

EVALUATING BIOFILTERS PERFORMANCE AFTER SHUTDOWN EPISODES AND STORED BIOMASS RECOVERY

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In order to prevent and reduce anthropogenic air pollution, gas emissions from a wide range of industrial activities are being limited by progressively more restrictive regulations. Therefore, the end-of-pipe treatment of gaseous emissions is often compulsory. One of the disadvantages of the traditional physical-chemical approaches to controlling air emissions is the shifting of pollution from one environment to another rather than completely removing the pollutant. On the contrary, biological techniques rely on microorganisms' activity to biodegrade the contaminants, rendering harmless by-products. Industrial-scale bioreactors are exposed to sudden concentration fluctuations or abrupt shutdowns that can negatively affect their performance. Depending on the impact of these incidences, inoculation of previously acclimated or stored biomass may be compulsory. The objective of this study was to evaluate biofilters performance after the sudden shutdown of the feeding gas flow under short-term (1 week) and long-term (3 months) incidences. Additionally, previously acclimated biomass was stored at 4 °C for 3 months, and subsequently, this biomass was used for re-inoculating the biofilter. It was concluded that shutdown periods shorter than one week did not negatively affect bioreactor's performance. On the contrary, biomass refrigerated longer than 3 months required a re-acclimation period to recover its original degradation activity.

Keywords: *Biofilter; Shutdown; Biomass re-acclimation*

EVALUACIÓN DE LA RESPUESTA DE BIOFILTROS TRAS EPISODIOS DE PARADA Y RE-ACTIVACIÓN DE BIOMASA ALMACENADA

Las emisiones gaseosas provenientes de diferentes sectores industriales están siendo reguladas de manera cada vez más restrictiva, con el fin de prevenir y reducir la contaminación atmosférica. Es por ello que, en muchas ocasiones, es necesario tratar dichas emisiones antes de su vertido. Una de las desventajas asociadas a las tecnologías de tratamiento físico-químicas es la transferencia de medio del contaminante. Por el contrario, las técnicas biológicas permiten la transformación de los compuestos a sub-productos no nocivos. Los bioreactores que tratan corrientes gaseosas industriales están expuestos tanto a variaciones en la concentración de entrada como a paradas repentinas. Estas incidencias pueden afectar de manera negativa a la efectividad de los reactores, y hacer necesaria la re-inoculación con biomasa activa. El objetivo de este trabajo fue la evaluación de la operación de biofiltros tras la parada de la corriente de alimentación durante periodos de duración corta (1 semana) y larga (3 meses). Además, se empleó biomasa previamente aclimatada y almacenada a 4 °C durante tres meses para re-inocular el biofiltro. Paradas de duración inferior a una semana no influyeron en la eficacia de los bioreactores. Por el contrario, la biomasa almacenada refrigerada requirió un periodo de re-aclimatación hasta alcanzar su actividad original.

