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Abstract

Combination of the electro-Fenton process with a post-biological treatment could represent a cost-effective solution for application of electrochemical advanced oxidation processes. The objective of this study was to assess this treatment strategy to assess a complex pharmaceutical mixture. First, main operating parameters ([Fe^{2+}] and current) of the electro-Fenton process were optimized. An optimal concentration of 0.2 mM of Fe^{2+} was obtained for mineralization of the pharmaceutical mixture. An optimal current of 400 mA was also obtained for degradation of caffeine and 5-fluorouracil alone. However, mineralization of the effluent was continuously improved when increasing the current owing to the promotion of mineralization of organic compounds at the BDD anode. Besides, energy efficiency was decreased at prolonged treatment time because of mass transport limitation. Interestingly, it was observed a strong biodegradability enhancement of the solution after short treatment times (<3 h) at 500 and 1000 mA, which can be related to the degradation of parent compounds into more biodegradable by-products. The need for an acclimation time of the biomass to the pre-treated effluent was also emphasized, most probably because of the formation of some toxic by-products as observed during acute toxicity tests. Therefore, a biological post-treatment could represent a cost-effective solution for the removal of biodegradable residual organic compounds as well as for the removal of nitrogen released from mineralization of organic compounds under the form of NO_3^- and NH_4^+ during electro-Fenton pre-treatment.

Keywords: Electro-Fenton, Pharmaceutical pollutants, Degradation, Mineralization, Biodegradation, Toxicity

1. Introduction

Electro-Fenton process is an electrochemical advanced oxidation process (EAOP) with an elevated interest for the removal of recalcitrant organic compounds form wastewaters (Brillas et al., 2009; Oturan and Aaron, 2014; Martínez-Huitle et al., 2015). This process is based on the well-known Fenton's reaction (Eq. (1)) for *in-situ* generation of hydroxyl radicals ($^{\bullet}OH$). Contrarily to the conventional Fenton process, Fe^{2+} is continuously regenerated at the cathode (Eq. (2)). It means that a catalytic amount of iron is initially added and steadily regenerated at the cathode throughout the treatment. Besides, aeration of the treated solution ensures continuous *in situ* production of H_2O_2 from reduction of dissolved oxygen at a suitable cathode material (Eq. (3)). Depending on the nature of both the anode material and inorganic matrix, further oxidant species such as $^{\bullet}OH$, $SO_4^{\bullet-}$, active chlorines can be also generated at the anode (Panizza and Cerisola, 2009; Rodrigo et al., 2010; Martínez-Huitle et al., 2015; Salazar et al., 2017; Garcia-Segura et al., 2018, Nidheesh et al., 2019). Therefore, electro-Fenton process has demonstrated a great potential for degradation and mineralization of different types of pollutants, including dyes, pesticides, pharmaceuticals etc. (Sirés et al., 2007; Özcan et al., 2008; Oturan et al., 2013; Nidheesh et al., 2014; Brillas and Martínez-Huitle, 2015; Mousset et al., 2018).

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^- \quad (1)$$

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \quad (2)$$

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \quad (3)$$

Research on the degradation of single compounds by the electro-Fenton process is an important step to understand the underlying mechanisms (Oturan et al., 2000; Yang et al., 2020). Besides, there is also a need to assess the efficiency of the process on solutions containing a mixture of organic compounds as well as on real effluents. Thus, the goal of this

study was to complement existing knowledge on electro-Fenton process by optimizing it for the treatment of a synthetic pharmaceutical mixture composed of 13 pharmaceuticals belonging to different therapeutic and pharmacological classes (Table SM-1). Each pharmaceutical selected was regarded as a representative of drugs with similar pharmaceutical action. The selection was made based on several publications that investigated the composition of hospital wastewater (Thomas et al., 2007; Kosma et al., 2010; Verlicchi et al., 2010, 2012; Escher et al., 2011; Sim et al., 2011). Among the multitude of identified compounds from these studies, a selection was done based on (i) the most frequently detected drugs with highest concentrations (Table SM-2) and, (ii) the risk or hazard they represent for humans and ecosystems (genotoxicity, antibiotic resistance in bacteria and various adverse effects on living organisms) (Martínez, 2008; Allen et al., 2010; Załęska-Radziwiłł et al., 2014; Dias et al., 2015; Diniz et al., 2015; Kovács et al., 2015; Zivna et al., 2015).

The objective of the electro-Fenton process detailed in this study is to provide an efficient solution for the removal of pharmaceutical in the range of mg L^{-1} concentrations. Such concentrations can be observed in effluents from the pharmaceutical industry effluents where contamination mainly arises from washing and rinsing procedures of tanks. For example, sulfonamide drugs were detected in an untreated drug waste at 400 – 700 mg L^{-1} (Kumar Gupta et al., 2005). High concentration of pharmaceutical compounds can be also analyzed in nanofiltration and/or reverse osmosis concentrates (Urtiaga et al., 2013). Hospitals are also another source of uncontrolled release of drugs into the environment with potential negative consequences (Mendoza et al., 2015). Hospital effluents are normally discharged to the common sewage system and undergo conventional treatment at municipal wastewater treatment facilities which do not constitutes an effective barrier for the removal of hardly biodegradable compounds (Heberer, 2002; Radjenović et al., 2009).

Particular emphasis has been given in this study to the potential combination of the electrochemical process with a biological post-treatment in order to improve the cost-efficiency of the process (Ganzenko et al., 2014; Olvera-Vargas et al., 2016a, 2016b; Monteil et al., 2018; El Kateb et al., 2019). Therefore the following objectives were pursued: (i) assessment of the influence of the mixture on degradation kinetics of two components of the pharmaceutical mixture (caffeine and 5-fluorouracil), (ii) determination of the effect of operating parameters (current, catalyst concentration, treatment time) on mineralization rate of the pharmaceutical mixture and determination of energy consumption, (iii) investigation of the evolution of inorganic species of nitrogen during the treatment, (iv) evolution of the acute toxicity of treated solutions and, (v) determination of the biodegradability enhancement of the solution after the electro-Fenton treatment.

