

## Electrified biotrickling filters as tertiary urban wastewater treatment

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### 1. Introduction

Nitrification-denitrification is a well-established method in wastewater treatment plants (WWTPs). Ammonium ( $\text{NH}_4^+$ ) is oxidized to nitrate ( $\text{NO}_3^-$ ) using oxygen ( $\text{O}_2$ ) as electron acceptor (nitrification) and  $\text{NO}_3^-$  is further reduced to dinitrogen gas ( $\text{N}_2$ ) under anoxic conditions using organic matter as electron donor (denitrification) [1]. However, secondary effluents can occasionally contain excessive nitrogen content [2].

Biofilters can be a suitable technology to reach the nitrogen standards, but the lack of electron donors in urban wastewater might hinder the performance of denitrification [3,4]. Microbial electrochemical technologies (MET) have been postulated as a promising alternative for nitrogen removal [5]. Full ammonium removal was reported for the first time in 2008 in METs [6]. Thereafter, different configurations have been studied. For example, simultaneous nitrification-denitrification was promoted in an aerated biocathode [7] or the integration of bioelectrochemical nitrogen removal in a WWTP configuration [8], among others. Following the principle of integrating METs into existing wastewater treatment technologies, electrified biotrickling filters (e-biofilters) aims at upgrading the current biotrickling filters by incorporating a submerged, electrified zone to promote bioelectrochemical denitrification [9]. Consequently, e-biofilters maintains nitrification activity and promotes denitrification processes in

wastewaters with a low Carbon/Nitrogen ratio, such as secondary wastewaters. For this reason, this work assesses for the first time the application of an e-biofilter to treat the secondary effluent of an urban WWTP.

### 2. Materials and methods

#### 2.1. Reactor set-up

The e-biofilter, originally constructed, inoculated and described in Pous et al. [9] consisted of a 1.39 L polyvinyl chloride (PVC) tubular reactor (100 cm height x 4.2 cm of internal diameter). The lower half of the reactor was filled with granular graphite (model 00514, diameter 1.5–5 mm, Enviro-cell, Germany), while the upper half was filled with PVC granules (effective volume 0.77 L) (Fig. 1). Two titanium rods (Grade 1, 8 mm diameter, Polymet Reine Metalle, Germany) connected to a power source (IMHY3, Lendher, Spain) were inserted in the reactor at 45 and 12 cm height, serving as anode and cathode current collectors, respectively. A stainless-steel mesh (30 cm height, mesh path light  $5 \times 5$  mm) was placed around the reactor inner wall to improve the cathode electrical distribution. An Ag/AgCl reference electrode (+0.197 V vs. SHE, SE 11, Xylem Analytics Germany Sales GmbH & Co. KG Sensor-technik Meinsberg, Germany) was placed next to the cathode collector to set a cathode potential of  $-0.3$  V (vs. Ag/AgCl) by routinely adjusting

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the power supply. The objective was to promote bioelectrochemical denitrification [10]. Influent wastewater was continuously supplied from the top of the reactor and it flowed down to the effluent. The upper section of the reactor was fully exposed to air (aerobic zone) to promote aerobic nitrification while the lower section was submerged to promote anoxic conditions. The height of the water level (WL) was initially set at 50 cm (50% WL). In the second part of the study, the WL was raised to 75 cm (75% WL) (Fig. 1b and c, respectively).

## 2.2. Experimental conditions

Synthetic wastewater, described by Pous et al. [9] was used as the influent for the first 10 days. Thereafter, the e-biofilter was fed with real secondary effluent of an urban WWTP (Quart, Catalonia, Spain). Secondary wastewater was stored in a 240 L refrigerated tank at 4 °C. It contained  $44.9 \pm 7.2$  mg N-NH<sub>4</sub><sup>+</sup> L<sup>-1</sup>,  $0.9 \pm 1.7$  mg N-NO<sub>2</sub><sup>-</sup> L<sup>-1</sup>,  $0.7 \pm 1.0$  mg N-NO<sub>3</sub><sup>-</sup> L<sup>-1</sup>, chemical oxygen demand (COD) of  $101.7 \pm 42.9$  mg COD L<sup>-1</sup> and a total suspended solids (TSS) content of  $105.3 \pm 95.1$  mg TSS L<sup>-1</sup>. Table 1 presents the operational configurations evaluated for the treatment of wastewater.

