



Combination of the Electro/Fe³⁺/peroxydisulfate (PDS) process with activated sludge culture for the degradation of sulfamethazine

A. Ledjeri, I. Yahiaoui, H. Kadji, F. Aissani-Benissad, A. Amrane, F. Fourcade

► To cite this version:

A. Ledjeri, I. Yahiaoui, H. Kadji, F. Aissani-Benissad, A. Amrane, et al.. Combination of the Electro/Fe³⁺/peroxydisulfate (PDS) process with activated sludge culture for the degradation of sulfamethazine. *Environmental Toxicology and Pharmacology*, 2017, 53, pp.34-39. 10.1016/j.etap.2017.04.022 . hal-01544476

HAL Id: hal-01544476

<https://univ-rennes.hal.science/hal-01544476>

Submitted on 5 Jul 2017

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Combination of the Electro/ Fe^{3+} /peroxydisulfate (PDS) process with activated sludge culture for the degradation of sulfamethazine

Amina Ledjeri¹, Idris Yahiaoui¹, Hakima Kadji¹, Farida Aissani-Benissad¹, Abdeltif Amrane² and Florence Fourcade²

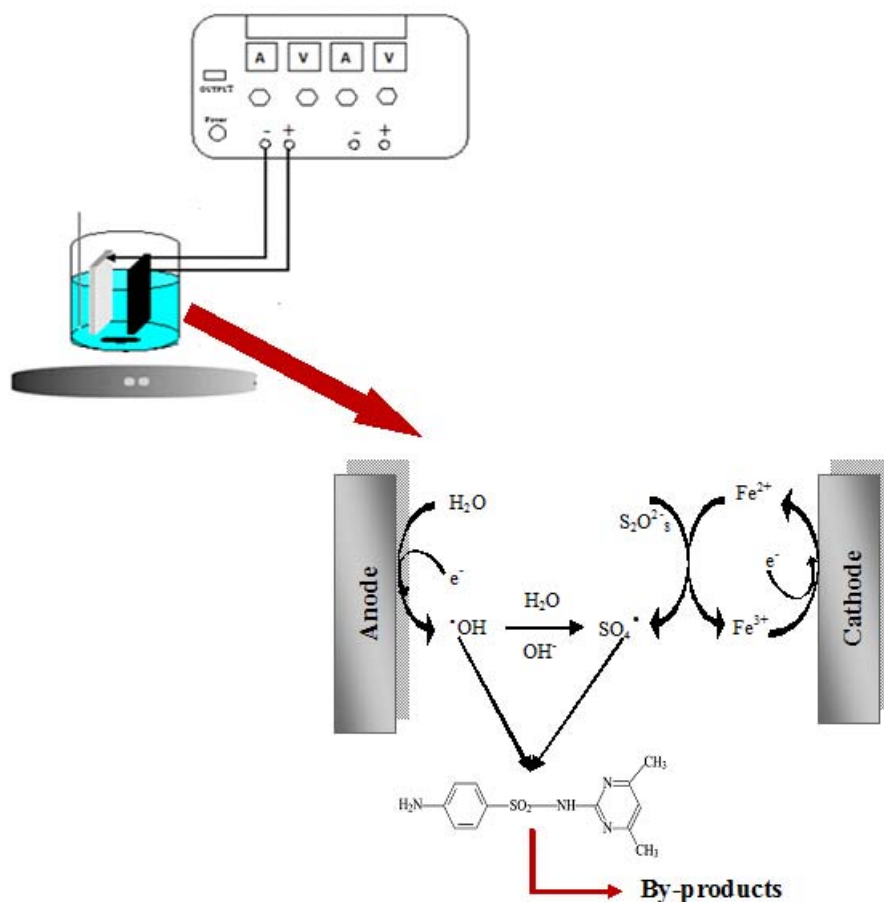
(1) Laboratoire de Génie de l'Environnement (LGE), Faculté de Technologie, Université de Bejaia, 06000, Bejaia, Algérie.

(2) Ecole Nationale Supérieure de Chimie de Rennes, Université Rennes1, CNRS, UMR 6226, Avenue du Général Leclerc, CS 50837, 35708 Rennes Cedex 7, France.

E-mail : ledjeri.amina@gmail.com

Tel/fax. + 213 34 21 51 88

Graphical abstract



Highlights

- The Electro/ Fe^{3+} /Peroxydisulfate process was used for degradation of sulfamethazine
- 40 mA cm^{-2} current density and 0.18 mM of TC concentration were the optimal values
- Optimal concentrations of PDS and Fe^{3+} were 10 mM and 1 mM , respectively
- The by-products formed after 6h of electrolysis were biodegradable
- The subsequent biological treatment increased the mineralization yield to 86%

Abstract

In this paper, the major factors affecting the degradation and the mineralization of sulfamethazine by Electro/ Fe^{3+} /peroxydisulfate (PDS) process (e.g. current density, PDS concentration, Fe^{3+} ions concentration and initial sulfamethazine (SMT) concentration) were evaluated. The relevance of this process as a pretreatment prior to activated sludge culture was also examined. Regarding the impact on SMT degradation and mineralization, the obtained results showed that they were significantly enhanced by increasing the current density and the PDS concentrations in the ranges 1 to 40 mA cm^{-2} and from 1 to 10 mM respectively; while they were negatively impacted by an increase of the initial SMT concentration and the Fe^{3+} concentration, from 0.18 to 0.36 mM and from 1 to 4 mM respectively. The optimal operating conditions were therefore 40 mA cm^{-2} current density, 10 mM PDS concentrations, 1 mM Fe^{3+} , and 0.18 mM SMT. Indeed, under these conditions the degradation of SMT and its mineralization yield were 100% and 83% within 20 min and 180 min respectively. To ensure a significant residual organic content for activated sludge culture after Electro/ Fe^{3+} /PDS pre-treatment, the biodegradability test and the biological treatment were performed on a solution electrolyzed at 40 mA cm^{-2} , 10 mM PDS concentrations, 1 mM Fe^{3+} , and 0.36 mM SMT. Under these conditions the BOD_5/COD ratio increased from 0.07 to 0.41 within 6 h of electrolysis time. The subsequent biological treatment increased the mineralization yield to 86% after 30 days , confirming the relevance of the proposed combined process.

Keywords: Antibiotics; sulfamethazine; Sulfate radicals; Ferric irons; Peroxydisulfate; Biological treatment.

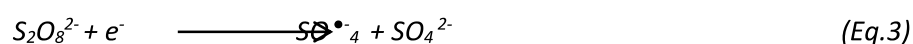
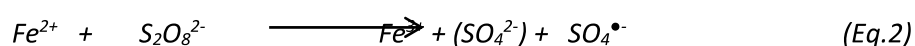
1. Introduction

Antibiotics are widely used to treat human and animal diseases. In China, 70% of the new drugs produced every year are antibiotics, with an annual production of 33,000 tons. The overuse of antibiotics in our life has caused serious losses in recent years (Chen et al., 2012; Song et al., 2010). Antibiotics residues is one of the largest source producers of non-biodegradable pollution leading to perturbations in the aquatic life (Yahiaoui et al., 2013; Mansour et al., 2012; Ferrag-Siagh et al., 2013; Belkheiri et al., 2011). Many antibiotics present in wastewater are poorly removed by conventional methods (Yahiaoui et al., 2015; Fan et al., 2015). Among them, SMT is widely used in livestock and aquaculture as an antimicrobial agent and growth promoter (Yahiaoui et al., 2015; Fan et al., 2015; Yahiaoui et al., 2013; Mansour et al., 2012). Run off from farms, leakage from septic tanks and direct discharge from aquaculture are pathways responsible for the occurrence of SMT in natural waters (Fan et al., 2015). Environmental concentrations of SMT generally range from nanogram per liter to microgram per liter. As a matter of fact, SMT concentrations in the range of 15 to 328 ng L⁻¹ were detected in tropical waters in the Mekong Delta, Vietnam (Fan et al., 2015). In China, 0.53–89.1 ng L⁻¹ of SMT was observed in the surface natural waters of Yangtze estuary (Fan et al., 2015; Yan et al., 2013; Li and Zhang, 2010) and in the Huangpu River (Shanghai) SMT concentrations of 2.05–623.27 ng L⁻¹ were observed (Fan et al., 2015; Li and Zhang, 2010). Such diffuse pollution is difficult to treat, and hence one solution would be to treat the considered pollution on site, to get low volumes highly concentrated.