2. Materials and methods

2.1. Chemicals

Analytical grades of 5-fluorouracil, acetylsalicylic acid (aspirin), atenolol, caffeine, diclofenac sodium salt, diatrizoate meglumine, erythromycin, naproxen, norfloxacin, acetaminophen (paracetamol), ranitidine, sulfamethoxazole and tetracycline hydrochloride were obtained from Sigma-Aldrich. Iron (II) sulfate heptahydrate and sodium sulfate were reagent grade obtained from Acros Organics and Sigma-Aldrich, respectively. All reagents listed in literature for COD and BOD analyses were reagent grade. For toxicity assessment with Microtox®, *Vibrio fischeri* bacteria were purchased from Hach Lange.

2.2. Preparation of the synthetic pharmaceutical mixture

The synthetic pharmaceutical solution was prepared by mixing 0.1 mM of each compound listed in sub-section 2.1 and Table SM-1 in water. All the solutions were prepared with ultrapure water produced by a Millipore Milli-Q (simplicity 185) system with resistivity

>18.2 MΩ cm. Solution was stirred until complete dissolution of all compounds and stored at 4 ℃ for maximum one week before use.

2.3. Experimental setup

Open undivided electro-Fenton glass reactor was operated in a batch mode at ambient temperature (T = 20±1 °C) and was filled with 200 mL of the synthetic pharmaceutical solution containing 0.05 M sodium sulfate and iron sulfate at concentration in the range 0.1 – 0.5 mM. The pH of the solution was adjusted to 2.9 ±0.1 with 1 M sulfuric acid. The carbon felt cathode (18.5 cm × 4.5 cm) circled the internal wall of the reactor. The boron-doped diamond (BDD) anode (6 cm × 4 cm) was positioned in the center on equal distances from the encircling cathode. The solution was continuously stirred at a speed of 450 rpm and aerated with compressed air (0.2 L min^{-1}) throughout the experiment. Aeration started 5 min prior to electrolysis in order to saturate the solution with oxygen. The current and voltage were monitored in real time using a power supply (HM8040-3, Hameg Instruments).

2.3. Instruments and analytical procedures

2.3.1. Total organic carbon (TOC)

TOC analysis was performed in order to determine the mineralization rate of the solution during the treatment. It was measured on a Shimadzu VCSH TOC analyzer by combustion with catalytic oxidation at 680 °C. A non-dispersive infrared detector was used. Standard potassium hydrogen phthalate solution was used for calibration. The injection volume was 50 µL.

2.3.2. Caffeine and 5-fluorouracil analysis by high performance liquid chromatography (HPLC)

Experiments on degradation kinetics of caffeine and 5-fluorouracil were followed by a reverse-phase HPLC. The equipment (Merck Hitachi) consisted of a column Purospher

STAR RP-18 endcapped (5 μm), a pump (Elite LaChrome, L-2130), UV detector (Elite LaChrome, L-2400) and a thermostat set at 40 °C (Jetstream Plus, series 140310). The mobile phase was a mixture of methanol and ultrapure water both buffered with 1% acetic acid. Injection volume was equal to 20 μL. UV detector was set to 275 nm. 5-Fluorouracil and caffeine exhibited well-defined peaks at retention time of 10 and 25.4 min, respectively, under gradient elution conditions (details of the procedure was given in Text SM-1)

2.3.3. Ion chromatography

The evolution of inorganic ions was followed with a Dionex ICS-1000 ion chromatography system equipped with an ASRS-ULTRA II (for anions) or CSRS-ULTRA II (for cations) self-regenerating suppressor to improve the sensitivity of the detector. The system was equipped with a DS6 conductivity detector containing a cell heated at 35 °C. An anion-exchange column (IonPac AS4ASC, 25 cm × 4 mm) was used for NO_3^- and NO_2^- analyses. NH_4^+ analysis was performed on a cation-exchange column (IonPac CS12A, 25 cm × 4 mm). A solution composed of 1.8 mM Na_2CO_3 and 1.7 mM $NaHCO_3$ at 2.0 mL min^{-1} was used as mobile phases for anion analysis. Mobil phase for cation analysis was a 9.0 mM H_2SO_4 solution at 1.0 mL min^{-1}. Identification and quantification of ions was done by comparison with elution time and peak areas of standard solutions.

2.3.4. Acute toxicity

Toxicity of solutions was measured by means of Microtox® test on bioluminescent bacteria *Vibrio fischeri*. Microtox® Model 500 Analyzer was used for this analysis. Each sample was adjusted to the pH in the range of 6.5-7.5 and filtered (0.2 μm regenerated cellulose filter) in order to remove precipitated iron. Sodium chloride 22% was added to the tubes with reactivated *Vibrio fischeri* for osmotic protection of bacteria. Finally, prepared samples were

147 added to the tubes in order to measure luminescence inhibition (as % of the initial
148 luminescence of bacteria) after 5 min of incubation.

149 *2.3.5. Chemical oxygen demand (COD)*

150 Chemical oxygen demand was measured using a reflux method in a closed system (tubes)
151 with potassium dichromate followed by a colorimetric dosage using a Spectroquant® TR 420
152 (Merck).

