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Sulfamethazine removal by means of a combined process coupling an oxidation pretreatment and activated sludge culture – Preliminary results

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Abstract

A coupled electrochemical process and biological treatment was used to remove a biorecalcitrant antibiotic: sulfamethazine (SMT). The pre-treatment was performed in a home-made flow cell involving graphite felt as a working electrode at potentials of 1 and 1.6 V/SCE; it was followed by a biological process involving activated sludge purchased from a local wastewater treatment plant. Activated sludge cultures of pretreated and non-pretreated sulfamethazine solution were carried out for 3 weeks, and different parameters were monitored, especially TOC and SMT concentration. HPLC results revealed that the target molecule was not assimilated by activated sludge. However, and confirming the improvement previously observed for the BOD_5/COD ratio, from 0.08 before electrolysis to 0.58 after electrolysis, a pre-treatment step in oxidation at 1.6 V/SCE led to a fast decrease of TOC during the subsequent biological treatment, since the mineralization yields increased from 10% for a non-pretreated SMT solution to 76.6% after electrolysis in oxidation (1.6 V/SCE), confirming the efficiency of coupling electro-oxidation process with a biological treatment for the mineralization of sulfamethazine. Moreover, when the electrolysis was performed at 1 V/SCE, no biodegradation was observed, underlining the importance of the electrochemical pretreatment.

Keywords: sulfamethazine; electro-oxidation pretreatment; activated sludge; biological treatment; combined process.

1. Introduction

Sulfamethazine (SMT) (Fig. 1) is an antibiotic that belongs to the pharmaceutically important group of heterocyclic sulfonamides. It is widely used in medicine and veterinary practice as an antibacterial drug in pharmaceutical preparations [1].

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Special attention is given to the treatment of waters contaminated with sulfonamides, which are not efficiently degraded in sewage treatment plants and are therefore transferred into water bodies [2]. Sulfamethazine is mentioned as the predominant sulfonamide found in livestock animal wastewater and a very emerging pollutant continuously delivered into waters bodies. It has attracted growing attention due to its recalcitrant behavior in the environment [3].

A variety of technologies have been developed to effectively remove this emerging pollutant and especially antibiotics, such as sorption on goethite [4], biological methods [5] photolysis [3,6,7] photo-catalysis with TiO_2 and ZnO as catalysts [1,8,9], anodic oxidation [10], photo-Fenton [2,11], Electro-Fenton [12] and photoelectro-Fenton processes [13] as well as other coupled processes [14-16]. Among these technologies, physical methods consist only in a transfer of the target compounds from water to a solid phase without any degradation. Although biological processes are economically interesting, they are not effective for antibiotics removal due to their high toxicity and resistance [2,14,17]. Several Advanced Oxidation Processes have demonstrated to be effective for the removal of sulfamethazine. These methods often lead to a total effluent mineralization but in this case they appear expensive. In some cases and according to the duration of treatment, they also favor the production of a great variety of by-products because of their absence of selectivity. From this, the combination of such physico-chemical processes to a biological treatment can appear relevant and have been previously recommended [18-25]; in this connection electrochemical processes have been recently tested to improve biodegradability of solution containing organic recalcitrant compounds including sulfamethazine [14,16,26,27], which were then treated by activated sludge cultures to complete the mineralization of the solutions and hence achieve the treatment [15,18,28-31]. Regarding the pretreatment step, advanced electrochemical oxidation process, namely electro-Fenton [14,15] or direct electrochemical oxidation [16] have been considered and showed promising results. Indeed, for 0.2 M initial

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SMT concentration and in the optimal electro-Fenton pretreatment conditions, mineralization yields of 61.4, 78.8 and 93.9% were obtained during the biological treatment for SMT solutions pretreated during 0.5, 1 and 4 h [15].