Physical and physico-chemical techniques have proved their efficiency for the removal of this pollution. Among the physical techniques, adsorption, flocculation, electro-flocculation, reverse osmosis, ultrafiltration and coagulation have been applied to remove recalcitrant pollutants (Arslan et al., 2000; Sarria et al., 2003; Homem and Santos, 2011). However, these conventional methods are non-destructive and merely transfer pollutants from one phase to another, which always result in a secondary pollution. Destructive methods, such as physico-chemical ones, should be therefore preferred. Among them, traditional AOPs based on the generation of highly oxidative hydroxyl radical ($\cdot\text{OH}$), such as Fenton ($\text{Fe}^{2+}/\text{H}_2\text{O}_2$), electro-Fenton, UV/ H_2O_2 , $\text{O}_3/\text{H}_2\text{O}_2$, or electrochemical oxidation

have been widely applied in wastewater treatment (Olvera-Vargas et al., 2014; Sopaj et al., 2015; Oturan and Aaron, 2014). However, the high cost requirement for expensive equipment and high reagent or energy requirement limit their use. For the degradation of persistent organic compounds contained in wastewater and in factory effluents, several studies recommended integrated processes, more especially the coupling of physico-chemical processes and biological treatment (Yahiaoui et al., 2014, 2013a, 2013b, 2012; Mansour et al., 2012; Ferrag-Siagh et al., 2013; Belkheiri et al., 2011).

More recently, sulfate radical ($\text{SO}_4^{\bullet-}$)-based AOPs gained a growing attention. $\text{SO}_4^{\bullet-}$ can be produced via electrochemical process coupled with $\text{Fe}^{3+}/\text{S}_2\text{O}_8^{2-}$ (EC/ $\text{Fe}^{3+}/\text{S}_2\text{O}_8^{2-}$) (Lin et al., 2013; Wu et al., 2012; Zhang et al., 2014). This process generates sulfate radicals ($\text{SO}_4^{\bullet-}$) which have a high standard redox potential ($E_0 = 2.6$ V), namely only slightly lower than that of hydroxyl radical ($E_0 = 2.7$ V), but with a longer lifetime (30–40 μs) than hydroxyl radical (10^{-3} μs) (Safari et al. (2015)). According to the results reported by Lin et al. (2013), Wu et al. (2012), Zhang et al. (2014), Fan et al. (2015) and Ledjeri et al. (2016) regarding the degradation of bisphenol A, acid orange 7, landfill leachate, sulfamethazine and tetracycline by the sulfate radical respectively, the Electro/ Fe^{3+} /peroxydisulfate (PDS) process has proven to be a very promising technique for the treatment of recalcitrant pollutants. Sulfate radicals are generated according to the following reactions (Ledjeri et al., 2016):



activated sludge culture for the degradation of sulfamethazine was therefore assessed. The effect of four operating parameters, namely the current density, the peroxydisulfate (PDS), the Fe^{3+} and the initial SMT concentration, on kinetic degradation of sulfamethazine were investigated, as well as their impact on biodegradability with the objective of combining Electro/ Fe^{3+} /peroxydisulfate process to a biological treatment for the degradation of sulfamethazine.

2. Materials and Methods

2.1. Experimental set-up

The experimental set-up is described in Figure 1. This installation prototype was mainly composed of the following parts: (1) power supply (Model GW insTEK GPS-2303); (2): plate cathode (stainless steel 304 L) (3): temperature sensor; (4): plate anode (Pb/PbO₂); (5): pyrex glass cell; (6): magnetic stirrer.

Fig. 1

2.2. Electrodes and products

Electrolysis of aqueous solutions of sulfamethazine was carried out in one-compartment pyrex glass cell. The total volume of Pyrex glass cell and the solution volume were 600 and 500 mL respectively, with a Pb/PbO₂ electrode (50 mm x 40 mm x 1 mm) as anode and stainless steel 304 L electrode (50 mm x 40 mm x 1 mm) as cathode. The composition of the 304 L stainless steel used was: C ≤ 0.07 %, Si ≤ 1%, Mn ≤ 2%, P < 0.045%, S ≤ 0.015%, N ≤ 0.1%, Cr: 17 to 19.5%, Ni: 8 to 10.5% and the balance being Fe (Ledjeri et al., 2016). Na₂S₂O₈ (99% purity) was purchased from Sigma-Aldrich; Na₂SO₄ (99% purity), H₂SO₄ (96% purity) and Fe₂(SO₄)₃ (100 % purity) were purchased from Biochem Chemopharma. The pH of the solutions was adjusted to 3 using concentrated sulfuric acid (96 % purity, Biochem Chemopharma) and distilled water was used to prepare the solutions. Electrolysis was performed at constant current controlled by a direct current (DC) power supply (Model GW insTEK GPS-2303). All experiments realized were triplicated.

2.3. Target compound

The SMT (C₁₂H₁₄N₄O₂, 99 % purity) was obtained from Alfa Aesar (Thermo Fisher Scientific, Germany); its characteristics are given in Table 1.

Table 1

2.4. Lead Surface Treatment and Formation of PbO₂

The details of the procedure used for the pretreatment of the lead substrate (50mm×40mm×1mm) used in this work were previously described by Yahiaoui et al. (Yahiaoui et al., 2014, 2013a, 2013b, 2012; Ledjeri et al., 2016).

2.3. Instruments and analytical procedures

2.3.1. Sulfamethazine analysis

Sulfamethazine was analyzed by High Performance Liquid Chromatography (HPLC YL9100). The HPLC was equipped with a standard degasser (YL 9101), a manual injector (20 µL), two pumps (Model Analytical SS-1) and a detector with visible ultraviolet ray (UV/Vis detector YL9120). The separation was achieved on a Thermo Fisher scientific (Germany) C18 (5 mm; 4.6 x 250 mm) reversed-phase column. The mobile phase consisted of acetonitrile/water (35/65 v/v) and the detection of sulfamethazine was carried out at 268 nm.

2.3.2. Dissolved organic carbon measurements

Dissolved organic carbon (DOC) was measured by TOC-V_{CPH/CPN} Total Organic Analyzer Shimadzu (France). Samples were taken and filtered through 0.45 µm membrane syringe filter (Satorius Stedim biotech GmbH, Germany) for the measurement of dissolved organic carbon (DOC) (Yahiaoui et al., 2014, 2013a, 2013b, 2012).