153 *2.3.6. Biological oxygen demand (BOD)*

154 The biological oxygen demand (BOD) was measured in order to follow the evolution of the
155 biodegradability of the solution. The analysis was performed following the method detailed
156 by (Rodier et al., 2009). The inoculum was activated sludge from a French municipal
157 wastewater treatment plant. Before the beginning of the experiment, sample, dilution water
158 and bacterial inoculum were aerated to reach oxygen saturation. The BOD values were
159 measured by respirometric method using OxiTop® Control System (WTW, Germany). Each
160 sample bottle of OxiTop® of 432 mL volume contained 100 mL of sample, 3 mL of buffer
161 solution (amount calculated to keep the ratio COD:N close to 100:5), 1 mL of allylthiourea
162 solution (to prevent nitrification), 273 mL of dilution water and 5 mL of biomass from
163 activated sludge. Before adding the inoculum, the solution was adjusted to circumneutral pH.
164 All the bottles contained a rubber sleeve containing sodium hydroxide pellets to absorb the
165 carbon dioxide produced during the bacterial respiration. Continuously stirred bottles were
166 incubated in dark place with temperature in the range 20(±1) °C during 5 days in order to
167 determine the BOD at 5 days (BOD_5) as well as during 17 days in order to observe the effect
168 of bacteria acclimation on the biodegradability of the solution. For each batch of analysis, a
169 blank (ultrapure water) was analyzed for evaluation of the endogenous respiration of bacteria.
170 Endogenous respiration was subtracted from each value obtained for the different samples.
171

3. Results and discussion

3.1. Influence of the mixture on degradation kinetics of caffeine and 5-fluorouracil.

The degradation kinetic of two components of the mixture was followed in order to determine the apparent rate constant (k_{app}) of the reaction with hydroxyl radicals. The degradation kinetics of pharmaceutical compounds fitted well with the pseudo-first order model ($R^2 > 0.99$) (Eqs. (4) and (5)):

$$d[Pharma]/dt = - k_{app} [Pharma], \quad (4)$$

$$k_{app} = k_{abs} [^{\bullet}OH] \quad (5)$$

Apparent rate constants for caffeine and 5-fluorouracil are given in Table 1 as a function of current applied. Apparent rate constants in the pharmaceutical mixture were compared with values obtained from the previous studies on individual molecules of caffeine and 5-fluorouracil (Ganzenko et al., 2015, 2018). As the experimental setup was identical, all these data allowed visualizing a change in the degradation rate of given compounds depending on the organic matrix of the solutions (compounds alone *vs* mixture of compounds).

It can be seen that the apparent rate constants for both molecules are close when comparing for same current intensities and same matrix. These results might be ascribed to a similar initial reaction mechanism and show that hydroxyl radicals really act as non-selective oxidants in this case. Besides, apparent rate constants decreased in the pharmaceutical mixture by a factor in the range 18 - 30 compared to experiments performed on single molecules. In fact, initial TOC of individual caffeine and 5-fluorouracil solutions was around 9.6 and 4.8 mg L^{-1} respectively, while the TOC of the synthetic mixture was 220 mg L^{-1} (including the same concentration of caffeine and 5-fluorouracil). These results show that hydroxyl radicals really act as non-selective oxidants. A slightly higher apparent reaction rate was observed for caffeine, as expected from absolute rate constants previously determined

196 (2.48×10^{-9} L mol^{-1} s^{-1} for caffeine and 1.52×10^{-9} L mol^{-1} s^{-1} for 5-florouracil) (Ganzenko et
197 al., 2015, 2018). As hydroxyl radicals are non-selective oxidants, they can react with caffeine
198 and 5-florouracil as well as with the other pharmaceuticals present in the mixture. Since 5-
199 florouracil and caffeine accounted for only 2.2 and 4.4% of the TOC of the mixture, the
200 apparent rate constants were strongly decreased because of the competition of other organics
201 for hydroxyl radicals. It can be noted that the apparent rate constants for both molecules were
202 close in the mixture, highlighting the non-selective potential of the electro-Fenton process.
203
204 Table 1 – Apparent (pseudo-first order) rate constants obtained for degradation of 5-flourouracil and
205 caffeine at different current intensities in the synthetic pharmaceutical mixture (Mix) and in solutions of
206 individual compounds (Alone). Optimal values for different types of solutions are indicated in bold
207 characters. Operating conditions: $[Fe^{2+}]$ = 0.2 mM, $[Na_2SO_4]$ = 0.05 M, V = 200 mL.
208

Current (mA)	5-fluorouracil		Caffeine	
	Mix	Alone	Mix	Alone
	k_{app} (min^{-1})	k_{app} (min^{-1})	k_{app} (min^{-1})	k_{app} (min^{-1})
200	0.038	0.61	0.034	0.73
300	0.040	**0.74**	0.036	**1.14**
400	**0.042**	0.60	**0.038**	0.64
700	0.03	-	0.023	-

209
210 An interesting observation was also linked to the fact that the optimal current for degradation
211 of both compounds in the pharmaceutical mixture was 400 mA. By comparison, the optimal
212 current for degradation of individual caffeine and 5-fluorouracil was 300 mA, with a strong
213 decrease of the apparent rate constant at 400 mA compared to 300 mA. This difference in the
214 optimal current can be mainly attributed to the higher TOC of the mixture that leads to a

different ratio between the amount of organic matter available for oxidation and the amount of hydroxyl radicals produced. The existence of an optimal value of current can be associated to the production of high amount of hydroxyl radicals leading to enhancement of the rate of parasitic reactions (Eqs. (4)-(7)) to the detriment of reaction with the organic matter (Brillas et al., 2009). Thus, the higher TOC in the mixture shifted the optimal current to a higher value as a greater fraction of hydroxyl radicals was consumed for the degradation of organic matter instead of propagation of parasitic reactions.

$$Fe^{2+} + {}^{\bullet}OH \rightarrow Fe^{3+} + OH^{-} \quad (4)$$

$$2BDD({}^{\bullet}OH) \rightarrow 2\ BDD + H_2O_2 \quad (5)$$

$${}^{\bullet}OH + HO_2{}^{\bullet} \rightarrow H_2O + O_2 \quad (6)$$

$${}^{\bullet}OH + H_2O_2 \rightarrow H_2O + HO_2{}^{\bullet} \quad (7)$$

3.2. Effect of operating parameters on mineralization of the pharmaceutical mixture.

Degradation of pharmaceutical compounds is not the only objective to achieve during the treatment of such effluent. It is also necessary to remove degradation by-products that can be potentially even more toxic than parent compounds. Total mineralization of organic compounds ensures a total decontamination of the solution due to the complete transformation of organic compounds into harmless inorganics such as CO_2, H_2O and inorganic ions. Therefore mineralization kinetics was followed through TOC analyses and the influence of two main operating parameters (catalyst concentration and current) on process efficiency was assessed (Fig. 1).