Palabras clave: *Biofiltro; Parada; Re-activación biomasa*

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1. Introduction

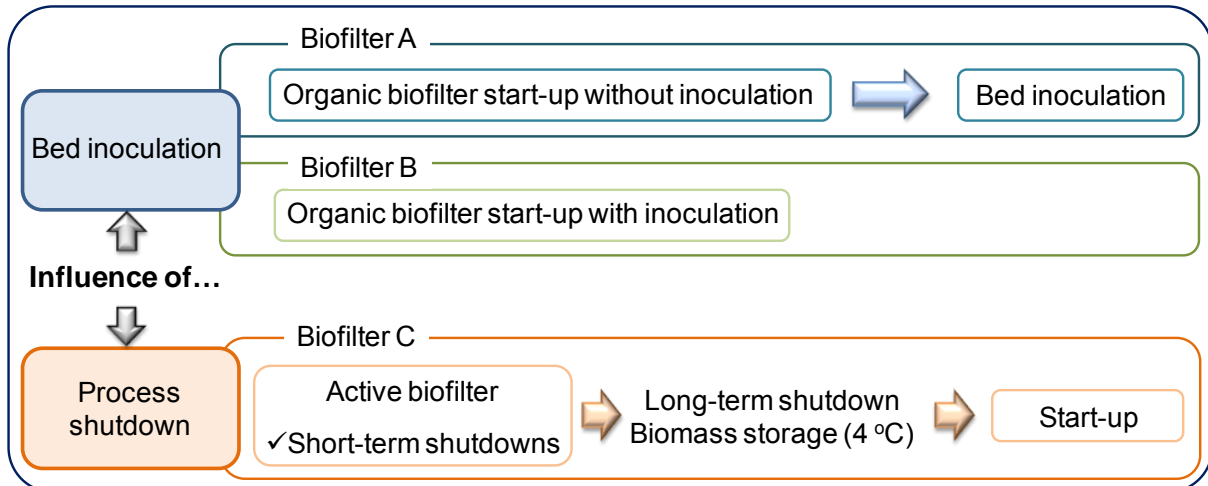
Biological technologies are among the best available techniques (BATs) in several industrial sectors for treating waste gas streams (European Commission [EC], 2003; EC, 2005; EC, 2006a; EC, 2006b). The viability of bioreactors treating emissions containing CS₂ at industrial scale has already been assessed in the literature (Kraakman, 2005, Kraakman & de Waal, 2006, Kraakman et al., 2012). Nevertheless, conventional biofilters for the treatment of these emissions are not very frequent at full-scale, as quick start-up and performance recovery after a shutdown period are still key issues that remain unresolved for the successful implementation of this technology.

Lengthy start-up is one of the operating problems in conventional biofilters treating CS₂ polluted gases. This is caused by both the microbial toxicity of the CS₂ itself (Hartel & Haines, 1992) and the scarce biodiversity of microbes capable of metabolizing this compound (Smet & Van Langenhove, 1998; Rojo et al. 2010). Therefore, the selection of a suitable inoculum is crucial for accelerating the start-up period and implementing this technique at industrial scale.

In addition, biofilters treating waste gas streams at industrial scale are exposed to abrupt shutdowns in the feed flow. These unexpected periods in which polluted gas is not generated are due to changes in the manufacturing process, interruptions in production, and technical failures. Depending on the nature of the feed interruption, a biofilter can be exposed to a long-term shutdown, negatively affecting biomass activity. Thus, the assessment of the biosystem's ability to recover its activity after a long-term shutdown is highly relevant for successful full-scale operation.

In this study, packing material inoculation was tested as an alternative for shortening the start-up period of biofilters treating CS₂ polluted streams. In addition, the influence of short-term and long-term process shutdown on biofilter performance recovery was studied. The main objectives are schematically summarized in figure 1.