2.3.3. COD and BOD₅ measurements

Chemical oxygen demand (COD) and biological oxygen demand in 5 days (BOD₅) were measured by Nanocolor 500D photometer type (Macherey-Nagel, Hoerd, France). All COD and BOD₅ measurements were triplicated and average results were considered. The determination of BOD₅ was carried out by tube test in the presence of added nutrients according to EN 1899-1-H51. Additionally, probable

influence of nitrification processes was inhibited by N-allythiourea. The incubation of the samples was carried out directly in the test tubes and the determination of oxygen dissolved in water was carried out after 5 days according to the Winkler method EN25813-G21 by photometric evaluation of iodine-color (Yahiaoui et al., 2013a, 2013b, 2014). The COD was measured by means of Kits Nanocolor® 15-160 mg L⁻¹ COD according to DIN ISO 15705 at 148 °C. The amount of oxygen required for the oxidation of the organic and mineral matter at 148 °C for 2 h was quantified after oxidation with K₂Cr₂O₇ at acidic pH and heating (Yahiaoui et al., 2014, 2013a, 2013b, 2012).

2.5. Media and culture conditions

The chemicals used in the culture medium were: K₂HPO₄ (99% purity, Biochem Chemopharma), Na₂HPO₄ 2H₂O (99% purity, Prolabo), CaCl₂ (96% purity, Biochem Chemopharma), MgSO₄ 7H₂O (99% purity, Biochem Chemopharma), NH₄Cl (99% purity, 99%, Biochem Chemopharma). The biological treatment was carried out in a shake-flask system (250 mL) at 25 °C, loaded with 150 mL of the electrolyzed SMT solution including the following mineral medium: 0.5 mL KH₂PO₄: 43.8 mg L⁻¹, 0.5 mL Na₂HPO₄: 33.4 mg L⁻¹, 0.150 mL CaCl₂: 27.5 g L⁻¹, 0.150 mL MgSO₄ 7H₂O: 22.5 g L⁻¹, 0.150 mL NH₄Cl: 3 g L⁻¹. The shake-flask was closed with a cellulose cap to ensure oxygenation and the system was magnetically stirred (300 rpm) (Ledjeri et al., 2016; Yahiaoui et al., 2014, 2013a, 2013b, 2012). The culture medium was inoculated with 0.5 g L⁻¹ of activated sludge (collected from a local wastewater treatment system (Sidi Ali Labhar Bejaia, Algeria)). The pH was adjusted to 7.0 with 1 mol/L NaOH (98% purity, Biochem Chemopharma) solution. It should be noted that no primary carbon source was added during the biological treatment; Samples were regularly taken and filtered through 0.45 µm membrane syringe filter (Sartorius Stedim biotech GmbH, Germany) for the measurement of the dissolved organic carbon (DOC) and all experiments were triplicated.

3. Results and Discussion

3.1. Effect of the Current density

The effect of the current density on the degradation of TC was examined. As can be seen from Figure 3, a significant improvement in sulfamethazine degradation was observed when the current density was increased, from 56 to 97 % within 60 min of reaction time when the current density increased from 10 to 40 mA cm⁻². This result can be attributed to a rapid ferrous ions production and regeneration rate according to Eq. 1 which improves the decomposition of PDS to generate sulfate radicals (Eq. 2). A higher current density improves the generation of sulfate radicals via an electron transfer reaction (Eq. 3) (Lin et al., 2013; Wu et al., 2012). According to the figure 2b, the increase of current density from 10 to 40 mA cm⁻² increased the mineralization yield from 25 to 46% after 60 min reaction time. The [DOC]_t/[DOC]₀ ratio remained then almost constant from 60 to 180 min due to the formation of recalcitrant by-products during electrolysis.

DOC removal at the end of experiment at 40 mA cm⁻² was close to 50% after 180 min reaction time.

Fig. 2

According to DOC data, the mineralization current efficiency (MCE) at a given current I (A) and a given electrolysis time t (h) can be estimated as follows (Eq.4) (Skoumal et al., 2009; Koumal et al., 2008) :

$$MCE (\%) = \frac{n F V_s \Delta(DOC)}{4.32 \cdot 10^7 m I t} \times 100 \quad (\text{Eq.4})$$

where n is the number of electrons consumed per SMT molecule (84 e⁻), F is the Faraday constant (96487 C mol⁻¹), V_s is the solution volume (L), $(DOC)_{exp}$ is the solution DOC decay (mg L⁻¹), 4.32×10^7 is a conversion factor to homogenize units ($3600 \text{ s h}^{-1} \times 12,000 \text{ mg of C mol}^{-1}$), m is the number of carbon atoms of SMT (12 C atoms) and I is the applied current (A), t is the time when a sample was collected.

The number of electrons (n) was calculated for each experiment according to the following mineralization reaction of SMT (Eq.5):



The mineralization current efficiencies in percentage (MCE%) versus time of electrolysis during the mineralization of SMT aqueous solution was presented in Fig. 3. It can be clearly seen that MCE % decreased drastically with the time of electrolysis. A rapid increase in MCE % at the beginning of the experiments performed at 10 and 20 mA/cm² was observed, suggesting a rapid destruction of products that are more easily oxidizable than the initial compound. In contrast, at long electrolysis reaction times the MCE % always underwent an important decrease due to the gradual formation of refractory by-products during the electrolysis, but the diminution of MCE % is far from being drastic. This could be attributed to the decrease of the concentration of organic matter during electrolysis, parasitic reactions occurred simultaneously and after a certain reaction time they became dominant compared to SMT and byproducts oxidation. In the case of 40 mA cm⁻², the increase of MCE % at the beginning of the reaction time was not observed, this effect can be attributed to parasitic reactions like oxygen evolution, which could be more significant at 40 mA cm⁻².

Fig. 3

3.2. Effect of the PDS concentration

Kinetic experiments were carried out with 100 mg L⁻¹ of SMT and the PDS concentration was varied in the range from 5 to 20 mM. According to the Figure 4, when the PDS concentration was increased from 5 to 10 mM, the SMT degradation and mineralization over 20 min of reaction time increased from 35

% to 64% and 23 % to 47% respectively, as a result of a larger amount of sulfate radicals being produced. An increase of the PDS concentration from 10 to 20 mM did not increase degradation and mineralization yields (Figure 4), as illustrated at the examination of the apparent rate constants of degradation and mineralization (table 2), probably due to the fact that an excess of PDS would lead to a side reaction between $S_2O_8^{2-}$ and $SO_4^{\bullet-}$ according to Eq. 6. The same results were reported by other authors (Ledjeri et al., 2016; Lin et al., 2013; Wu et al., 2012).