In the case of direct electrochemical SMT oxidation, the impact of the pretreatment on biodegradability was previously assessed [16]. The pre-treatment was achieved in an electrochemical flow cell using a graphite felt electrode of high specific surface area. Under optimal conditions, the biodegradability based on the BOD_5 on COD ratio measurement was improved from 0.08 initially to 0.58 after electrolysis [16], namely above the threshold limit value (0.4) [20,32]. However, this positive impact of the electrochemical pretreatment was not confirmed by a subsequent biological treatment. Therefore, to confirm the relevance of the proposed combined process for sulfamethazine, treatment should be assessed; this task was the main purpose of this paper.

2. Materials and Methods

2.1. Chemicals and materials

Sulfamethazine (purity 99%) was obtained from Alfa Aesar (Schiltigheim, France). Inert supporting electrolyte Na_2SO_4 (purity 99%) was purchased from Carlo Erba Reactif-SDS Acetonitrile (purity 99.9%) was HPLC grade obtained from Sigma-Aldrich (Saint-Quentin Fallavier, France). Graphite felt (RVG 4000) was supplied by Mersen (Paris La Defense). Its specific area measured by the BET method, its volume density and its carbon content were 0.7 $m^2\ g^{-1}$, 0.088 g cm^{-3} and 99.9%, respectively.

2.2. Materials for the electrochemical pre-treatment

Electrochemical pre-treatment, in continuous system, was performed in a home-made flow cell [26]. Two interconnected PAPYEX carbon papers supplied by Mersen (France) were used as counter-electrodes (85 mm × 85 mm) and compartments were separated by cationic

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exchange membranes (Ionac 3470 – Lanxess SAS, Courbevoie, France). The reference electrode (Saturated Calomel Electrode – SCE) was positioned in the middle of the graphite felt (48 mm diameter and 12 mm width) and the potential control was performed using a potentiostat. To ensure a good homogeneity of the potential distribution in the three dimensional working electrode, the felt was located between the two counter-electrodes [33]. The cell was thoroughly rinsed with distilled water before and after each experiment. The solution (50 mg L^{-1} sulfamethazine in 0.1 M Na_2SO_4) percolated the porous electrode at various flow rates monitored by a Gilson minipuls 2 peristaltic pump (Middleton, WI, USA).

2.3. Biological treatment

Activated sludge obtained from a local wastewater treatment plant (Beaurade, Rennes, France) was used in this study. It was washed at least five times with water and centrifuged at 3000 rpm for 10 min to remove any residual carbon and mineral source. Cultures were at least carried out in duplicates at 25 °C in 250 mL erlenmeyers flasks containing 100 mL of medium with 0.5 g L^{-1} of activated sludge. The following mineral basis was used for all experiments (g L^{-1}): Na_2HPO_4 $2H_2O$, 33.4; KH_2PO_4, 8.5; K_2HPO_4, 20.8; $MgSO_4.7H_2O$, 22.5; $CaCl_2$, 27.6; $FeCl_3$, 0.26 and NH_4Cl, 75 10^{-3}. The pH was then adjusted to 7.0 with NaOH solution. Samples (5 mL) were taken every 2 or 3 days and filtered on 0.45 µm.

2.4. Analytical Procedures

2.4.1 High Performance Liquid Chromatography (HPLC)

The residual sulfamethazine concentration was determined by HPLC using a Waters 996 system equipped with waters 996 PDA (Photodiode Array Detector) and Waters 600 LCD Pump. The separation was achieved on a Waters C-18 (5 µm; 4.6 × 250 mm) reversed-phase and the mobile phase consisted of a mixture of acetonitrile/ultra-pure water (35/65, v/v) delivered at a flow rate of 1 mL/min. Detection of sulfamethazine was carried out at 268 nm and the retention time was approximately 5 min.