## 2.3. Chemical analyses and calculations

NH<sub>4</sub><sup>+</sup>, nitrite (NO<sub>2</sub><sup>-</sup>), NO<sub>3</sub><sup>-</sup>, COD and TSS concentrations, pH and conductivity were routinely measured at the influent and the effluent of the reactor, following the American Public Health Association standards [11]. Nitrous oxide (N<sub>2</sub>O) was measured at the effluent using an N<sub>2</sub>O liquid-phase microsensor (Unisense, Denmark). The hydraulic retention time of the reactor (HRT) was determined by using the reactor net volume and the different influent flow rates applied. Ammonium and total nitrogen (NH<sub>4</sub><sup>+</sup> + NO<sub>2</sub><sup>-</sup> + NO<sub>3</sub><sup>-</sup>) removal rates were calculated as the difference between the influent and the effluent, divided by the HRT. The energy required to removed nitrogen content (kWh g N<sup>-1</sup>) was calculated from the voltage and the current applied together with the nitrogen removal observed.

**Table 1**

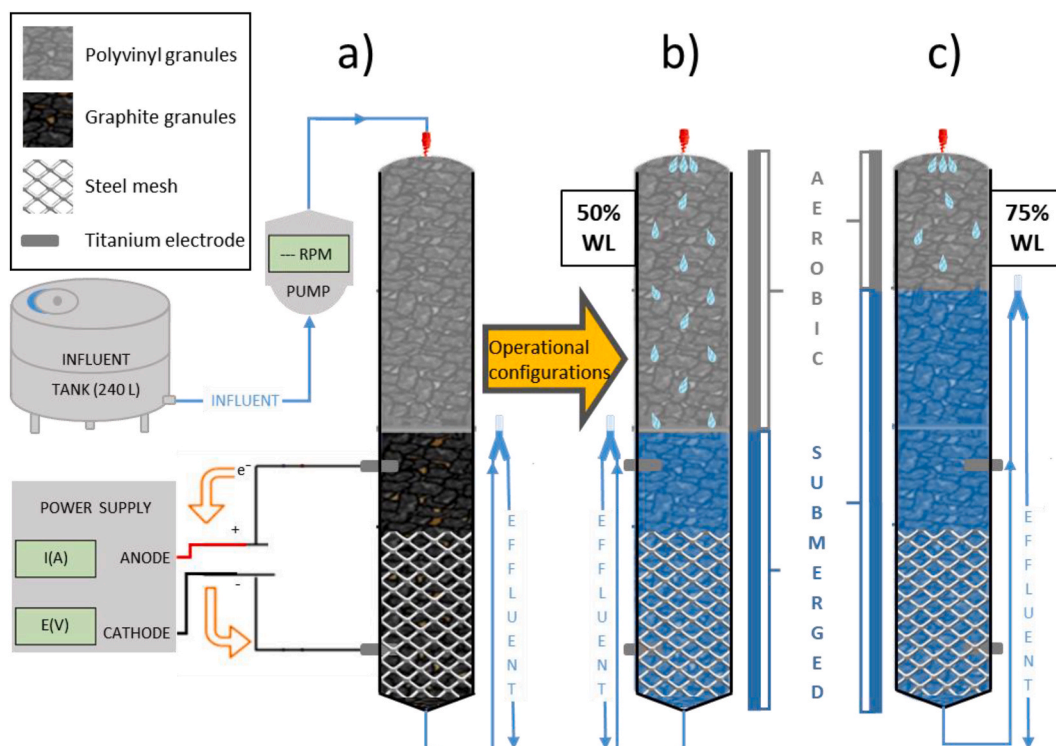
Set of operational conditions tested during the experimental study.

Operational condition	HRT 1.4 d (50% WL)	HRT 0.4 d (50% WL)	HRT 1.4 d (75% WL)	HRT 0.7 d (75% WL)	HRT 0.3 d (75% WL)
Water level height (cm)	50	50	75	75	75
Flow rate (L d <sup>-1</sup> )	0.6 ± 0.0	2.1 ± 0.3	6.0 ± 0.0	1.1 ± 0.0	2.3 ± 0.1
HRT (days)	1.4 ± 0.1	0.4 ± 0.0	1.4 ± 0.0	0.7 ± 0.0	0.3 ± 0.0
Experimental time duration (days)	40	10	7	7	7