First, the influence of Fe^{2+} (catalyst) concentration, which influences greatly the formation of hydroxyl radicals, was analyzed. Results obtained for three different Fe^{2+} concentrations (0.1, 0.2 and 0.5 mM) were depicted in Fig. 1A. It can be seen that a double increase in Fe^{2+}

concentration from 0.1 to 0.2 mM led to a faster TOC removal. However, a further increase to 0.5 mM showed that the mineralization was slower than for 0.2 mM Fe^{2+}. The existence of an optimal value for catalyst concentration during electro-Fenton process for the removal of organic pollutants is mainly attributed to enhancement of the parasitic reaction between hydroxyl radicals and Fe^{2+} in the presence of excess Fe^{2+} (Eq. (4)) (Brillas et al., 2009; Yang et al., 2019). Therefore, the concentration of 0.2 mM Fe^{2+} was chosen for all further experiments.

Then, the influence of current was studied in the range 100 to 1500 mA and the results were presented in Fig. 1B. It was observed that the higher the current the faster the mineralization of pharmaceuticals, without existence of an optimal threshold value. For example, after 0.5 h of electrolysis the mineralization rate was at 20, 33, and 50% for 100, 500 and 1500 mA, respectively. This behavior is different from the mineralization of single pharmaceuticals (caffeine and 5-florouracil) for which an optimal value of 400 mA was observed. These results can be explained by the fact that degradation is mainly ascribed to oxidation of organic compounds in the bulk through the electro-Fenton process, while mineralization is also strongly enhanced through anodic oxidation at the BDD anode. While there is an optimal current for the electro-Fenton process (because of parasitic reactions, Eqs. (4)-(7)), it is usually observed a continuous increase of mineralization rates when increasing current during anodic oxidation process (Panizza and Cerisola, 2009).

However, it is worth noticing that the mineralization rate was much faster at the beginning of the treatment compared, particularly at high current. After 1 h of electro-Fenton treatment with an intensity of 1000 mA almost 62% of organic matter was removed, while during next 1 h only additional 21% mineralization was achieved. Such behavior can be attributed to a stronger mass transfer limitation after removal of the main portion of the organic matter. In fact, the level of production of hydroxyl radicals was constant throughout the treatment, while the organic matter was being gradually mineralized. The ratio between the amount of

hydroxyl radicals and the amount of organic matter becomes higher, resulting in excess of hydroxyl radicals and thus promoting parasitic/ wasting reactions instead of reaction with organic compounds (Mousset et al., 2019).

This phenomenon led to a decrease of the energy efficiency (EC) of the process during the treatment. Thus, the EC was calculated according to Eq. (7) in terms of kWh consumed per kg of TOC removed during the process:

$$EC = \frac{E_{cell} \cdot I \cdot t}{(\Delta TOC)_t \cdot V_s} \quad (7)$$

where E_{cell} is the cell voltage (V), I is the applied current (A), t is the treatment time (h), $(\Delta TOC)_t$ is the decay of TOC (g L^{-1}) at time t and V_s is the volume of the solution treated (L).

At 500 mA, energy consumption was 97.8, 130, 181, 289 and 407 kWh per kg of TOC removed after 0.5, 1, 2, 4 and 6 hours of treatment, respectively. This strong increase in energy consumption with treatment time is directly related to the slower mineralization kinetics.