Figure 1. Outline of the study's main objectives



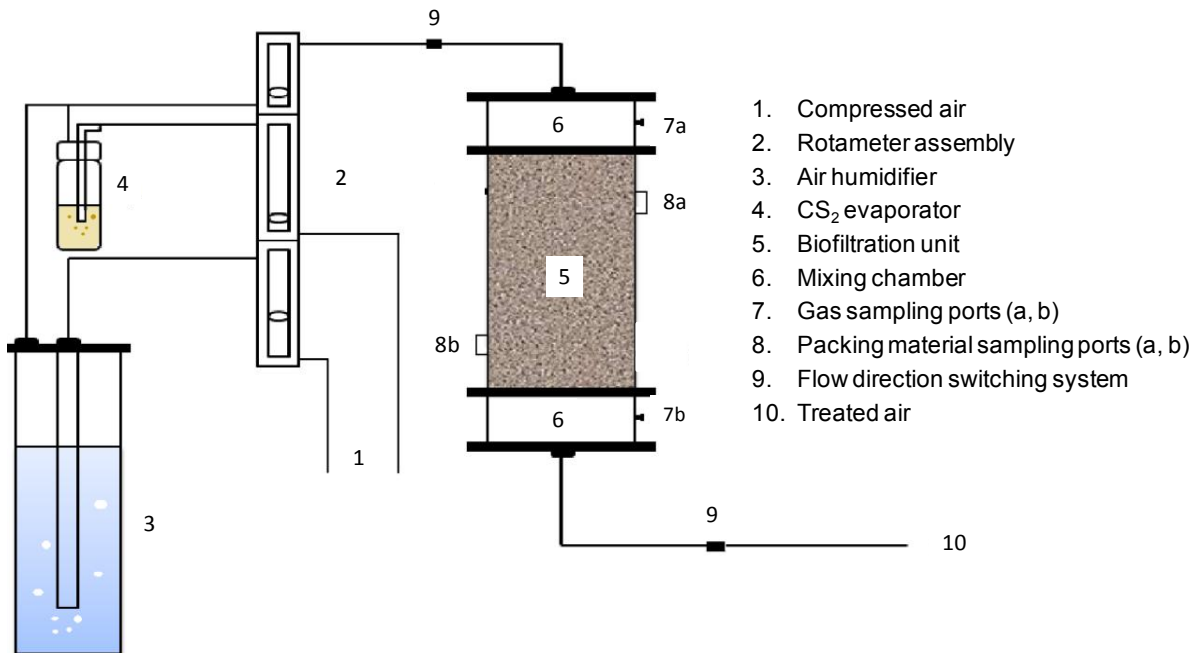
2. Materials and methods

2.1. Experimental setup

Three biofilters were operated at laboratory scale. Each biofilter consisted of a PVC module with a total volume of 1.2 L and two gas mixing chambers ($V = 0.5$ L each) located in the

upper and lower part of the module, respectively. Inlet CS_2 concentration was regulated by mixing a CS_2 -saturated stream with a CS_2 -free humidified air stream in different proportions. Pollutant concentration was periodically measured in both mixing chambers (inlet and outlet concentration, IC and OC, respectively). Two sampling ports were located at 3 and 11 cm from the biofilter inlet for the regular measurement of moisture and sulfate content in the packing material. The outline of the laboratory scale plant is shown in figure 2.

Figure 2. Outline of the laboratory-scale biofiltration system



2.2. Start-up without packing material inoculation

The removal of CS_2 was initially studied in a biofilter packed with an organic support material that had not been previously exposed to the target pollutant (biofilter A). This packing material was a pelletized mixture of composted pig manure and sawdust (Abonlir, SLIR), and it has been reported to contain a diverse microbial community (Prenafeta-Boldú et al., 2014). The bed was not therefore inoculated with specific biomass.

Biofilter A was operated at room temperature (21 ± 2 °C), and at a 240 s Empty Bed Residence Time (EBRT). A continuous gaseous stream containing 0.24 ± 0.08 g $\text{CS}_2 \cdot \text{m}^{-3}$ was fed into the reactor at switch flow mode (weekly upflow/downflow switching frequency).

The biofilter was operated under optimum bed moisture conditions (35-40%) (Rojo et al., 2012). The packing material was unpacked, manually mixed and irrigated using 300 mL of deionized water per kilo of packing material at the beginning of the experiment and on day 53.

2.3. Packing material inoculation

After day 105 of operation without inoculation, biofilter A's support material was mixed with the support material collected from an active CS_2 biofilter available in the laboratory. The active:non-active packing material weight ratio was 1:4 (dry basis).

A second biofilter (biofilter B) was initially packed with a mixture of the aforementioned active support and new packing material that had not previously been exposed to the contaminant.

The 1:1 weight ratio (dry basis) was selected in order to evaluate the influence of the active:non-active packing material mixture on the removal efficiency from the very first moment of operation.

The active packing material used in both biofilters A and B (and collected from the biofilter available in the laboratory) degraded up to $25 \text{ g CS}_2 \text{ g m}^{-3} \text{ h}^{-1}$ before being mixed with the corresponding non-active packing material.

Inoculated biofilters A and B were operated for 145 and 75 days, respectively. The operating conditions of both biofilters are summarized in table 1.

Table 1. Operating conditions in inoculated biofilters A and B

Parameter	Biofilter A	Biofilter B
Flow mode	Switch flow	Switch flow
Temperature	Room temperature	Room temperature
EBRT (s)	240	240
IC ($\text{g}\cdot\text{m}^{-3}$)	0.36 ± 0.15	0.32 ± 0.08

The moisture content in both mixed beds was initially adjusted to optimum values (35-40%) using 300 mL of deionized water per kg of packing material. On days 42 and 85, the beds were unpacked, manually mixed (separately) and irrigated using the same water volume (300 mL) in order to recover bed moisture content and partially wash out the sulfates accumulated on the packing material during the experimental period.