## 3. Results and discussion

The performance of the e-biofilter was assessed at different operational conditions (WL 50% and 75%, HRT from 0.3 to 1.4 days). The system was initially operated at HRT  $1.4 \pm 0.1$  days and WL 50%. Almost all ammonium was oxidized ( $1.7 \pm 1.5$  mg N-NH<sub>4</sub><sup>+</sup> L<sup>-1</sup> in the effluent, Fig. 2a). However, most of the NO<sub>x</sub><sup>-</sup> (NO<sub>2</sub><sup>-</sup> + NO<sub>3</sub><sup>-</sup>) produced by nitrification was not removed, yielding a concentration of  $27.3 \pm 5.6$  mg N-NO<sub>x</sub><sup>-</sup> L<sup>-1</sup> in the effluent. No N<sub>2</sub>O was detected during the experiment. When the HRT was reduced to  $0.4 \pm 0.0$  days, both ammonium and nitrogen removal rates increased ( $43.4 \pm 13.1$  g N-NH<sub>4</sub><sup>+</sup> m<sup>-3</sup> d<sup>-1</sup> and  $35.7 \pm 14.6$  g N m<sup>-3</sup> d<sup>-1</sup>, Fig. 2b), but also the ammonium content at the effluent ( $40.8 \pm 7.1$  mg N-NH<sub>4</sub><sup>+</sup> L<sup>-1</sup>, Fig. 2a).

In the second round of tests, the water level was lifted to 75 cm (WL 75%) aiming to boost bioelectrochemical denitrification by reducing the potential presence of oxygen in the submerged zone. As a trade-off, halving the volume of the aerobic zone could hinder nitrification. At an HRT of  $1.4 \pm 0.0$  days, the nitrogen content at the effluent decreased to  $5.8 \pm 6.2$  mg N-NH<sub>4</sub><sup>+</sup> L<sup>-1</sup> and  $10.6 \pm 3.0$  mg N-NO<sub>x</sub><sup>-</sup> L<sup>-1</sup> (Fig. 2a). Subsequently, the decrease of the HRT to  $0.7 \pm 0.0$  and  $0.3 \pm 0.0$  days increased the NH<sub>4</sub><sup>+</sup> effluent concentration to  $11.8 \pm 4.0$  mg N-NH<sub>4</sub><sup>+</sup> L<sup>-1</sup> and  $18.8 \pm 3.0$  mg N-NH<sub>4</sub><sup>+</sup> L<sup>-1</sup>, respectively (Fig. 2a). Nevertheless, the NO<sub>x</sub><sup>-</sup> content slightly moved from the values observed at an HRT of 1.4



**Fig. 1.** Schematic representation of the e-biofilter design (a) and the WL configurations (WL 50% (b) and WL 75% (c)).