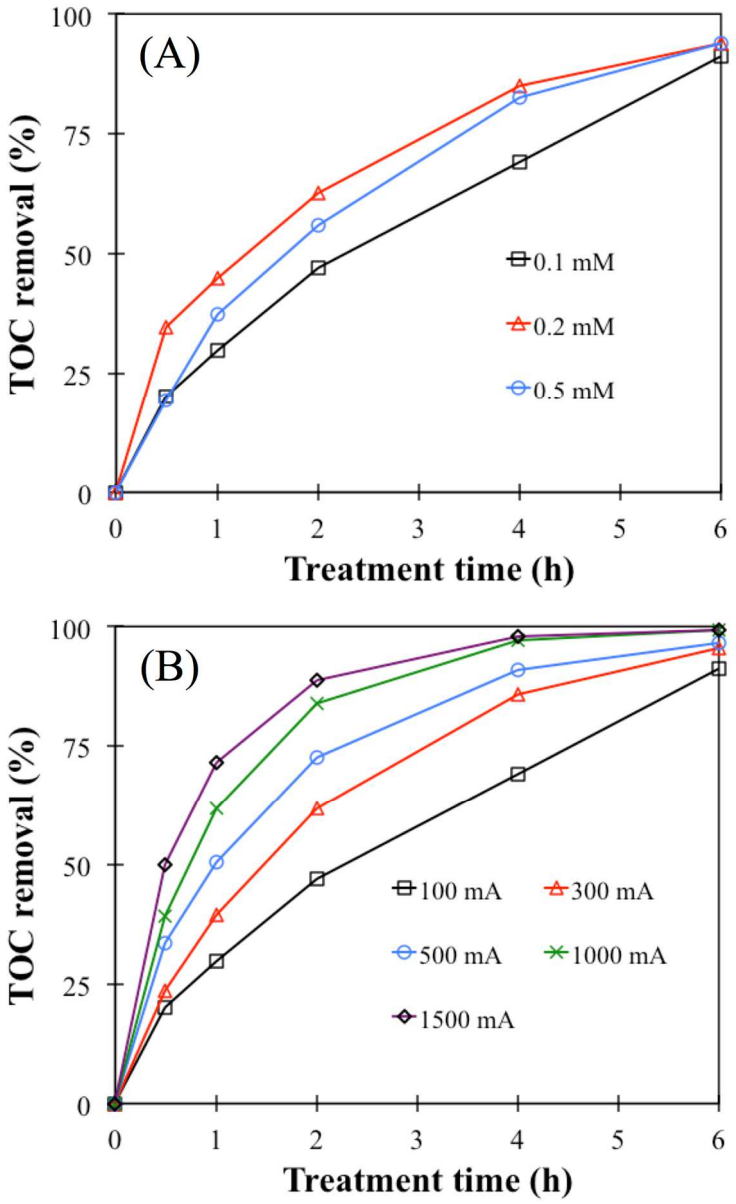
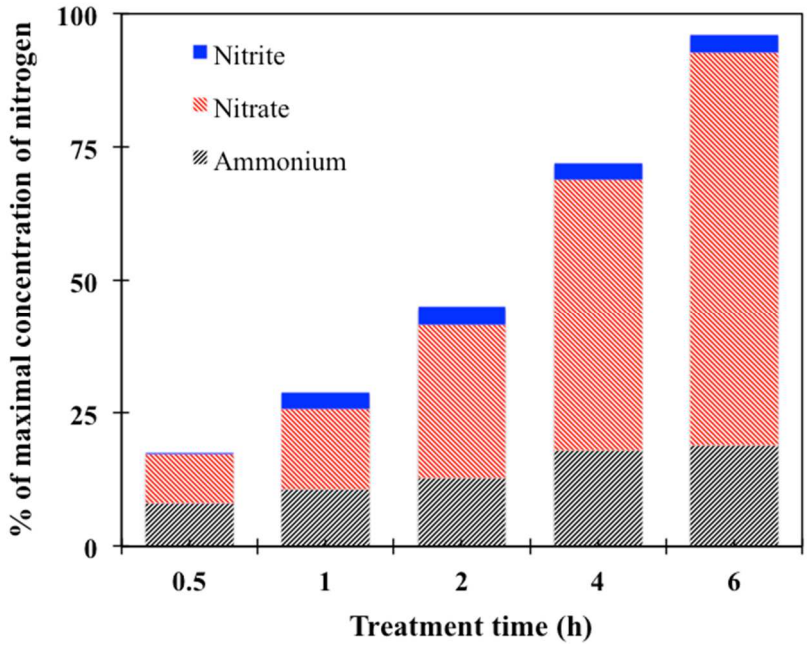


Fig. 1 - Effect of operating parameters on TOC removal during the treatment of the pharmaceutical mixture by electro-Fenton process. A: Effect of Fe^{2+} concentration; [Fe^{2+}] = 0.1 - 0.2 - 0.5 mM; operating conditions: *I* = 300 mA, [Na_2SO_4] = 50 mM, V = 200 mL. B: Effect of current; *I* = 100 - 300 - 500 - 1000 - 1500 mA; operating conditions: [Fe^{2+}] = 0.2 mM, [Na_2SO_4] = 0.05 M, V = 200 mL.

3.3. Formation and monitoring of inorganic nitrogen species

Mineralization of organic compounds results in the formation of inorganic species depending on the nature of heteroatoms in the structure of parent compounds. In the pharmaceutical mixture, 0.2 mM of fluorine, 0.2 mM of chlorine, 0.3 mM of iodine, 0.2 mM of sulfur and 2.6

mM of nitrogen were present as heteroatoms. N being the main heteroatom present in organic molecules, the formation of different forms of inorganic N was followed during the treatment. The evolution of nitrite (NO_2^-), nitrate (NO_3^-) and (NH_4^+) is presented in Fig. 2 as a percentage of the initial N concentration (2.6 mM). The concentration of these ions gradually increased till the end of the treatment, when total inorganic nitrogen reached 95% of total initial N content while the TOC removal rate was 91% at the end of the treatment. These results show that almost all the organic nitrogen was converted into inorganic nitrogen. A little fraction of N might be also converted into gaseous products such as N_2, NO_2 or N_2O_5 (Garcia-Segura et al., 2017; Mousset et al., 2018). It can also be noticed that organic nitrogen was transformed mainly into nitrate (73%) and ammonium (19% N), while the percentage of nitrite was low throughout the whole treatment (<3%). These results are consistent with previous studies on mineralization of single compounds by the electro-Fenton process (Ganiyu et al., 2019). The amount and nature (oxidation state) of inorganic nitrogen species accumulated in the solution is related to (i) the release of N from degradation of organic compounds (ii) oxidation and reduction of inorganic N species at the electrodes (particularly the oxidation of NH_4^+ and NO_2^- into NO_3^- at the anode) and, (iii) reduction of NH_4^+ at the cathode or its reaction with HClO that can be generated from oxidation of Cl^- at the anode (however, initial Cl concentration from heteroatoms in organic compounds was much lower than N concentration (0.2 and 2.6 mM, respectively) (Mousset et al., 2018). The evolution of inorganic N has to be carefully monitored since it could constitute a secondary contamination after mineralization of organic compounds. For example, it could be necessary to implement a post-biological nitrification and denitrification process for the removal of inorganic N species.