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2.4.2. Liquid chromatography–mass spectrometry (UPLC-MS/MS)

2.4.2.1. Ultra-pressure liquid chromatography.

The analytes were separated by a Waters Acquity UPLC system (Waters Corporation, Milford, MA, USA) consisting of an Acquity UPLC binary solvent manager, an Acquity UPLC sample manager and an Acquity UPLC column heater equipped with a Waters Acquity UPLC BEH C18 column (2.1 mm x 100 mm, 1.7 µm particle size) (Milford, MA, USA)) maintained at 45°C. Isocratic LC elution was performed with 0.1% formic acid in acetonitrile as mobile phase A and an ultrapure water

9.5:0.5 acetonitrile (v/v) mix, with added 0.1% (v/v) of formic acid as mobile phase B. Separation of the analytes on the column was performed with a mobile phase consisting of a mixture of phase A/phase B (5/95, v/v) delivered at a flow rate of 0.4 mL min^{-1}.

2.4.2.2. andem mass spectrometry.

The separated compounds were detected with a Waters Micromass Quattro Premier (Waters Corporation, Manchester, UK) triple quadrupole mass spectrometer. It was operated with an electrospray source in positive ionization mode with a cone potential of 40 V. The ionization source conditions were: capillary voltage of 3.0 kV, source temperature of 120°C and desolvation temperature of 350°C. The cone and desolvation gas flows were 50 L h^{-1} and 750 L h^{-1}, respectively; they were obtained from an in-house nitrogen source. High-purity argon (99.99%, Air Liquid, Paris, France) was used as collision gas and was regulated at 0.1 mL min^{-1}. Analyses were performed in full scan and daughter scan modes. Spectra were acquired between 50 and 300 m/z and the data were treated with Micromass Mass-Lynx 4.1 software.

2.4.3 Total Organic Carbon (TOC) measurements

The solutions were filtered on Sartorius Stedim Minisart 0.40 µm GF prefilters (Goettingen, Germany). TOC was measured by means of a TOC-$V_{CPH/CPN}$ Total Organic Analyzer Schimadzu. Organic carbon compounds were combusted and converted to CO_2, which was

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detected and measured by a non-dispersive infrared detector (NDIR). Reproducible TOC values were always obtained using the standard NPOC (Non Purgeable Organic Carbon) method. For each sample, each measurement was triplicated.

2.4.4 Chemical Oxygen Demand (COD) measurements

Chemical Oxygen Demand was measured by means of a Test Nanocolor® CSB 160 and 300 from Macherey-Nagel (Düren, Germany). The amount of oxygen required for the oxidation of the organic and mineral matter at 164°C for 30 min was quantified after oxidation with $K_2Cr_2O_7$ at acidic pH and heating.

2.4.5 Biological Oxygen Demand (BOD_5) measurements

Biodegradability was deduced from BOD_5 measurements, as previously reported [16].

3. Results and discussion

3.1. Electrochemical pretreatment prior to biological treatment

Electrochemical oxidation of sulfamethazine on carbon felt was previously investigated [12] and showed an enhancement of the biodegradability of sulfamethazine solution after electrolysis. The electrochemical behavior of sulfamethazine (50 mg L^{-1}) was first studied in neutral salts (Na_2SO_4 0.1 mol L^{-1}) by cyclic voltammetry on a glassy carbon electrode, showing an electroactivity in oxidation (1 V/SCE). The pre-treatment was then carried out using an electrochemical flow cell with a graphite felt electrode as working electrode at 1 and 1.6 V/SCE. After only a single pass through the cell, the analysis of the electrolyzed solution showed high degradation yield (more than 90%) while mineralization remained limited (it did not exceed 23%). The influence of different parameters such as the flow rate and the applied potential on the degradation of the molecule and the biodegradability of by-products was examined. As presented in table 1 and in agreement with previous results [16], the BOD_5/COD ratio increased from 0.08 before electrolysis to 0.58 after electrolysis. To confirm

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these promising results, a biological treatment should be assessed out to check the biodegradability improvement after pretreatment.

3.2. Biological treatment

In order to confirm the encouraging results obtained after electrochemical pretreatment [16], biological treatment on activated sludge of pure sulfamethazine solution and electrolyzed solution at 1 V and 1.6 V were carried out.