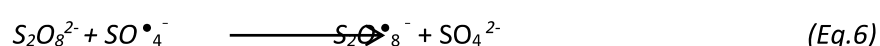


Fig. 4

Table 2

3.3. Effect of the Fe^{3+} concentration

In the same way, the influence of the Fe^{3+} ions concentration on the degradation and on the mineralization of SMT was examined. According to Figure 5, increasing the Fe^{3+} concentration had a negative impact on both SMT degradation and its mineralization, only slightly for an increase from 1 to 2 mM and significantly for a further increase to 4 mM. Fe^{2+} . Indeed, this latter can activate the persulfate anion leading to sulfate free radical (Eq.2), but an excess of Fe^{2+} can also react with the sulfate free radical (Eq.7) and this reaction is faster than Eq.2, and integration of Eq.2 in Eq.7 leads to Eq.8 (Li et al., 2016). This result allows to conclude that a low concentration of Fe^{3+} is enough to degrade SMT. However, this result is inconsistent with the findings reported by other authors (Ledjeri et al., 2016 and Lin et al., 2013). In other words, the effect of this parameter seems to depend on the nature of the molecules treated:

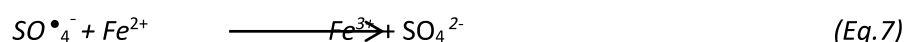
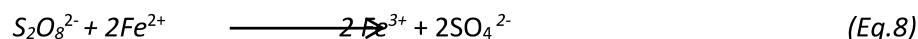


Fig. 5



3.4. Effect of the initial SMT concentration

The initial SMT concentration was varied from 0.18 mM to 0.36 mM. The increase of the initial SMT concentration impacted negatively the yields of SMT degradation and mineralization (Fig.6), as illustrated at the examination of the apparent rate constants k_{app} , which decreased from 0.1665 to 0.0524 min⁻¹ and from 0.071 to 0.0328 min⁻¹ for SMT degradation and mineralization, respectively (Table 2). This could be attributed to a competitive consumption of oxidizing SO₄^{•-} radicals between SMT antibiotic and the generated intermediate compounds formed during experiments. To examine degradation and mineralization kinetics, time-courses of ln([SMT]₀/[SMT]_t) was examined during the initial step of the experiments (insert of figure 6). The apparent kinetic rate constant (k_{app}) values corresponded to the slopes of the linear fits of the plots of ln([SMT]₀/ [SMT]_t) versus time (figure 6). A good linear relationship between ln([SMT]₀/[SMT]_t) and time t was obtained (table 2) and k_{app} decreased with increasing of the initial SMT concentration. Moreover, the SO₄^{•-} radicals are very reactive species, with very short lifetime (30-40 μs) and hence do not accumulate in the reaction medium; As a result, the assumption of a stationary state has been applied to the concentration of SO₄^{•-} radicals indicating that the degradation and the mineralization of SMT by SO₄^{•-} radicals followed pseudo-first-order kinetics.

Fig.6

3.5. Biodegradability test and Biological treatment

3.5.1. Biodegradability test

The biodegradability tests were realized on the solutions electrolyzed in the optimal conditions except for the initial concentration of SMT, namely $i = 40 \text{ mA.cm}^{-2}$, $\text{Na}_2\text{SO}_4 = 50 \text{ mM}$, $\text{PDS} = 10 \text{ mM}$, $\text{Fe}^{3+} = 1 \text{ mM}$, $\text{pH} = 3$, $T = 30^\circ \text{C}$, $\omega = 360 \text{ rpm}$ and 0.36 mM . This latter high initial amount was considered to allow significant residual organic carbon for a possible subsequent biological culture. Under these conditions, total removal of SMT was observed after 60 min, while 40 % of the dissolved organic carbon (DOC) remained after electrolysis. According to table 3, BOD_5/COD ratio increased from 0.07 initially to 0.41 after 6 h electrolysis, namely slightly above the limit of biodegradability (0.4), showing the biodegradability of the generated by-products. This pre-treatment time, 6 h, was therefore considered for the subsequent biological treatment.

3.5.2. Biological treatment

According to figure 7, an absence of biodegradation by activated sludge for the non-pretreated solution of SMT (0.36 mM) was shown, owing to the constant values of the dissolved organic carbon ratio $[\text{DOC}]_t/[\text{DOC}]_0$ observed throughout the culture (30 days); this result confirmed the biorefractory character of SMT.

The biological treatment of the solution electrolyzed during 6 h under the optimal conditions except for the initial concentration of SMT led to a significant mineralization yield of 67% (Fig.7), leading to an overall DOC removal by means of the combined process close to 86 %.

It should be observed that these promising results cannot be attributed to a possible biosorption of the by-products generated during electrolysis, as it has been previously shown for the by-products obtained after pretreatment of SMT by classical electro-Fenton (Dorsaf et al. 2015) and by electrochemical oxidation (Saidi et al. 2016).

The efficiency of the proposed combined process for the treatment of SMT was therefore shown.

Fig.7

Table 3

4. Conclusion

Experiments were realized to evaluate the performance of $SO_4^{\bullet-}$ radicals to remove and to enhance the biodegradability of sulfamethazine. According to the results, the following conclusions can be drawn:

- SMT can be rapidly and effectively degraded and mineralized under 40 mA cm^{-2} .
- Regarding their impact on degradation and mineralization efficiencies, the PDS concentration showed an optimal value of 10 mM, while they were negatively impacted by the Fe^{3+} amount in the range of concentrations tested, 1-4 mM
- The degradation of SMT followed pseudo-first order kinetics, and the rate constant decreased with increasing the initial SMT concentration.
- The optimal operating conditions appeared to be 40 mA cm^{-2} current density, 10 mM PDS concentrations, 1 mM Fe^{3+} and 0.18 mM SMT. Under these conditions, SMT and mineralization yields were 100% and 83% within 20 min and 180 min, respectively.
- The BOD_5/COD ratio increased from 0.07 initially (0.36 mM SMT) to 0.41 after 6 h electrolysis under the optimal conditions. The combined process was therefore tested showing 86 % of DOC abatement after 6 h electrolysis followed by 30 days of activated sludge culture.

References

- Arslan, I., Bacioglou, I.A., Tuhkanen, T., Bahnemann, D., 2000. $\text{H}_2\text{O}_2/\text{UV-C}$ and $\text{Fe}^{2+}/\text{H}_2\text{O}_2/\text{UV-C}$ versus $\text{TiO}_2/\text{UV-A}$ treatment for reactive dye wastewater. *J Environ Eng.* 126, 903–911.
- Belkheiri, D., Fourcade, F., Geneste, F., Floner, D., Ait-Amar, H., Amrane, A., 2011. Feasibility of an electrochemical pre-treatment prior to a biological treatment for tetracycline removal, *Sep. Purif. Technol.* 83, 151-156.
- Chen, J., Zhou, X., Zhang Y., Gao, H., 2012. Potential toxicity of sulfanilamide antibiotic: Binding of sulfamethazine to human serum albumin. *Sci. Total. Environ.* 432, 269-274.
- Fan, Y., Ji Y., Kong, D., Lu, J., Zhou, Q., 2015. Kinetic and mechanistic investigations of the degradation of sulfamethazine in heat-activated persulfate oxidation process. *J. Hazard. Mater.* 300 39-47.
- Ferrag-Siagh, F., Fourcade, F., Soutrel, I., Aït-Amar, H., Djelala, H., Amrane, A., 2013. Tetracycline degradation and mineralization by the coupling of an electro-Fenton pretreatment and a biological process. *J. Chem. Technol. Biotechnol.* 88, 1380-1386.
- Homem, V., Santos, L., 2011. Degradation and removal methods of antibiotics from aqueous matrices. *A Rev J Environ. Manage.* 92, 2304-2347.
- Ledjeri, A., Yahiaoui, I., Aissani-Benissad, F., 2016. The electro/ Fe^{3+} /peroxydisulfate (PDS) process coupled to activated sludge culture for the degradation of tetracycline. *J Environ. Manage.* 184, 249-254.
- Li, B., Zhang, T., 2010. Biodegradation and adsorption of antibiotics in the activated sludge process, *Environ. Sci. Technol.* 44, 3468–3473.
- Li, Z., Yang, Q., Zhong, Y., Li, X., Li Zhou, L., Xin Liab, X., Zengab, G., 2016. Granular activated carbon supported iron as a heterogeneous persulfate catalyst for the pretreatment of mature landfill leachate. *RSC Adv.* 6, 987–994.