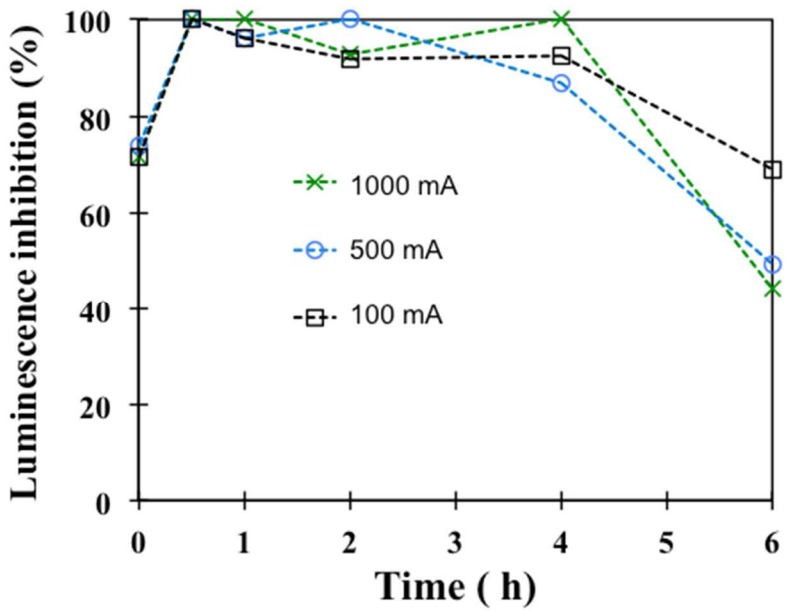
311

312 Fig. 2 - Evolution of inorganic species of nitrogen (nitrite, nitrate, ammonium) during electro-Fenton
313 treatment of the pharmaceutical mixture. Data are presented as a mass balance (%) of the initial
314 amount of organic nitrogen (2.6 mM) in the pharmaceutical mixture. Operating conditions: I = 100 mA,
315 $[Fe^{2+}]$ = 0.2 mM, $[Na_2SO_4]$ = 50 mM, V = 200 mL.

316

317 ***3.4. Evolution of acute toxicity of the pharmaceutical mixture***

318 The evolution of acute toxicity of the pharmaceutical mixture during the electro-Fenton
319 process was monitored through a series of Microtox® tests and results are presented on Fig. 3.
320 The initial solution had already a rather high acute toxicity with a *Vibrio Fisheri*
321 luminescence inhibition of 70%. After 30 min of treatment, *Vibrio Fisheri* luminescence
322 inhibition increased to 100%, indicating the formation of degradation by-products with
323 higher toxicity (Le et al., 2017). Then, luminescence inhibition started to decrease from 4 h of
324 treatment at 500 and 1000 mA reaching 42% inhibition (40% lower than initial inhibition) at
325 the end of 6 h treatment. This result might be ascribed to the degradation of toxic by-products
326 into harmless by-products such as carboxylic acids (Le et al., 2017). Contrarily to 500 and
327 1000 mA, a lower decrease was observed at 100 mA because of the slower
328 oxidation/mineralization kinetics.



329

330 Fig. 3 - Evolution of luminescence inhibition of *Vibrio fisheri* as a function treatment time during
331 electro-Fenton process as a function of f current (100, 500 and 1000 mA). Operating conditions: [Fe^{2+}]
332 = 0.2 mM, [Na_2SO_4] = 0.05 M, V = 200 mL.

333

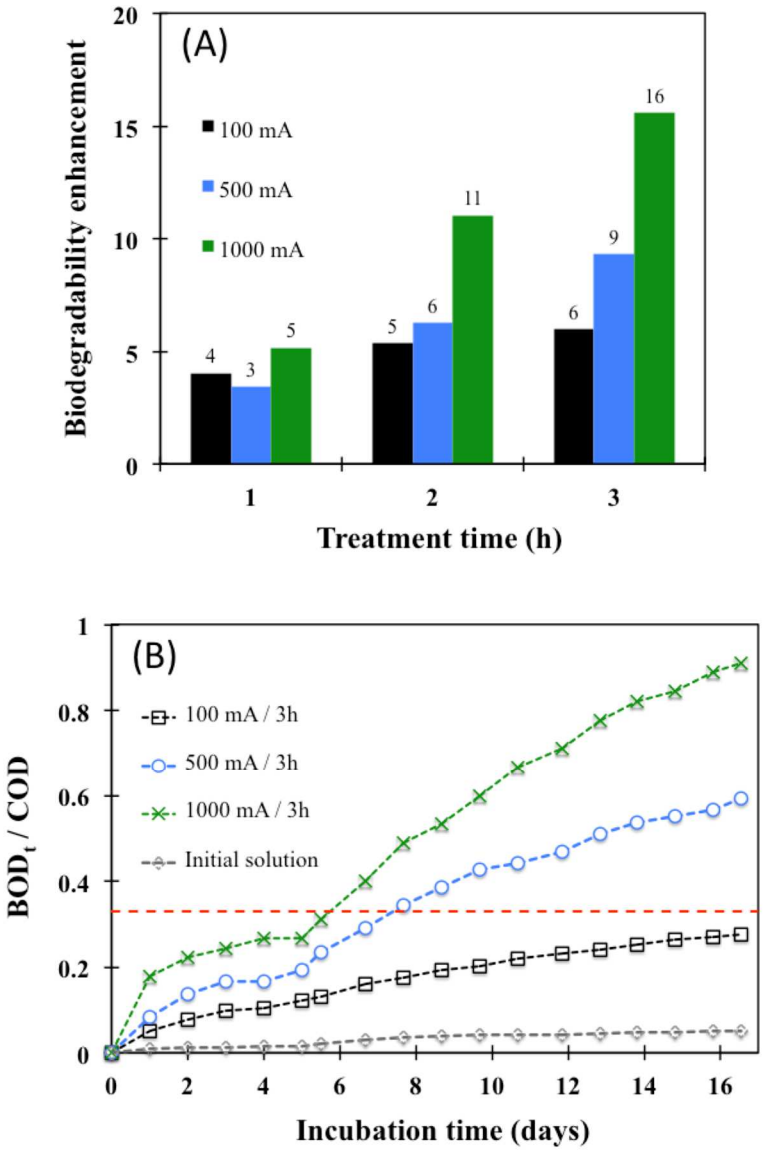
334 ***3.5. Biodegradability enhancement***

335 The possibility to combine the electro-Fenton process with a post-biological process for
336 removing organic compounds in a more cost-effective way has been investigated. In fact,
337 operation of a conventional biological process requires lower energy consumption than
338 electrochemical processes. However, conventional heterotrophic biological processes are
339 only effective for the removal of biodegradable organic compounds. First, the ratio
340 BOD_5/COD was used as indicator of the biodegradability of the effluent under examination.
341 It is usually assumed that a value above 0.33 is required for treatment of an effluent by a
342 biological process. The ratio BOD_5/COD of the initial pharmaceutical mixture was only
343 0.017, indicating that it would not be efficient to implement directly a biological treatment.
344 Then, it was investigated the evolution of the biodegradability of the effluent during the
345 electro-Fenton treatment. The factor of biodegradability enhancement was calculated from
346 Eq. (8).