3.2.1. Biosorption

Prior, to the biological treatment, biosorption on activated sludge of SMT and by-products from SMT oxidation should be assessed. Given that, sorption is a rapid mechanism which take only few hours, TOC and residual SMT concentrations were monitored during the first 2 hours of activated sludge culture on pure SMT and the electrolyzed solutions (E=1 V and 1.6 V, flow rate of 1 mL min^{-1}).

As displayed in Fig. 2, neither SMT nor its by-products appeared significantly biosorbed on activated sludge, owing to the observed stability of TOC values and the residual SMT concentrations.

From these results, no significant involvement of biosorption of the target compound SMT or its degradation products of electrolysis have to be considered during the biological treatment, and hence any decrease of the SMT amount and the TOC values can be attributed to biodegradation.

Based on a review of the related literature, biosorption of organic compounds depends on various factors (molecular size, degree of ionization, solubility, charge, hydrophobicity [34].

Yang et al. [35] investigated the biosorption of sulfonamide antibiotics (sulfamethoxazole, sulfadimethoxine, sulfamonomethoxine) onto activated sludge. They found that the sorption phenomenon depended on the molecular structure. Indeed, after 2 h of contact, 7, 12 and

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18.7% of sulfamethoxazole, sulfamonomethoxine and sulfadimethoxine were respectively biosorbed at pH 7, for 2.56 $g.L^{-1}$ of activated sludge. The differences observed were mainly due to the structure of the pyrimidinic ring and biosorption was the weakest for sulfamethoxazole, the closest structure to that of sulfamethazine.

Biosorption depends also on pH [36] and weaker biosorption was observed when sulfonamide antibiotics were in their anionic form. pKa of sulfamethazine are 2.07 and 7.65; in our biological operating conditions (neutral pH), a non-negligible part of sulfamethazine was therefore in an anionic form, which is not in favor of biosorption. Moreover, in neutral pH conditions, sulfamethazine responded to a low biodegradability and a weak biosorption [37].

The absence of significant biosorption of SMT on activated sludge experimentally observed was therefore in accordance with all these literature data.

3.2.2. SMT Biodegradation

Biological treatments were carried out in aerobic conditions and somes parameters, SMT concentration and TOC, were monitored during the 18 days of culture; samples were regularly taken and were duplicated in order to check the reproducibility of the results.

Time-course of SMT concentration during the biological treatment did not show significant removal, since low degradation yield were recorded: 3.4 ± 1.8% after 18 days (Fig. 2). TOC evolution (Fig. 3) confirmed the non-biodegradability of the target compound in these culture conditions, since it remained nearly constant during the biological treatment of non pretreated SMT, the mineralization yield was close to 5% after 18 days. This result was in good agreement with the low value obtained for the BOD_5/COD ratio (0.08) [16] and with previous results recorded during the treatment of sulfamethazine by means of a combined process coupling an electro-Fenton pretreatment with a biological treatment [15], which also observed an absence of biodegradability of sulfamethazine, owing to the nearly constant TOC values obtained during 20 days of activated sludge culture.

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3.2.3. Biodegradation of the electrolyzed solution

After only a single pass through the electrochemical flow cell the electrolyzed solution (E=1 V and 1.6 V, flow rate of 1 mL min^{-1}) was collected for a subsequent biological treatment.

As observed in Fig. 4, no really significant TOC decrease was measured during culture for SMT solution oxidized at 1 V/SCE; only nearly 5 % of the carbon was mineralized after 18 days, indicating an almost total absence of biodegradability of the by-product resulting from oxidation (1 V/SCE). This result was in agreement with the only low increase of the BOD_5/COD ratio values after the oxidation (1 V/SCE) step, from 0.08 initialy to 0.14 after electrolysis (Table 1).

Contrarily, a significant reduction of the TOC was obtained for the SMT solution oxidized at 1.6 V/SCE during activated sludge culture, 72.3 ± 1.3 % TOC removal was measured after 18 days, confirming the increase of the BOD_5/COD ratio, since a value of 0.58 was obtained after electrolysis at 1.6 V/SCE (Table 1). Oxidation at 1.6 V/SCE led therefore to the formation of some by-products readily biodegradable. From this, an overall mineralization yield of 79.3% was obtained after the biological treatment of SMT previously oxidized at 1.6 V/SCE.