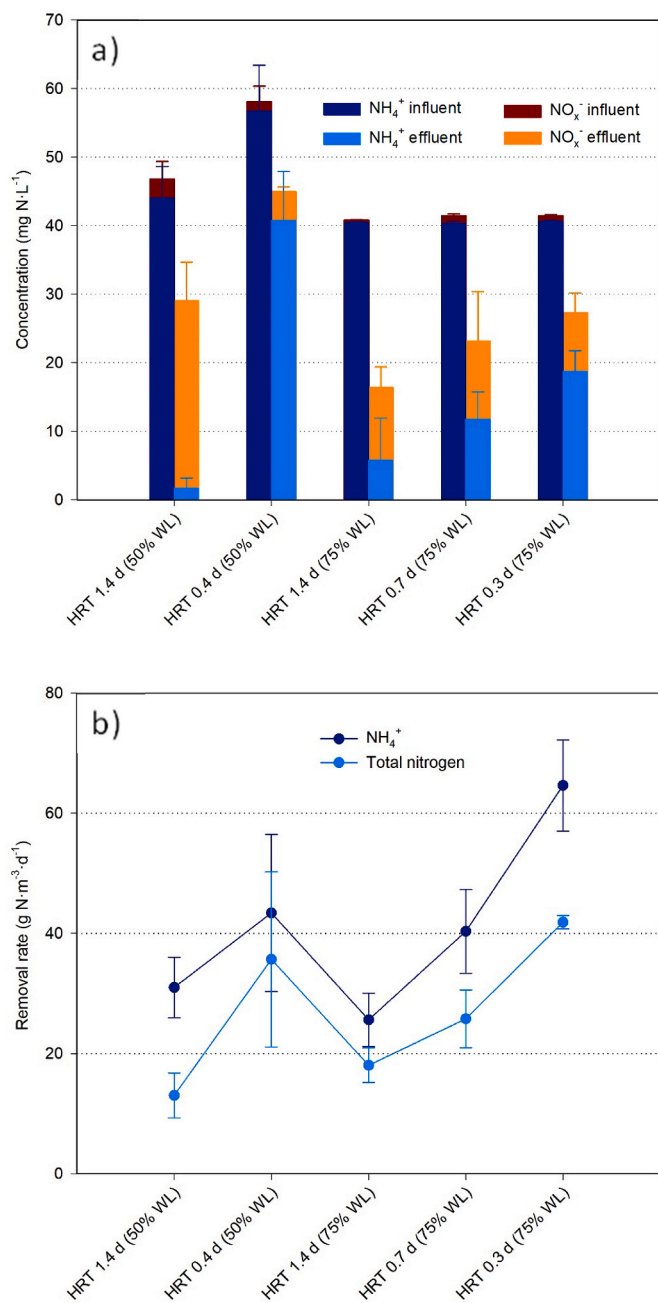


Fig. 2. Influent and effluent  $\text{NH}_4^+$  and  $\text{NO}_x^-$  ( $\text{NO}_2^- + \text{NO}_3^-$ ) average concentrations (a) and ammonium and total nitrogen average removal rates (b) for each experimental condition. Error bars represent standard deviation ( $n > 3$ ).

days. A further decrease of the HRT to 0.3 days improved the ammonium and total nitrogen removal rates to  $64.6 \pm 7.6 \text{ g N-NH}_4^+ \text{ m}^{-3} \text{ d}^{-1}$  and  $41.9 \pm 1.1 \text{ g N m}^{-3} \text{ d}^{-1}$ , respectively (Fig. 2b). These results implied a slight improvement of the performance compared to HRT 0.4 days WL 50% ( $43.4 \pm 13.1 \text{ g N-NH}_4^+ \text{ m}^{-3} \text{ d}^{-1}$  and  $35.7 \pm 14.6 \text{ g N m}^{-3} \text{ d}^{-1}$ ). This unexpected enhancement on the nitrification observed at WL 75% could be linked to a difference in the influent COD ( $36.7 \pm 8.2 \text{ mg COD L}^{-1}$  at HRT 0.3 WL 75% vs.  $102.5 \pm 6.4 \text{ mg COD L}^{-1}$  at HRT 0.4 WL 50%, Fig. 3). Organic matter competed with  $\text{NH}_4^+$  for  $\text{O}_2$ , hampering nitrification. However, COD could also serve as the electron donor for heterotrophic denitrification, contributing alongside bioelectrochemical denitrification to overall nitrogen removal. On average, the e-biofilter removed  $63.1 \pm 19.3\%$  of the influent COD, yielding similar COD concentrations at the effluent for the different experimental conditions

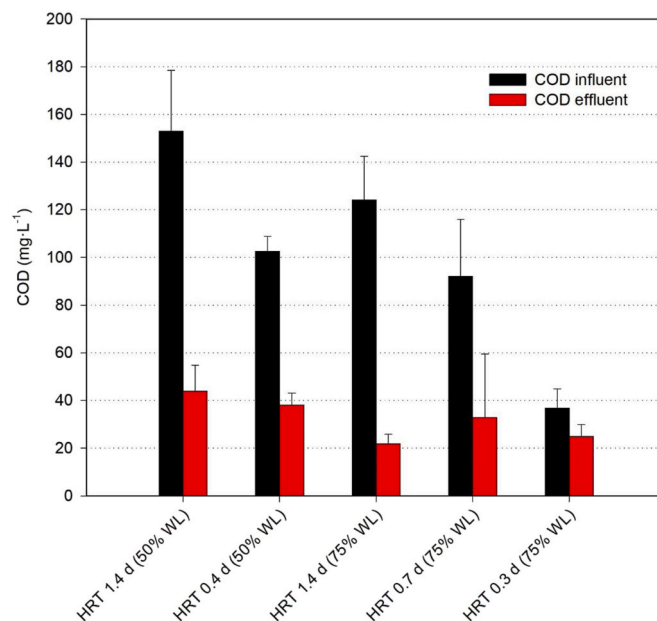


Fig. 3. Influent and effluent average COD at each experimental condition. Error bars represent standard deviation ( $n > 3$ ).

evaluated (between  $43.9 \pm 11.0$  and  $21.8 \pm 4.0 \text{ mg COD L}^{-1}$ , Fig. 3). Solids removal was also higher ( $82.4 \pm 18.7\%$  mean TSS removal), with effluent concentrations ranging from  $57.5 \pm 24.7$  to  $1.1 \pm 1.6 \text{ mg TSS L}^{-1}$  (Table 2). These values upgrade e-biofilters to a holistic treatment with a high potential to produce an effluent water valuable for reuse [13].