2.4. Shutdown

A third biofilter (biofilter C) was packed with the previously described active organic packing material. The biofilter was operated in switch flow mode at a 240 s EBRT, and it was exposed to inlet concentrations (IC) up to $0.8 \text{ g CS}_2\cdot\text{m}^{-3}$. Biofilter C was operated for 100 days under these operating conditions.

Two short-term shutdown episodes were simulated over the 100-day operating period. Thus, the CS_2 evaporating system was closed and, consequently, the contaminant was stopped from entering the biofilter for 24 hours and for four consecutive days (two short-term shutdown episodes). Only water-saturated air was fed into the system.

The influence of a long-term process shutdown on biofilter C's performance was studied after 150 operating days by completely shutting down the system (not even air was fed). The active packing material containing the degrading biomass was stored for seven months at 4°C . After this period, biofilter C was filled with that refrigerated packing material and operated for a further 80 days. The biofilter was operated in switch flow mode, at a 240 s EBRT. The concentration in the inlet stream for the last 80 days was $0.21\pm 0.06 \text{ g CS}_2\cdot\text{m}^{-3}$.

On day 53, the packing material in biofilter C was unpacked, manually mixed and irrigated using 300 mL of deionized water per kg of packing material.

2.5. Analytical methods

CS_2 concentration was measured using a micro-gas chromatograph (Varian, the Netherlands) equipped with auto-sampling injection, a TCD detector and using He as carrier gas. Sulfate concentration in the bed was determined by ion chromatography using a Dionex ICS-3000 system (DIONEX, Sunnyvale, USA). Bed pH was measured with a CRISON pH-Meter GLP 21+ (Barcelona, Spain). The moisture content within the packing material at different bed heights was determined by a Moisture Analyzer HB43-S (Mettler Toledo) by

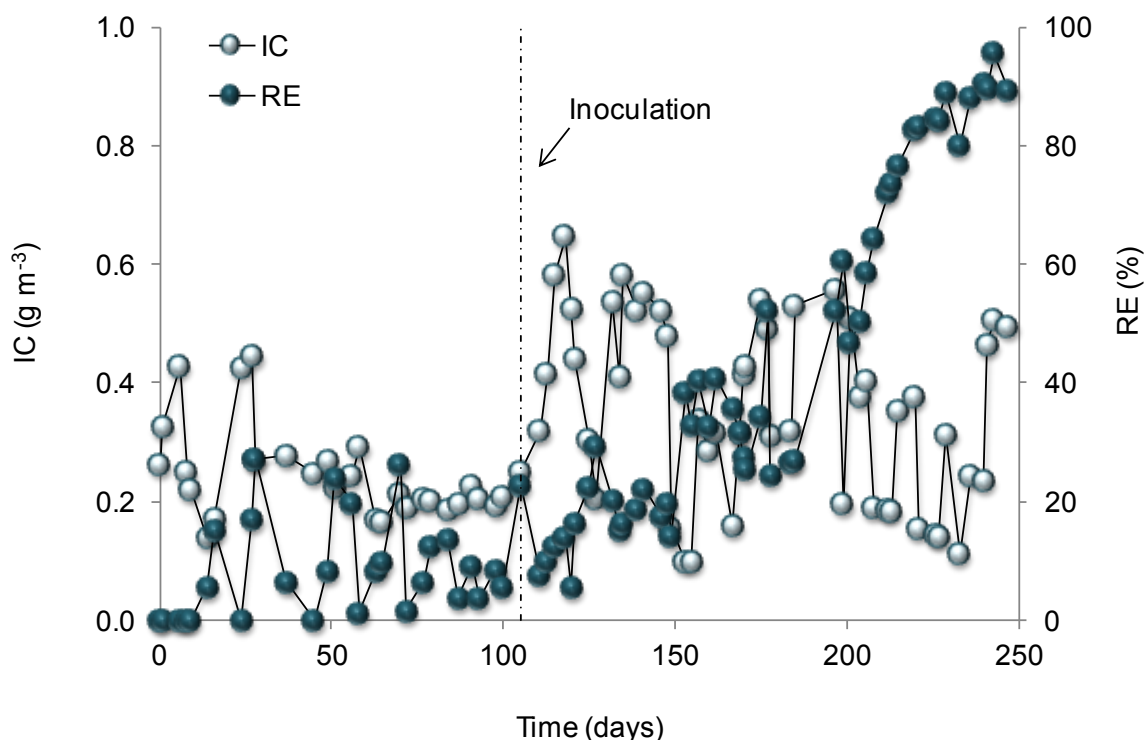
periodically collecting 2 – 3 g of support material from each sampling port. All the analytical methods are further described in Prenafeta-Boldú et al. 2014.