The main intermediates identified after the sulfamethazine pretreatment were 2-hydroxy-4,6-dimethylpyrimidine, 2-Amino-4,6-dimethylpyrimidine, 4-((4,6-dimethyl-2-pyrimidinyl)-amino)phenol and *N*-(4-aminophenyl)-4,6 dimethyl-2-pyrimidinamine (Table 2).

If we compare the solutions electrolyzed at 1 V and 1.6 V, 2-hydroxy-4,6-dimethylpyrimidine was not detected at 1.6 V. 2-Amino-4,6-dimethylpyrimidine and *N*-(4-aminophenyl)-4,6 dimethyl-2-pyrimidinamine are less concentrated at 1.6 V while the amount of 4-((4,6-dimethyl-2-pyrimidinyl)-amino)phenol was similar in the two electrolyzed solutions.

Pyrimethanil [38] is a pesticide that is known to interfere with the secretion of fungal enzymes that are necessary for infection by pathogens. Its chemical structure is close to *N*-(4-

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aminophenyl)-4,6 dimethyl-2-pyrimidinamine except the presence of an amino group in the aromatic ring.

Few microorganisms are able to metabolize pyrimidine: *Pseudomonas aeruginosa* [39] and *Saccharomyces kluyveri* [40]. Escherichia coli K-12 can grow on pyrimidine compounds and metabolize them as sole nitrogen source by means of Rut (pyrimidine utilization) pathway composed of seven proteins. This pathway enzymes can cleave the pyrimidine ring but with the production of reactive and toxic intermediates [41].

Moreover, in anaerobic culture in serum bottles, pyrimidine was partially biodegraded to methane and carbon dioxide by soil microorganisms but the degradation needed around one year to reach 83% with initial concentration near 350 µM [42].

Finally, Cambon et al. [43] have observed in their study the accumulation of 2-amino-4,6-dimethylpyrimidine in same amount in both sterile and non sterile soil. They concluded on the slight biodegradation of the target compound with less than 10.4% of removal in non sterile soil.

All these studies showed that pyrimidinamine and pyridimine derivatives are not easily biodegradable and the present results seem to suggest that their concentration in the electrolyzed solution is a key factor for biodegradability.

When an electro-Fenton pretreatment was carried out prior to a biological treatment [15], the evolution of biodegradability did not show similar trend. Indeed, after an electro-Fenton pretreatment, an acclimation of the sludge to the byproducts was observed, owing to the constant TOC values observed until 10 days of culture, and a clear decrease then occurred until total mineralization (97.3%); while after direct oxidation on the carbon felt, a rapid TOC decrease was observed during activated sludge culture. This shows that even if total target compound degradation and low mineralization yields were observed for both pretreatments, and even if some similarities were found between degradation products, the degradation

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pathway involved in direct oxidation on the carbon felt electrode (this work) and in electrochemical advanced oxidation process, electro-Fenton [15], were not the same. It was most likely the consequence of differences in the amounts of by-products and/or the formation of other unidentified by-products.

4. Conclusion

This study demonstrated the efficiency of coupling an electrochemical oxidation with a biological treatment for enhancing the mineralization of sulfamethazine, a sulfonamide drug. Pre-treatments in oxidation were performed in a home-made flow cell at 1 and 1.6 V/ESC on graphite felt. Preliminary tests showed an increase of the biodegradability with the oxidation potential, the BOD_5/COD ratio increased from 0.08 before electrolysis to 0.14 and 0.58 after electrolysis in oxidation at 1 and 1.6 V/SCE respectively, namely above the limit of biodegradability for the highest potential. This enhancement of biodegradability was confirmed during biological treatment, since 79.3% of total organic carbon (TOC) was removed by means of the combined process, namely after biological treatment of a solution electrolyzed at 1.6 V/SCE. In order to try to reduce the working potential on the one hand and to improve mineralization during the biological process on the other hand, an acclimation of the activated sludge to the degradation products resulting from electrolysis could be subsequently investigated.