347 Biodegradability enhancement = R_t / R_i (8)

348 where R_t is BOD_5/COD ratio at time t and R_i is initial BOD_5/COD ratio.

349 Evolution of biodegradability of pharmaceutical mixture during electro-Fenton treatment is
350 presented on Fig. 4A. It was observed that the biodegradability after 5 days of incubation for
351 100 and 500 mA was enhanced in the range of 3-9 times from the initial value and tends to
352 increase with longer treatment duration. When a current of 1000 mA was applied, the
353 biodegradability enhancement reached 5, 11 and 16 after 1, 2 and 3 h of treatment,
354 respectively. These results highlight that the electro-Fenton process is able to degrade initial
355 compounds into more biodegradable by-products. Particularly, short-chain carboxylic acids
356 are well known to be easily biodegradable. Finally, their formation requires multiple steps of
357 degradation of pharmaceutical compounds as described in studies on single compounds.
358 Therefore, longer treatment times and higher currents allow for greater enhancement of
359 biodegradability. However, even after 3 h of treatment at 1000 mA, the BOD_5/COD value
360 was only 0.27.



361

362 Fig. 4 - A - Biodegradability enhancement (after 5 days of incubation) after electro-Fenton treatment
363 of the pharmaceutical mixture under 3 different as a function of current applied. B - evolution of BOD_t /
364 COD ratio as a function of incubation time during BOD tests, depending on the current applied for the
365 electro-Fenton treatment of the pharmaceutical mixture during 3 h (B). The red dotted line indicates
366 the value 0.33 of the ratio BOD_t / COD. Operating parameters: $[Fe^{2+}]$ = 0.2 mM, $[Na_2SO_4]$ = 50 mM, V
367 = 200 mL.

368

369 Values of BOD_5 can strongly depend on the nature of the inoculum chosen for the analyses
370 since different bacterial population could result in different biodegradation rate of organic
371 compounds. In this study, it was chosen to use an activated sludge from a municipal
372 wastewater treatment plant in order to obtain data that could be useful in view of the

373 combination of the electrochemical process with a conventional biological process. However,
374 acclimation of the biomass to this specific effluent might result in different biodegradation
375 rate. Therefore, it has been investigated the evolution of BOD/COD ratio over incubation
376 time longer than the conventional 5 days. A set of BOD experiments was conducted for 17
377 days and results are graphically presented on Fig. 4B. Prolonged incubation time did not
378 significantly change the biodegradability of the initial effluent. However, it was observed a
379 different behavior in the effluents pre-treated by electro-Fenton process. First, BOD_t/COD
380 ratio increased rapidly during the first 3 days of incubation, most probably owing to the
381 biodegradation of short-chain carboxylic acids. For instance, a maximal BOD_t/COD value of
382 0.18 was reached after 1 d of incubation of electro-Fenton pre-treated mixture at 1000 mA for
383 3 h. In fact, the higher amount of carboxylic acids was expected for this effluent because of
384 the higher current and treatment time used for the pre-treatment. Interestingly, a second phase
385 of fast increase of BOD_t/COD ratio was observed from days 5-6, particularly for the effluents
386 pre-treated at 500 and 1000 mA currents. That means that an acclimation time of the biomass
387 was required for degradation of some degradation by-products generated during the electro-
388 Fenton pre-treatment. Results from Microtox® tests indicating that some degradation by-
389 products have higher acute toxicity than the parent compound are consistent with these
390 results showing the necessity of an acclimation time of the biomass to the pre-treated
391 effluent. Trellu et al. (2016) observed similar results for the treatment of soil washing
392 solutions by combining anodic oxidation and biological treatment. Thus, after 17 days of
393 incubation, BOD_t/COD ratio reached 0.59 and 0.91 for effluents pre-treated at 500 and 1000
394 mA respectively. These values are much higher than the threshold value of 0.33, indicating
395 that a conventional biological treatment might be applied to these pre-treated effluents. Such
396 combined treatment would allow the application of the electro-Fenton process only for short
397 treatment times in order to keep the electrical energy consumption at a minimal level, while
398 the biological process would allow the removal of the biodegradable residual organic matter

399 in a more cost-effective way than the electro-Fenton process. Acclimation of the biomass to
400 the pre-treated effluent would be a crucial parameter. However, using continuous biological
401 reactors will easily solve this issue. The results obtained also confirm the limited relevance of
402 using the BOD_5/COD ratio alone to assess the biodegradability of an effluent. Finally, it can
403 be noticed that NO_3^- released from mineralization of organic compounds could also act as
404 electron acceptors in place of O_2 for heterotrophic bacteria degrading organic compounds.
405 Thus, presence of NO_3^- would be also an advantage as it can decrease the aeration cost of the
406 biological treatment.

407 ## 4. Conclusions

408 This study has investigated the potential of the electro-Fenton process for degradation and
409 mineralization of a complex mixture of pharmaceuticals. Degradation/mineralization of 2 of
410 the 13 pharmaceuticals was also comparatively studied in single compound solutions and in
411 the mixture. Optimal Fe^{2+} concentration and current for degradation of the pharmaceutical
412 mixture were found as 0.2 mM and 400 mA, respectively. However, the mineralization rate
413 was continuously increased when increasing the current without any threshold value owing of
414 the strong contribution of anodic oxidation process with BDD anode. Mineralization of
415 pharmaceuticals was confirmed through monitoring of TOC removal and nitrogen ions
416 released into the solution mainly under the form of NO_3^- and NH_4^+. These results highlight
417 that optimal operating conditions strongly depends on hydroxyl radical scavenging. Such
418 competition phenomena depend on the nature of each specific effluent and should be further
419 study for the different kinds of effluent for which the EF process could be applied.