3. Results and discussion

3.1. Influence of packing material inoculation on biofilter start-up

An uninoculated biofilter (biofilter A) was initially operated for 105 days. This period was characterized by a poor CS₂ removal efficiency (RE), lower than 20% (Figure 3). Biofilter inoculation on day 105 led to a gradual increase in RE, and values higher than 75% were recorded 110 days after inoculation. RE remained quite constant beyond day 220 (average RE 87±4%) despite IC fluctuations. The maximum elimination capacity reported in this biofilter over the entire experimental period was 6.6 g CS₂ m⁻³ h⁻¹.

Figure 3. IC and RE of CS₂ in biofilter A throughout time before and after inoculation



It has been reported that the start-up of biofilters packed with the support material studied here and operated under xerophilic conditions can be as long as 400 days (at similar EBRT and ICs) (Prenafeta-Boldú et al., 2014). Therefore, the combined effect of optimum moisture content (30-35%) and bed inoculation in a 1:4 active:non-active packing material weight ratio significantly improved biofilter performance. Nevertheless, a shorter start-up period is required if biofilters are to be a competitive gas treatment option at industrial scale.

As expected, the higher active:non-active packing material ratio studied in biofilter B (1:1 w:w dry basis) led to a significant reduction in the start-up period (Figure 4). Thus, biofilter B achieved an RE higher than 75% only 19 days after start-up, in comparison to the 110 days biofilter A required to achieve similar RE values. Nevertheless, despite the fast start-up, biofilter performance remained quite constant at 70±4% until the end of the experiment (Figure 4). This average RE is lower than the results obtained in previous experiments carried out using only active packing material, and under similar operating conditions (Rojo et

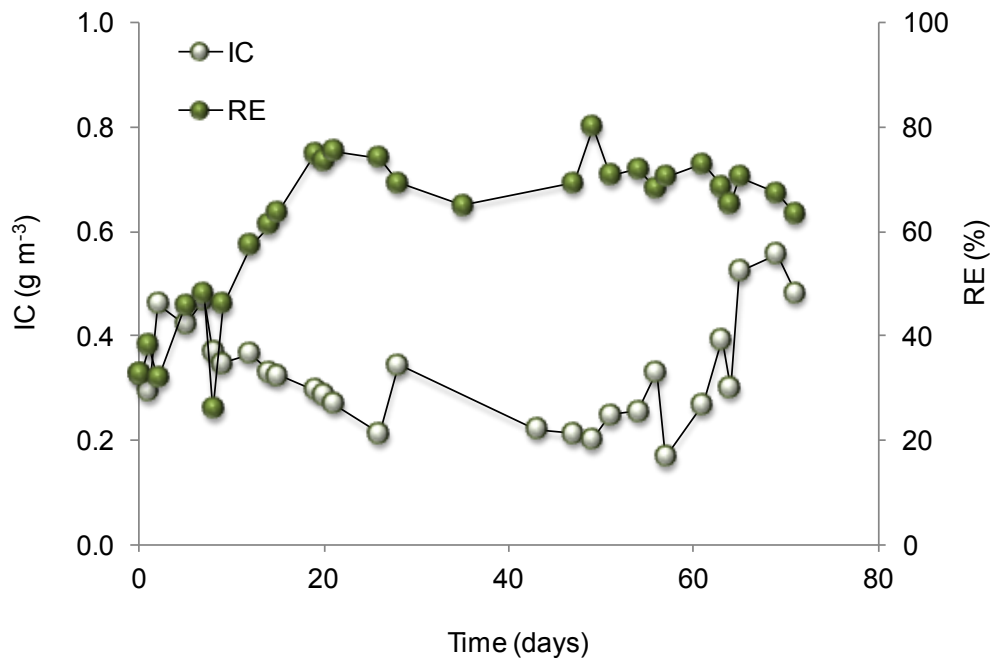
al., 2012, Rojo et al. 2013). This behavior could be attributed to the lower amount of microorganisms capable of biodegrading CS₂ in the active:non-active mixed bed.