- Lin, H., Wu, J., Zhang, H., 2013. Degradation of bisphenol A in aqueous solution by a novel electro/ Fe^{3+} /peroxydisulfate process. *Sep. Purif. Technol.* 117, 18–23.
- M.A. Oturan, M.A., Aaron, J.J., 2014. Advanced oxidation processes in water/wastewatertreatment: principles and applications. A review, *Crit. Rev. Environ. Sci. Technol.* 44, 2577–2641.
- Mansour, D., Fourcade, F., Soutrel, I., Hauchard, D., Bellakhal, N., Amrane, A., 2015. Relevance of a combined process coupling electro-Fenton and biological treatment for the remediation of sulfamethazine solutions -Application to an industrial pharmaceutical effluent. *C. R. Chimie.* 18, 39–44
- Mansour, D., Fourcade, F., Bellakhal, N., Dachraoui, M., Hauchard, D., Amrane, A., 2012. Biodegradability Improvement of Sulfamethazine Solutions by Means of an electro-Fenton Process, *Water Air Soil Pollut.* 223, 2023-2034.
- Olvera-Vargas, H., Oturan, N., Brillas, E., Buisson, D., Esposito, G., Oturan, M.A., 2014. Electrochemical advanced oxidation for cold incineration of the pharmaceutical ranitidine: Mineralization pathway and toxicity evolution. *Chemosphere.* 117, 644-651
- Safari, G. H., Nasser, S., Mahvi, A. H., Yaghmaeian, K., Nabizadeh, R., Alimohammadi, M., 2015. Optimization of sonochemical degradation of tetracycline in aqueous solution using sono-activated persulfate process. *j. environ. health sci. eng.* DOI: 10.1186/s40201-015-0234-7, 1-15.
- Saidi, I., Fourcade, F., Floner, D., Soutrel, I., Bellakhal, N., Amrane, A., Geneste, F., 2016. Sulfamethazine removal by means of a combined process coupling an oxidation pretreatment and activated sludge culture – Preliminary results. *Environmental Technology* DOI : 10.1080/09593330.2016.1273395
- Sarria, V., Kenfack, S., Guillod, O., Pulgarin, C., 2003. An innovative coupled solarbiological system at field pilot scale for the treatment of biorecalcitrant pollutants. *J Photochem Photobiol A-Chem.* 159, 89-99.

- Skoumal, M., Rodriguez, R.M., Cabot, P.L., Centellas, F., Garrido, J.A., Arias, C., Brillas, E., 2009. ElectroFenton, UVA photoelectro-Fenton and solar photoelectro-Fenton degradation of the drug ibuprofen in acid aqueous medium using platinum and boron-doped diamond anodes, *Electrochimica Acta*. 54, 2077-2085.
- Skoumal, M., Arias, C., Cabot, P.L., Centellas, F., Garrido, J.A., Rodriguez, R.M., Brillas, E., 2008. Mineralization of the biocide chloroxylenol by electrochemical advanced oxidation processes. *Chemosphere*. 71,1718-1729.
- Song, C., Gao, N.Y., Gao, H.W., 2010. Transmembrane distribution of kanamycin and chloramphenicol: insights into the cytotoxicity of antibacterial drugs. *Mol. Biosyst.* 6, 1901-1910.
- Sopaj, F., Rodrigo, M. A., Oturan, N., Podvorica, F.I., Pinson, J., Oturan, M.A., 2015. Influence of the anode materials on the electrochemical oxidation efficiency. Application to oxidative degradation of the pharmaceutical amoxicillin. *Chem. Eng. J.* 262, 286-294
- Wu, J., Zhang, H., Qiu, J., 2012. Degradation of Acid Orange 7 in aqueous solution by a novel electro/Fe²⁺/peroxydisulfate process. *J. Hazard. Mater.* 215- 216, 138-145.
- Yahiaoui, I., Aissani-Benissad, F., Fourcade, F., Amrane, A., 2012. Response surface methodology for the optimization of the electrochemical degradation of phenol on Pb/PbO₂ electrode, *Environ. Prog. Sustainable Energy*. DOI10.1002/ep.10572, 31,515-523.
- Yahiaoui, I., Aissani-Benissad, F., Fourcade, F., Amrane, A., 2013a. Removal of tetracycline hydrochloride from water based on direct anodic oxidation (Pb/PbO₂electrode) coupled to activated sludge culture. *Chem. Eng.J.*221, 418-425.
- Yahiaoui, I., Aissani-Benissad, F., Madi, K., Benmehdi, N., Fourcade, F., Amrane, A., 2013b. Electrochemical Pre-Treatment Combined with Biological Treatment for the Degradation of Methylene Blue dye: Pb/PbO₂ electrode and Modeling-optimization through Central Composite Design. *Ind. Eng. Chem. Res.* dx.doi.org/10.1021/ie401367q.,52,14743-147451.

- Yahiaoui, I., Aissani-Benissad, F., Fourcade, F., Amrane, A., 2014. Combination of an Electrochemical Pre-Treatment with a Biological oxidation for the Mineralization of Nonbiodegradable Organic Dyes: Basic Yellow 28 Dye. *Environ. Prog. Sustainable Energy*. DOI 10.1002/ep.11774,33,160-169.
- Yahiaoui, I., Aissani-Benissad, F., Fourcade, F., Amrane, A., 2015. Removal of a mixture of antibiotics (tetracycline-tylosin) from water based on direct anodic oxidation on a glassy carbon electrode coupled to activated sludge culture. *Environmental Technology*. 36, 1837-1846.
- Yan, C., Yang, Y., Zhou, J., Liu, M., Nie, M., Shi, H., Gu, L., 2013. Antibiotics in the surfacewater of the Yangtze Estuary: occurrence, distribution and risk assessment. *Environ. Pollut.* 175, 22–29.
- Zhang, H., Wang, Z., Liu, C., Guo, Y., Shan, N., Meng, C., Sun, L., 2014. Removal of COD from landfill leachate by an electro/ Fe^{2+} /peroxydisulfate process. *Chem. Eng. J.* 250, 76-82

Figure captions

Figure 1: Experimental set-up (Ledjeri et al.; 2016)

Figure 2: Effect of the current density.

Conditions: SMT = 0.36mM, PDS = 10 mM, Fe^{3+} = 2 mM, Na_2SO_4 = 50 mM, pH=3, T=30 °C and ω =360 rpm, (a): Degradation of SMT, (b): mineralization of SMT

Figure 3: Effect of is the applied current on the mineralization current efficiency (MCE)

Conditions: SMT = 0.36mM, PDS = 10 mM, Fe^{3+} = 2 mM, Na_2SO_4 = 50 mM, pH=3, T=30 °C and ω =360 rpm

Figure 4: Effect of the PDS concentration.

Conditions : i = 40 mA.cm⁻², SMT = 0.36mM, Fe^{3+} = 2 mM, Na_2SO_4 = 50 mM, pH=3, T=30 °C and ω =360 rpm, (a): Degradation of SMT, (b): Mineralization of SMT

Figure 5: Effect of the Fe^{3+} concentration.

