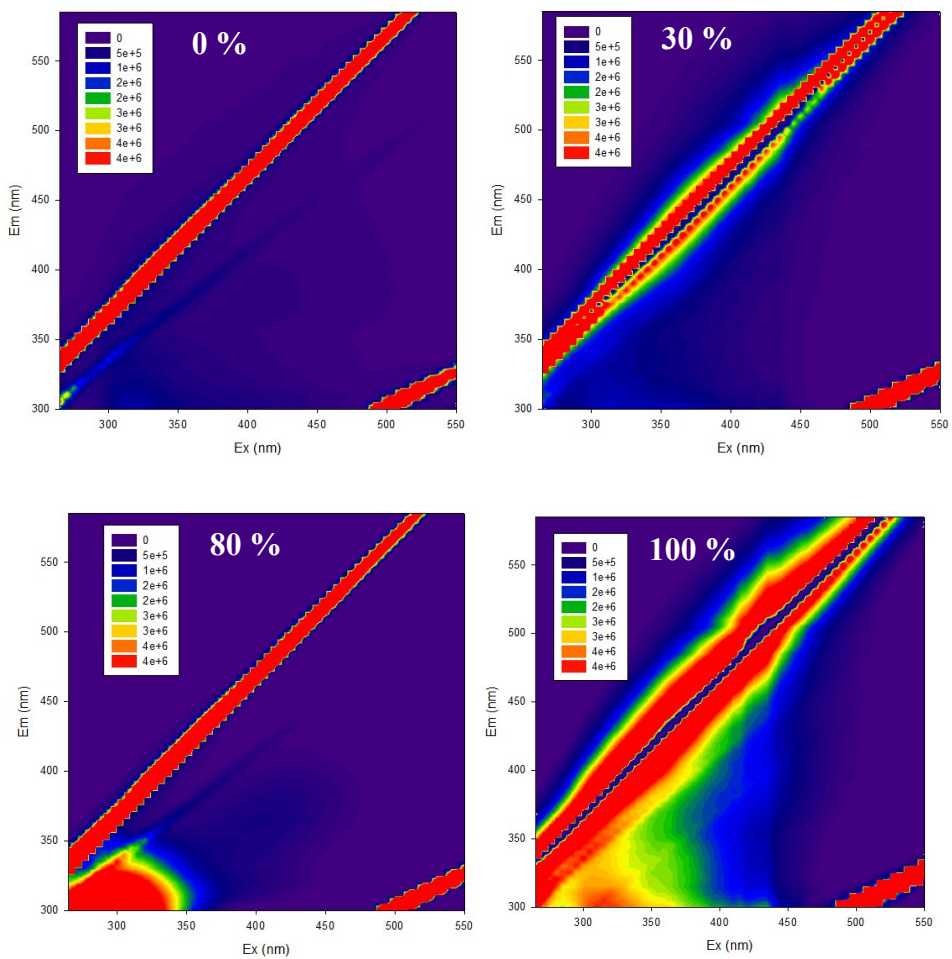
411   for reductive experiments carried out at different pH values.

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415   Figure 3: Excitation emission matrices of Pentachlorophenol (PCP); 2,4-Dichlorophenol

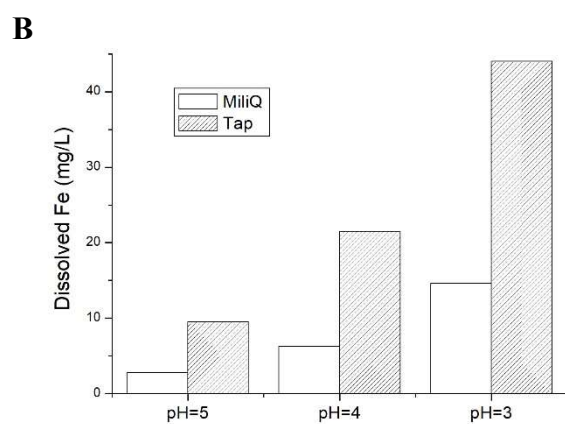416   (2,4-DCP); 4-Chlorophenol (4-CP) and Phenol (From left to right, top to bottom).