It is worth noting that an almost twofold increase in the IC during the last six days did not significantly impact biofilter RE. By contrast, and due to the higher inlet load (IL), the EC_{max} in biofilter B (5.6 g·m⁻³·h⁻¹) was recorded during this final period.

Bed moisture content remained in the optimum range (35-40%) during the 75-day experiment. Maximum recorded sulfate concentration over the packing material was 35.5 mg S per gram of dry pellet. This value was lower than the maximum concentration reported in similar biofilters (data not shown). Therefore, sulfate accumulation and water content were not considered limiting factors in biofilter B's performance.

In short, although the strategy of using a 1:1 w:w packing material ratio dramatically reduced the start-up period, a 100% RE was not achieved.

Figure 4. IC and RE of CS₂ in biofilter B throughout time



3.2. Shutdown influence on biofilter performance

Biofilter C, filled solely with packing material containing active biomass, was successfully operated for 100 days (RE 100%), achieving an EC_{max} of 11.5 g CS₂·m⁻³·h⁻¹ (data not shown).

Two short-term shutdowns of the CS₂ feed into the system for 24 hours and four days, respectively, did not affect biofilter performance (data not shown).

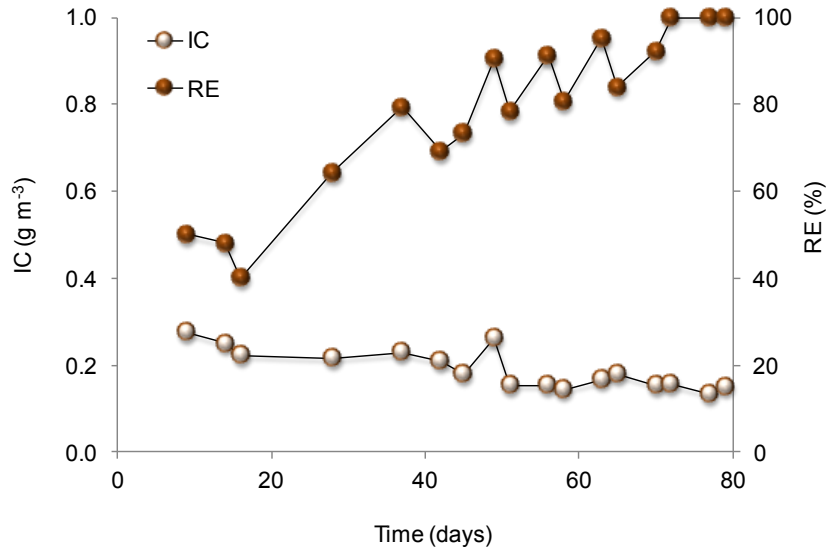
Nevertheless, long-term biofilter shutdown for seven months and biomass storage at 4 °C for the same period had a negative impact on biomass activity when biofilter operation was restored for 80 days (Figure 5).

As shown in figure 5, biofilter performance after restoring the feed was clearly affected by the long-term shutdown, as RE was lower than 50% until day 20, in comparison to the 100% recovery recorded before the shutdown. A gradual increase in RE was observed in this biofilter beyond day 20, and a 70% RE was recorded after a 40-day period. Finally, the biofilter completely recovered its initial activity, and 100% RE was recorded from day 70 until

the end of the assay. The maximum elimination capacity of biofilter C after the long-term shutdown episode was $3.5 \text{ g CS}_2 \cdot \text{m}^{-3} \cdot \text{h}^{-1}$ (day 49).