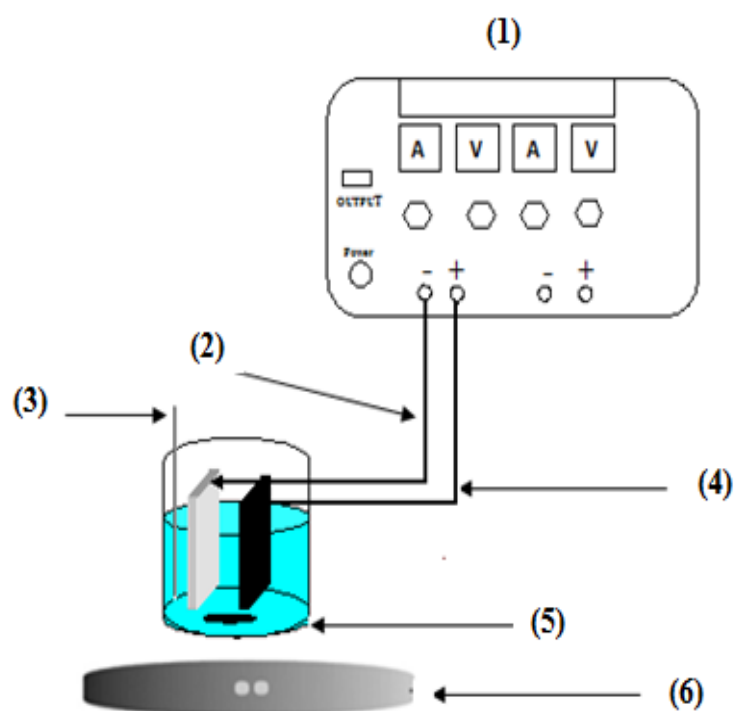
Conditions : i = 40 mA.cm⁻², SMT = 0.36mM, Na_2SO_4 = 50 mM, PDS=10mM, pH=3, T=30 °C et ω = 360 rpm, (a): Degradation of SMT, (b): Mineralization of SMT

Figure 6: Influence of the initial sulfamethazine concentration.

Conditions: i = 40 mA.cm⁻², Na_2SO_4 = 50 mM, PDS=10 mM, Fe^{3+} = 1 mM, pH=3, T=30 °C and ω =360 rpm, (a): Degradation of SMT, (b): Mineralization of SMT

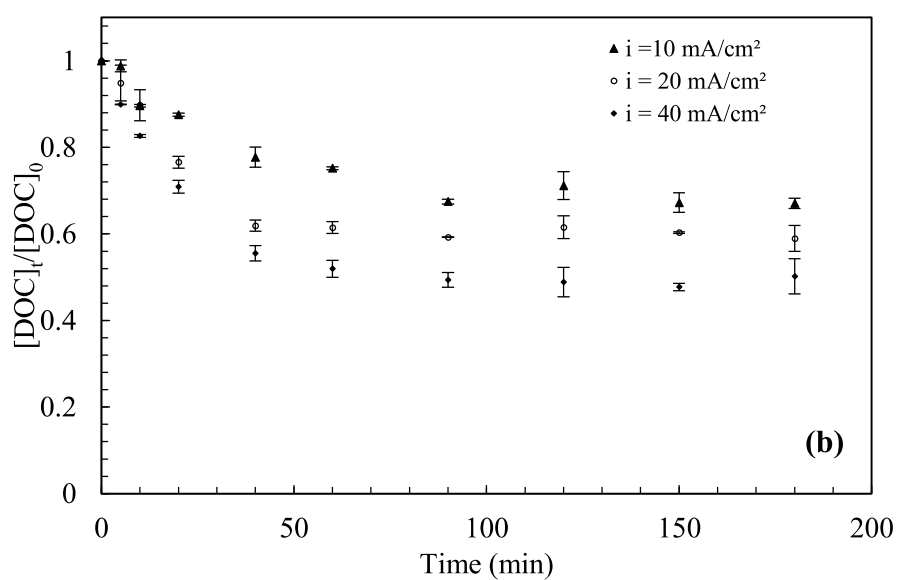
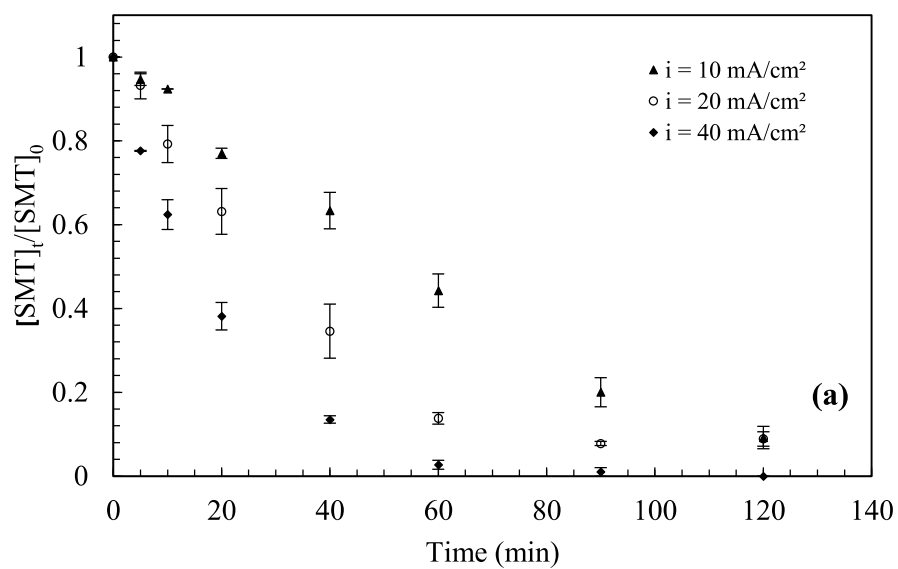
Figure 7: Time-courses of $[\text{COD}]_t/[\text{COD}]_0$ values during activated sludge culture on non-treated SMT solution (\diamond) and after 6 h electrolysis pre-treatment (\blacklozenge) on 0.5 g L⁻¹ activated sludge, pH=7, T=25 °C and ω =300 rpm.

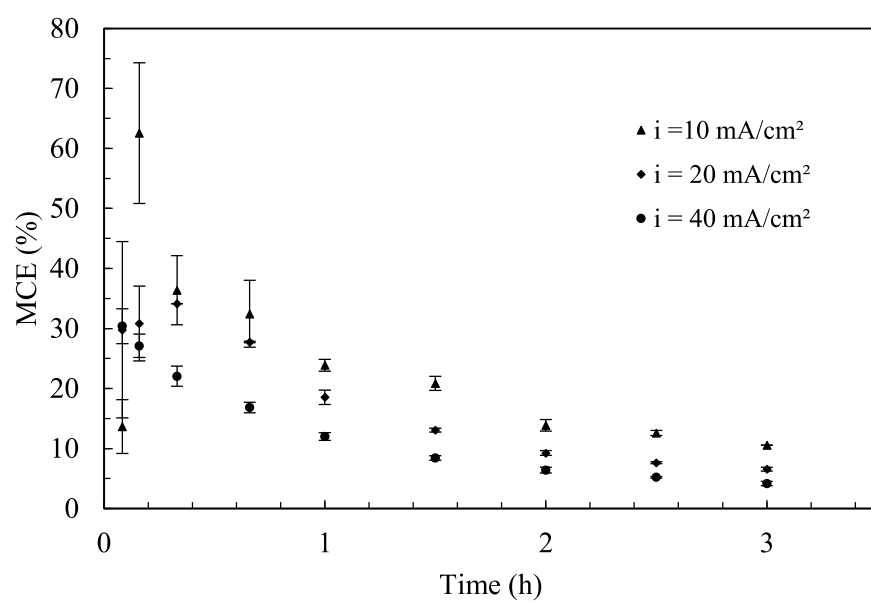
Figures



- (1): DC power supply (Model GW insTEK GPS-2303)
- (2): Cathode (304L Stainless steel plate)
- (3): Thermocouple
- (4): Anode (Pb/PbO₂ plate)
- (5): Pyrex glass cell (600 mL)
- (6): Plate Stirrer