Accepted manuscript

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Table 1: Impact of the applied potential on the biodegradability and the mineralization of the electrolyzed solutions [16]. Electrolysis conditions: $[SMT]_0$= 50 mg L^{-1}, 1 mL min^{-1}.

Applied potential (V)	BOD_5/COD[a]	TOC(mg L^{-1})[a]
-	0.08 ± 0.01	23.2 ± 1.3
1	0.14 ± 0.00	18.0 ± 2.7
1.6	0.58 ± 0.10	20.0 ± 2.1

[a]Uncertainties are based on two reproducibility measurements

Table 2: Intermediates products formed during the electrochemical oxidation of sulfamethazine [16]. Electrolysis performed at 1V/SCE, at a flow rate of 1 mL min-1, with an initial sulfamethazine concentration of 50 mg L-1, and 0.1M Na_2SO_4.

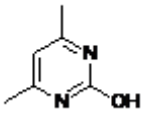
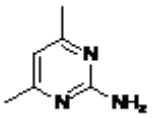
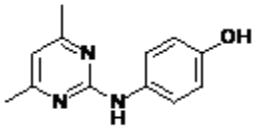
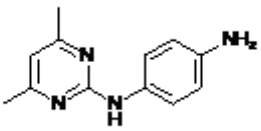
Name	Chemical structure
2-hydroxy-4,6-dimethylpyrimidine	
2-Amino-4,6-dimethylpyrimidine	
4-((4,6-dimethyl-2-pyrimidinyl)-amino)phenol	
N-(4-aminophenyl)-4,6 dimethyl-2-pyrimidinamine	

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Figure legends

Fig.1. Chemical structure of sulfamethazine.

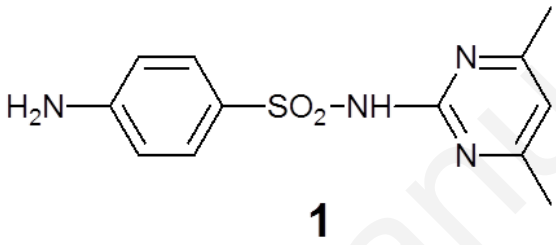

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Fig. 2. Time-courses of the residual SMT concentrations (⊠) and the TOC values of SMT (■), and SMT solutions oxidized at 1 V (○) and 1.6 V (▲) during biosorption on activated sludge (0.5 g L^{-1}) Error ± 2% is based on 3 measurements.