The  $\text{NH}_4^+$  and nitrogen removal rates registered at an HRT of 0.3 days with a WL of 75% ( $64.6 \text{ g N-NH}_4^+ \text{ m}^{-3} \text{ d}^{-1}$  and  $41.9 \text{ g N m}^{-3} \text{ d}^{-1}$ , Fig. 2b) were higher than the ones observed in electroconductive biofilters treating urban wastewater ( $15.0 \text{ g N-NH}_4^+ \text{ m}^{-3} \text{ d}^{-1}$  and  $6.7 \text{ g N m}^{-3} \text{ d}^{-1}$  [12]) and close to those achieved by soil trickling biofilters treating swine wastewater digested liquid ( $78.2 \text{ g N-NH}_4^+ \text{ m}^{-3} \text{ d}^{-1}$  and  $49.2 \text{ g N m}^{-3} \text{ d}^{-1}$  [4]) or e-biofilters treating synthetic aquaponics wastewater ( $94 \text{ g N-NH}_4^+ \text{ m}^{-3} \text{ d}^{-1}$  and  $43 \text{ g N m}^{-3} \text{ d}^{-1}$  [9]). Nevertheless, the e-biofilter presented a nitrogen removal energetic efficiency higher in real wastewater (consuming between  $1.0 \times 10^{-2}$  and  $3.9 \times 10^{-2} \text{ kWh g N}^{-1}$ , Table 2) than in synthetic aquaponics wastewater (2.7

Table 2

Dynamics of different parameters depending on the experimental condition applied.

Experimental condition	HRT 1.4 d (50% WL)	HRT 0.4 d (50% WL)	HRT 1.4 d (75% WL)	HRT 0.7 d (75% WL)	HRT 0.3 d (75% WL)
<b>Influent TSS</b> ( $\text{mg L}^{-1}$ )	$230.0 \pm 141.4$	$97.5 \pm 46.0$	$87.8 \pm 5.4$	$93.0 \pm 108.9$	$18.0 \pm 2.8$
<b>Effluent TSS</b> ( $\text{mg L}^{-1}$ )	$57.5 \pm 24.7$	$25.0 \pm 21.2$	$2.1 \pm 3.0$	$10.0 \pm 8.5$	$1.1 \pm 1.6$
<b>Cathode potential</b> (V vs. Ag/AgCl)	$-0.3 \pm 0.1$	$-0.3 \pm 0.3$	$-0.4 \pm 0.2$	$-0.1 \pm 0.1$	$-0.3 \pm 0.3$
<b>Energy efficiency</b> ( $\text{kWh g N}^{-1}$ )	$3.9 \times 10^{-2}$	$1.0 \times 10^{-2}$	$3.4 \times 10^{-2}$	$3.9 \times 10^{-2}$	$2.6 \times 10^{-2}$
<b>Influent pH</b>	$8.2 \pm 0.3$	$8.1 \pm 0.1$	$7.9 \pm 0.1$	$7.8 \pm 0.2$	$7.9 \pm 0.1$
<b>Effluent pH</b>	$7.9 \pm 0.3$	$8.0 \pm 0.1$	$7.4 \pm 0.2$	$7.2 \pm 0.3$	$7.4 \pm 0.1$
<b>Influent conductivity</b> ( $\text{mS cm}^{-1}$ )	$1.3 \pm 0.1$	$1.5 \pm 0.0$	$1.5 \pm 0.2$	$1.3 \pm 0.0$	$1.3 \pm 0.0$
<b>Effluent conductivity</b> ( $\text{mS cm}^{-1}$ )	$1.1 \pm 0.1$	$1.4 \pm 0.0$	$1.2 \pm 0.1$	$1.1 \pm 0.0$	$1.2 \pm 0.0$

$\times 10^{-1}$  to  $8.3 \times 10^{-2}$  kWh g N<sup>-1</sup> [9]).

#### 4. Conclusions

E-biofilters were applied, for the first time, for the treatment of real secondary wastewater. The e-biofilter was shown as a promising technology for nitrogen polishing in secondary effluents. The operation at WL 50% enhanced aerobic nitrification, which decreased the effluent ammonium concentration to 1.7 mg N-NH<sub>4</sub><sup>+</sup> L<sup>-1</sup>. The operation at WL 75% favoured bioelectrochemical denitrification, which reduced the effluent total nitrogen concentration to 16.4 mg N L<sup>-1</sup>. The highest NH<sub>4</sub><sup>+</sup> and total nitrogen removal rates were achieved when applying low HRTs (0.3 days), yielding 64.6 g N-NH<sub>4</sub><sup>+</sup> m<sup>-3</sup> d<sup>-1</sup> and 41.9 g N m<sup>-3</sup> d<sup>-1</sup>, respectively. Better effluent qualities were obtained when working at higher HRTs (e.g. 1.4 days). In addition, high removal efficiencies in terms of organic matter (63.1% COD) and solids (82.4% TSS) were achieved, showcasing the ability of e-biofilters to polish a set of pollutants that are the key for generating an effluent suitable for water reuse.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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