Fig.1

**Fig.2**

**Fig.3**

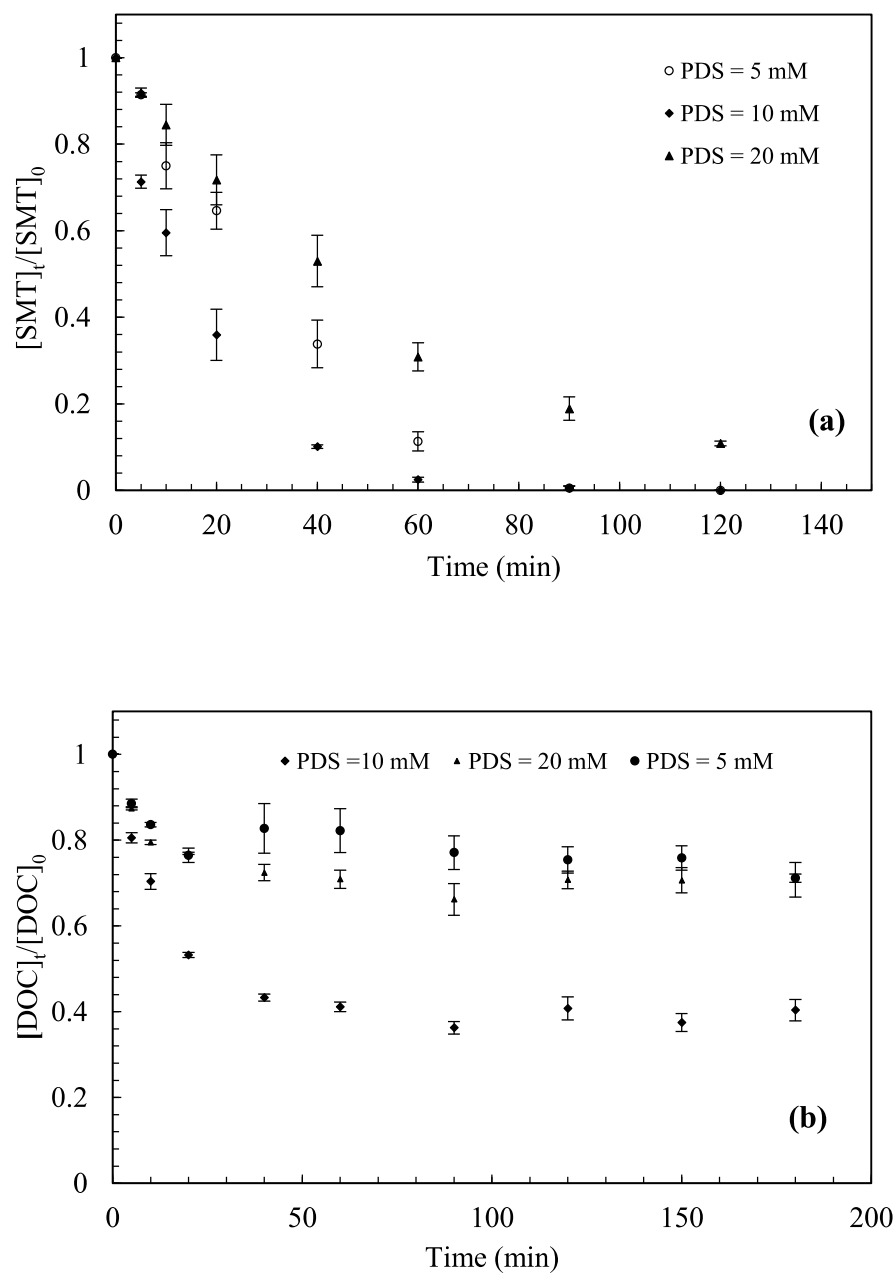


Fig.4

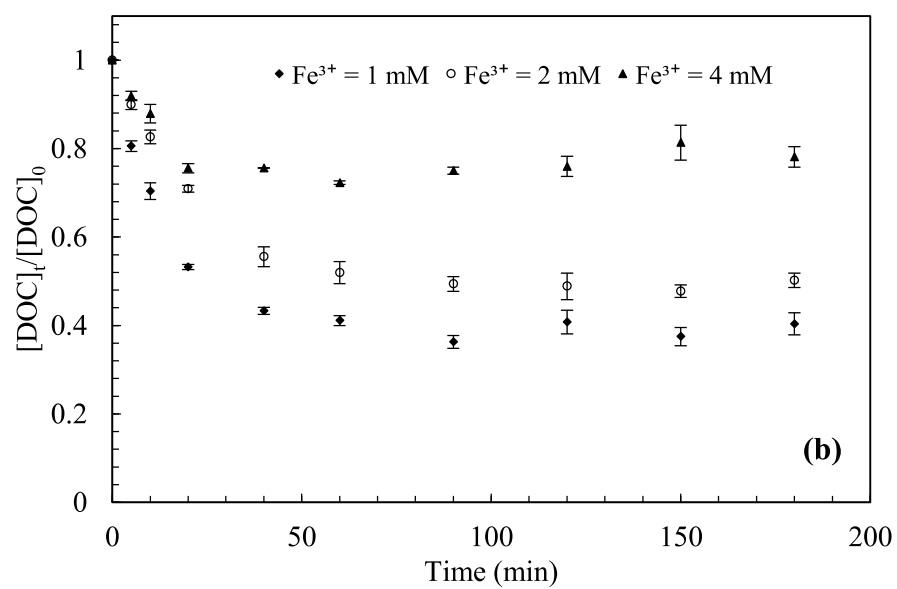
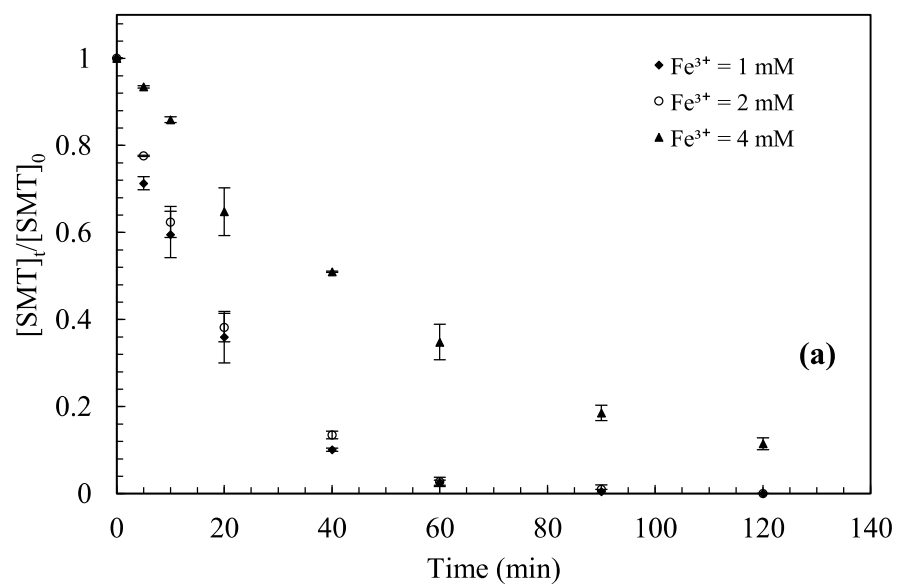