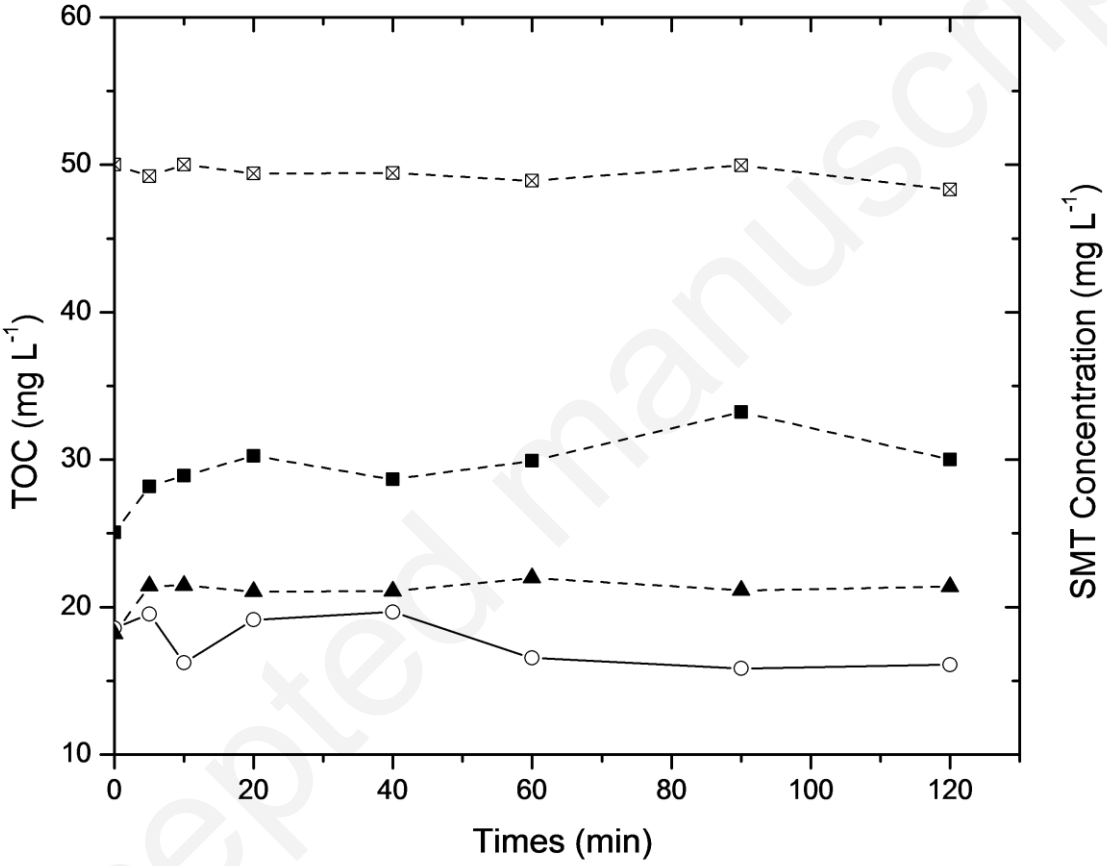

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Fig. 3. Time-course of non-pretreated SMT (50 mg L^{-1}) during activated sludge culture (0.5 g L^{-1}).