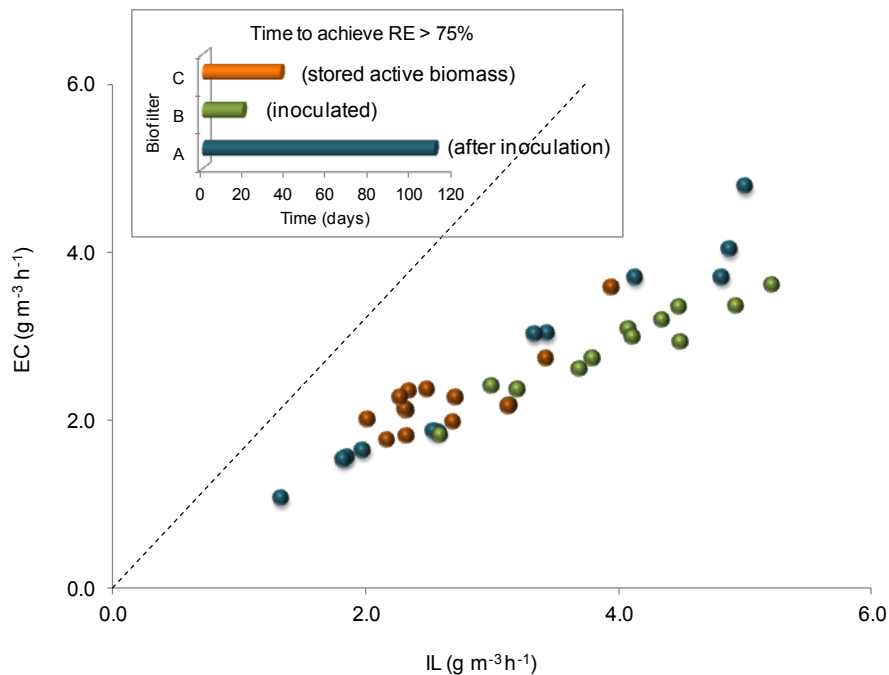
Bed water content remained in the optimum range during the 80-day experiment, and sulfate concentration in the packing material fell within the range of values reported in similar prior experiments.

Figure 5. IC and RE of CS_2 in biofilter C after a long-term shutdown (seven months)



The relationship between inlet load and elimination capacity in the three biofilters (in the two inoculated biofilters A and B, and in biofilter C during the additional 80 operating days) is shown in figure 6. Only the IL and EC values corresponding to RE higher than 75% have been plotted in figure 6.

Figure 6. IL versus EC of CS_2 in the three biofilters (the two inoculated biofilters A and B, and biofilter C during the additional 80 operating days)



It is worth pointing out that once RE exceeded 75%, the IL-EC relationship was similar in all the biofilters, regardless of the initial nature of the packing material, i.e., active:non-active support mixture or refrigerated packing material containing active biomass (Figure 6). Thus, a 1:1 active:non-active (w:w, dry basis) packing material mixture seems to be a promising option for shortening the start-up period for biofilters treating CS₂.

4. Conclusions

The mixture of active packing material (previously used in another biofilter, and thus containing biomass) and non-active (fresh) packing material in a 1:4 active:non-active weight ratio (dry basis) did not significantly accelerate biofilter start-up. By contrast, a 1:1 active:non-active packing material ratio (w:w, dry basis) dramatically reduced this period, and RE higher than 75% was recorded in 19 days. Nevertheless, beyond day 20, the average RE in this biofilter remained quite constant at a moderate value (70±4%) until the end of the experiment.

Short-term shutdown periods did not influence the performance of a biofilter packed with active support material (RE = 100%). By contrast, a long-term shutdown for seven months and the corresponding biomass storage at 4°C negatively affected biomass activity, as a period of 40 days was required for the biofilter to once again record an RE higher than 75%. After 70 days, the biofilter recovered its original activity, recording a 100% RE.

Acknowledgments

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