420 The energy consumption related to electro-Fenton process is a crucial parameter for cost
421 efficiency of the process. Thus, the possibility to combine this process with a post-biological
422 treatment was investigated through monitoring the evolution of the biodegradability of
423 electro-Fenton pre-treated effluent. Acclimation of the biomass to the pre-treated effluent was

observed to be an important parameter since some degradation by-products were observed to have higher acute toxicity than the parent compounds. Short treatment time (3 h maximum) at 500 and 1000 mA were effective operating conditions for increasing sufficiently the biodegradability of the effluent. Therefore, the electro-Fenton process allows the degradation of non-biodegradable pharmaceuticals into more biodegradable compounds that could be removed in a more cost-effective way by a post-biological treatment.

Acknowledgment

The authors thank the EU for providing financial support through the Erasmus Mundus Joint Doctorate Program ETeCoS$_3$ (Environmental Technologies for Contaminated Solids, Soils and Sediments, grant agreement FPA no. 2010-0009).

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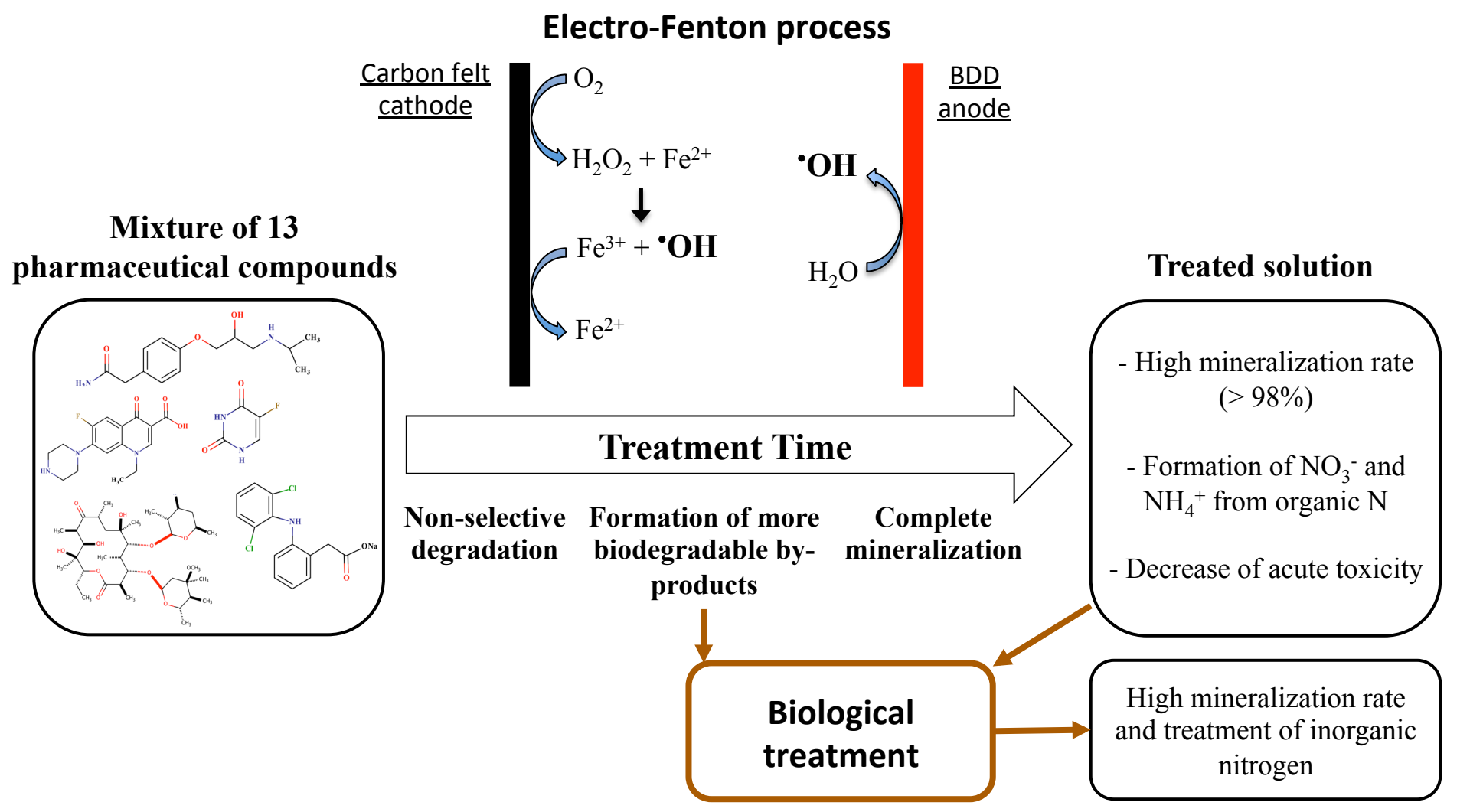
Electro-Fenton process
Carbon felt cathode
O_2
$H_2O_2 + Fe^{2+}$
$Fe^{3+} + {}^{\bullet}OH$
Fe^{2+}
BDD anode
${}^{\bullet}OH$
H_2O
Mixture of 13 pharmaceutical compounds
Treatment Time
Non-selective degradation
Formation of more biodegradable by-products
Complete mineralization
Treated solution
- High mineralization rate (> 98%)
- Formation of NO_3^- and NH_4^+ from organic N
- Decrease of acute toxicity
Biological treatment
High mineralization rate and treatment of inorganic nitrogen