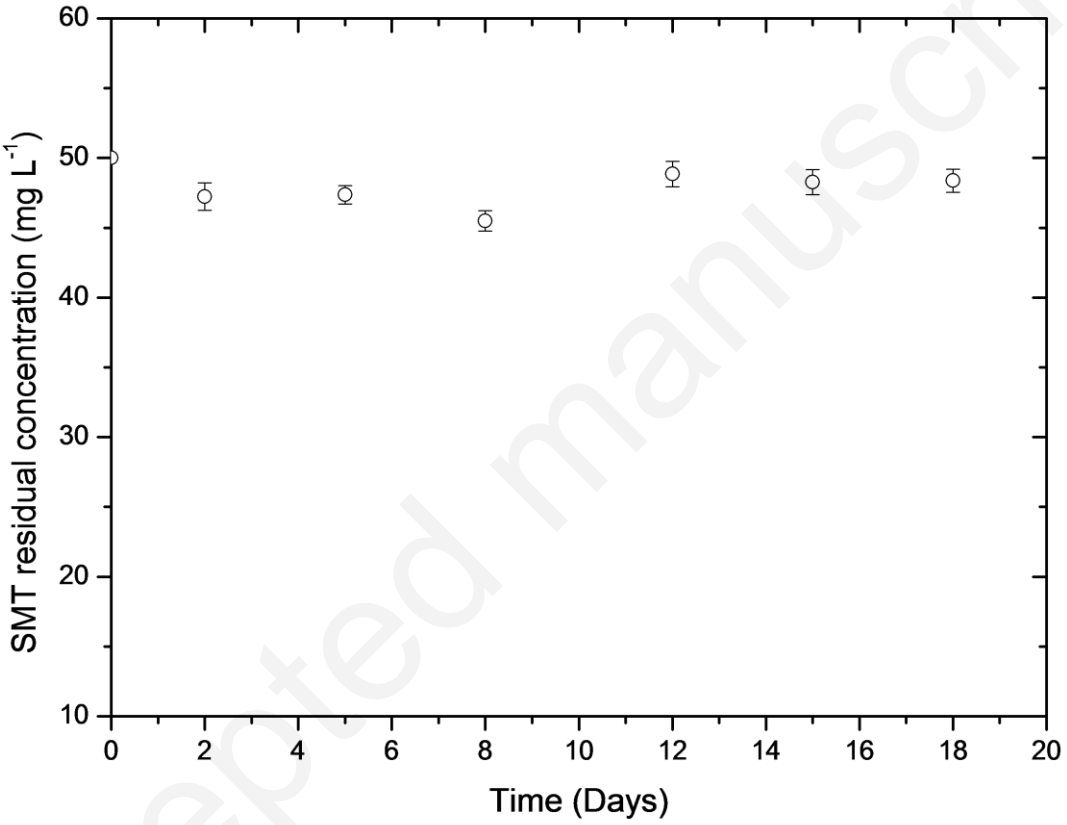

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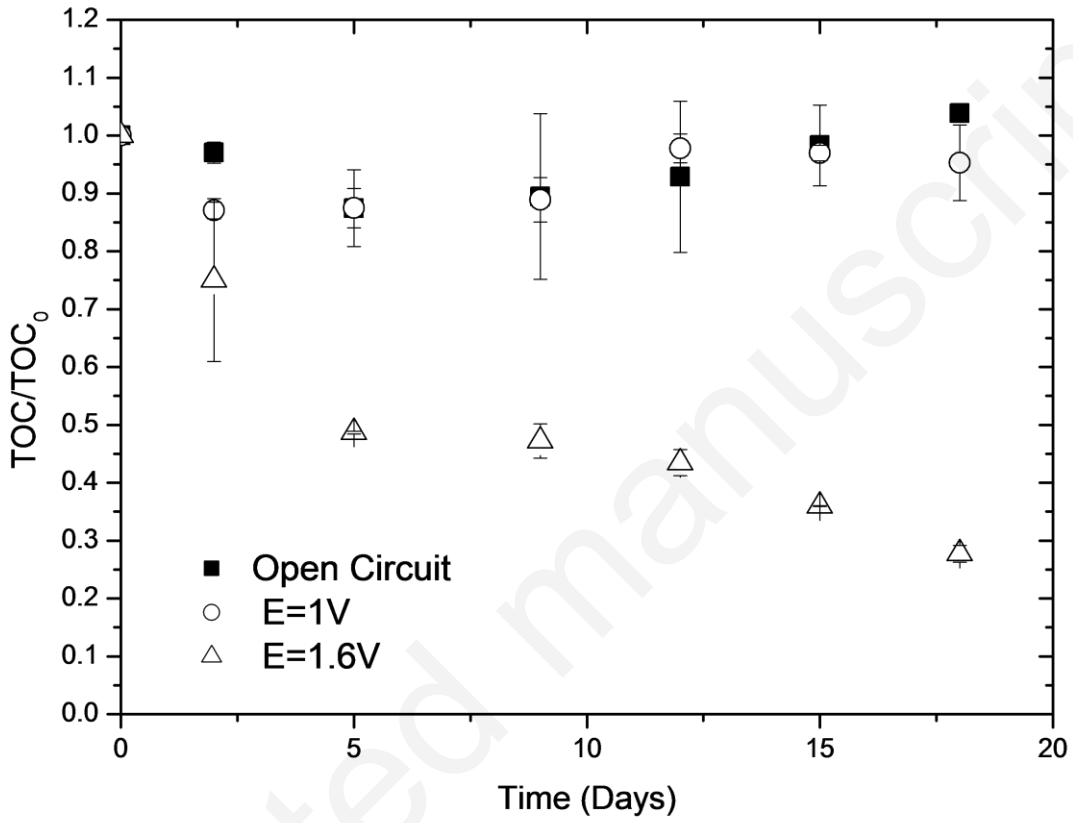
Fig. 4. TOC/TOC_0 time-courses during activated sludge culture (0.5 g L^{-1}) of SMT (50 mg L^{-1}) (■), and SMT solutions oxidized at 1 V (○) and 1.6 V (△).



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