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419

420 Figure 4: Excitation emission matrices of Pentachlorophenol (PCP) at different

421 percentages of removal: 0, 30, 80 and 100% (From left to right, top to bottom).
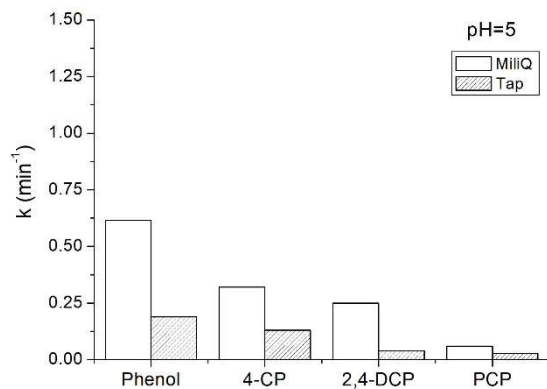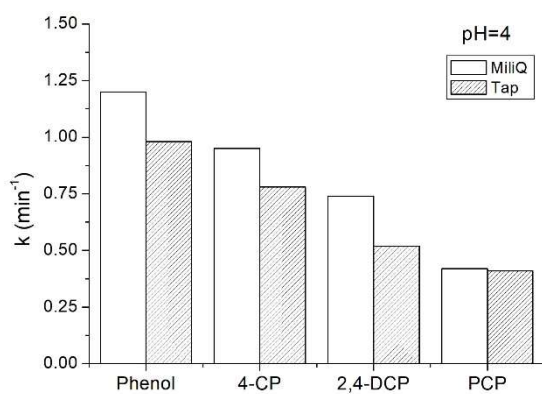
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A

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B
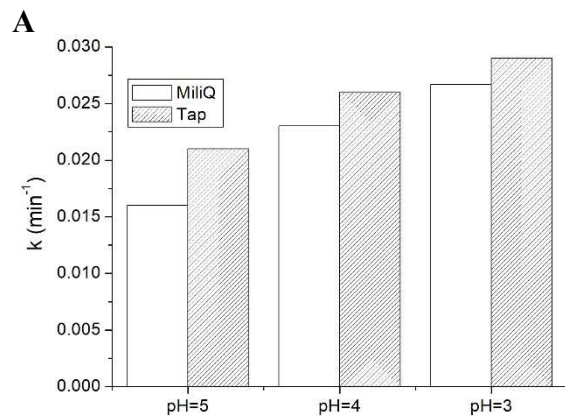
424

425   Figure 5: Pseudo-fist order kinetic constants for the reductive degradation of PCP using

426   Mili-Q and tap water at different pH values (A). Dissolved iron at the end of the

427   reductive process using Mili-Q and tap water at different pH values (B).
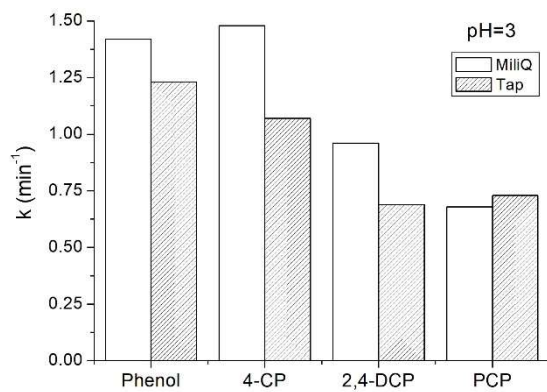
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Figure 6: Pseudo-fist order kinetic constants degradation of different compounds employing the photo-Fenton process at different initial pH values. Empty bars represent Mili-Q water solutions while lined bars represent tap water solutions.

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436

437   Table 1: Tap water composition and main characteristics

pH	7.8	Cl^- (mg/L)	26.8
Conductivity (µS/cm)	493	NO_3^- (mg/L)	2.63
$CaCO_3$ (mg/L)	147	SO_4^{2-} (mg/L)	28.1
Free Chlorine (mg/L)	1.15	Na^+ (mg/L)	18.7

438