Fig.5

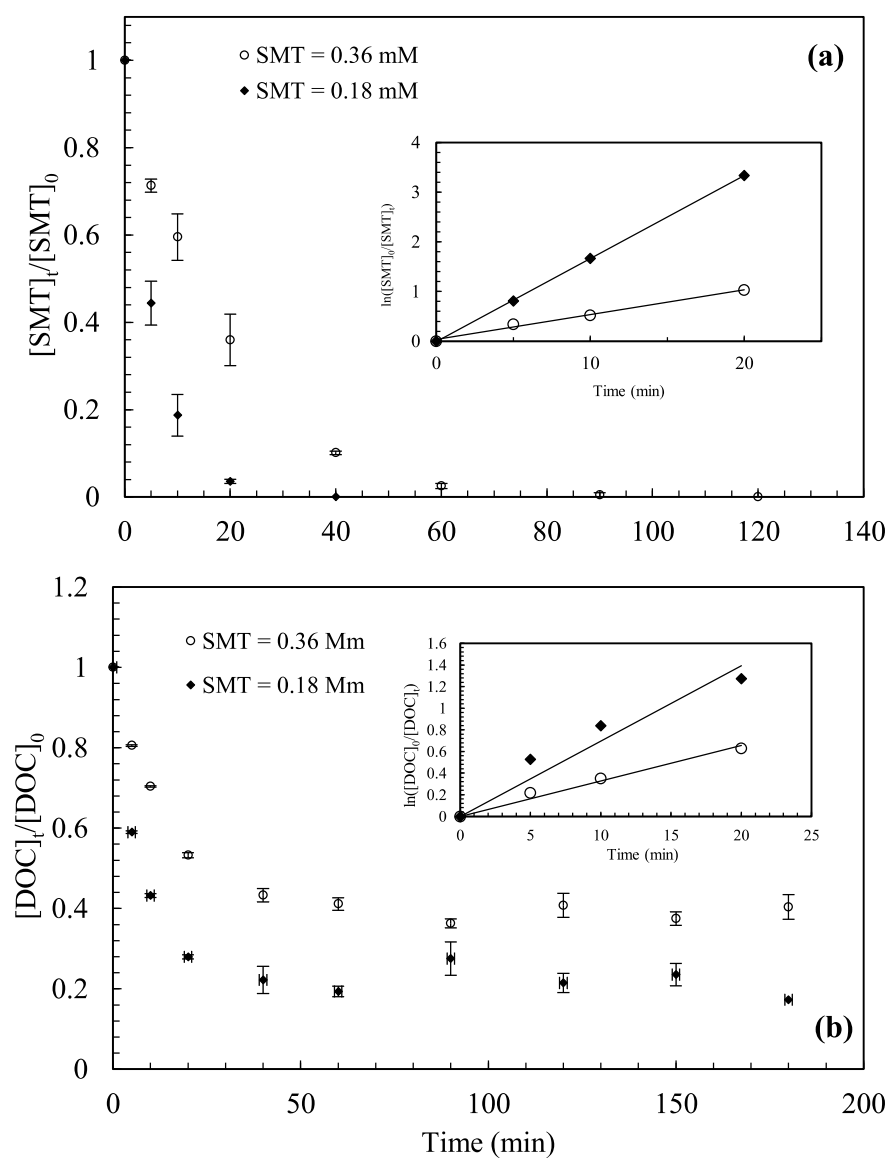


Fig.6

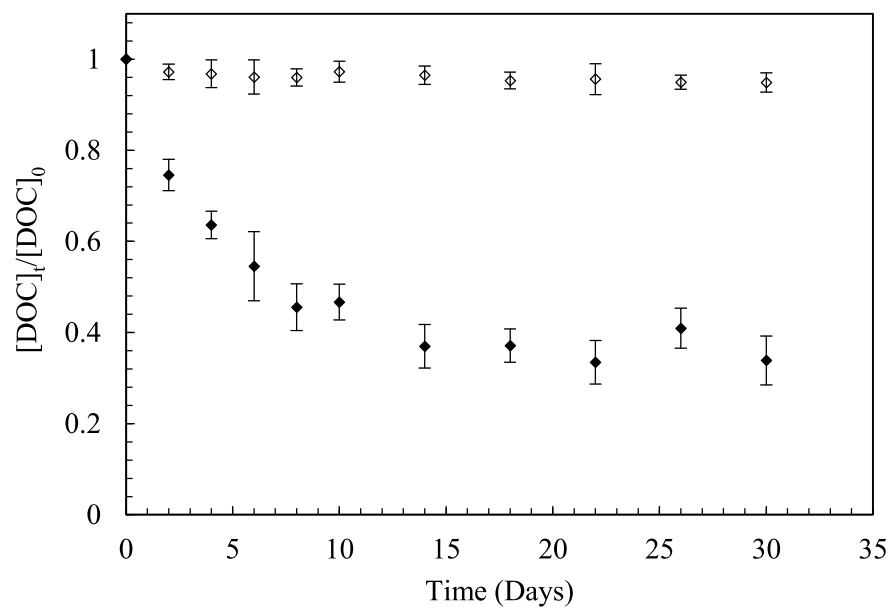
**Fig.7**

Table 1: SMT characteristics

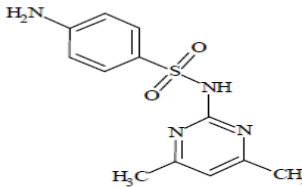
Chemical formula	Structure	M _w (g/mol)	λ _{max} (nm)	pKa	Solubility in water (g/L)
C ₁₂ H ₁₄ N ₄ O ₂ S		278.33	260	pKa ₁ = 2.65 pKa ₂ = 7.65	1.5

Table 2: Apparent Rate Constants (k_{app}) of degradation and mineralization of SMT

SMT (mg L ⁻¹)	PDS (mg L ⁻¹)	k_{app} of degradation (min ⁻¹)	R^2	k_{app} of mineralization (min ⁻¹)	R^2
100 mg L ⁻¹	5	0.0325	0.96	0.0148	0.91
	10	0.0595	0.99	0.0328	0.98
	20	0.0184	0.98	0.0148	0.91
	SMT (mM)	k_{app} of degradation (min ⁻¹)	R^2	k_{app} of mineralization (min ⁻¹)	R^2
	0.18	0.1665	0.99	0.0671	0.93
	0.36	0.0524	0.98	0.0328	0.98

Table 3: Biodegradability test of electrolyzed SMT solution in the following conditions: $i = 40 \text{ mA.cm}^{-2}$, $\text{Na}_2\text{SO}_4 = 50 \text{ mM}$, $\text{PDS} = 10 \text{ mM}$, $\text{Fe}^{3+} = 1 \text{ mM}$, $\text{pH} = 3$, $T = 30 \text{ }^\circ\text{C}$, $\omega = 360 \text{ rpm}$ and $\text{SMT} = 0.36 \text{ mM}$

	SMT(mM)	0h	3h	6h
BOD ₅ /COD	0.36	0.07	0.13	0.41