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Capillary membrane bioreactor for abatement of low soluble compounds in waste gas

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3   1   # Capillary membrane bioreactor for abatement of low soluble
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5   2   # compounds in waste gas
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24   17   **ABSTRACT**
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27   18   BACKGROUND: The removal of problematic volatile organic compounds (VOCs)
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29   19   from polluted gas (toluene, iso-octane and hexane) has been investigated in a membrane
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31   20   bioreactor (MBR) by adapting a commercial capillary microporous polypropylene
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33   21   membrane. The MBR performance was carried out under several operational conditions.
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35   22   The influence of the empty bed residence times (EBRT), the liquid velocity and the inlet
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37   23   concentration was evaluated.
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40   24   RESULTS: For toluene, it was possible to treat higher loading rates than 1600 $g \cdot m^{-3} \cdot h^{-1}$
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42   25   with a maximum elimination capacity (EC) of 1309 $g \cdot m^{-3} \cdot h^{-1}$, removal efficiencies (RE)
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44   26   of ~80%. However, iso-octane was poorly degraded as a single pollutant. Hexane
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46   27   presented lower EC values (400 $g \cdot m^{-3} \cdot h^{-1}$) than toluene. The synergistic effect of hexane
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48   28   degradation in two different mixtures was also considered.
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51   29   CONCLUSION: Our results demonstrate that a commercial membrane for wastewater
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53   30   treatment can be adapted for biological gas treatment, becoming a potential alternative

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1   to conventional biological treatment technologies, especially for pollutants with low

2   solubility.

3   **Key Words:** membrane bioreactor, VOCs, waste gas, hydrophobic compound

Nomenclature	
VOCS	Volatile Organic Compounds
MBR	Membrane BioReactor
IL	Inlet Load
EC	Elimination Capacity
RE	Removal Efficiency
EBRT	Empty Bet Residence Time
K_La	Volumetric overall mass transfer coefficient
TSS	Total Suspended Solids
Log Kow	Octanol-water partition coefficients

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6   **1. INTRODUCTION**

7   Volatile organic compounds are commonly found in waste gases from a wide

8   range of industrial processes. Several of these compounds are toxic air pollutants which

9   may cause serious health effects as well as environmental problems. Among them,

10 toluene, and n-hexane are enlisted in the EPA (United States Environmental Protection

11 Agency) hazardous air pollutants list[1]. These two compounds are widely used as

12 solvents in industry such as paints, adhesives and fuel production. On the other hand,

13 iso-octane is a major component of gasoline and it is a very recalcitrant substrate.

14   Different physicochemical techniques such as absorption, adsorption and

15 thermal and catalytic oxidation have been used in order to reduce air pollutants. In the

16 last decades, biological gas treatment techniques such as bio(trickling)filtration,

17 bioscrubbing and membrane biofiltration have been widely studied and implemented as

18 alternatives for the traditional physical–chemical techniques[2-4]. Biological technologies

1 present several advantages over conventional physicochemical ones, such as low

2 operating cost, low energy requirements, and the absence of waste products that require

3 further treatment or disposal. However, these biotechniques have some limitations like

4 large size reactors, hard control of moisture and pH (biofilters), channelling and,

5 specially, low removal efficiencies for highly hydrophobic pollutants (biotrickling

6 filters)[5,6]. Hydrophobicity involves poor transfer of the pollutants from the gaseous to

7 the liquid (and biofilm) phase where biodegradation occurs, as a result of a reduced

8 concentration gradient (driving force). In this sense, lower mass transfer rates means

9 higher gas residence times and higher bioreactor volumes. Due to their low solubility,

10 toluene, iso-octane and hexane have shown low elimination performances by traditional

11 biotechniques[7,8].

12 In membrane biological reactors (MBRs), two phases (gas and liquid) are

13 physically separated by the membrane. Pollutants dissolved in air pass through the

14 membrane by diffusion and are degraded by the microorganisms attached on the other

15 side where the culture medium is continuously recycled. The polymeric material of the

16 membrane is regarded as a mass transfer vector[9] with the consequent improvement of

17 mass transfer of the poorly soluble compounds. In this regard, the use of membrane

18 bioreactor (MBR) for waste gas treatment is able to overcome these mass transfer

19 limitations due to the high permeability of some particular membranes for hydrophobic

20 pollutants[10]. Since the membrane provides a physical separation between the liquid

21 phase and the gas phase, it is possible to change the liquid and gas flow independently,

22 without evaporation or overgrow problems and pH can be easily controlled. In MBR,

23 the membrane also serves as a support for the development of the microbial biofilm

24 responsible for pollutant biodegradation.

3

1   The physical separation between the gas and liquid phase is also beneficial in

2   applications where direct contact of the air being treated with microorganisms is

3   undesirable[11] such as hospitals or cleanrooms. Moreover, the polymeric membrane has

4   the capability to retain a certain amount of pollutant. The adsorbed pollutant can be used

5   by the microorganisms as a secondary substrate source. Thus, the system can be capable

6   to treat inlet flows with sudden pollutant variation, typically found in industrial

7   facilities, avoiding starvation periods[12]. This key parameter has been established in

8   several water treatment by MBR studies[13,14] . However, the adsorption capacity in MBR

9   for waste gas treatment remains unstudied.

10   Different MBR configurations have been described: hollow fibre (diameter

11   <0.5mm), capillary (0.5<diameter<10mm), tubular (diameter>10mm), flat sheet and

12   spiral-wounded[15]. For waste gas treatment, hollow fibres and flat sheet are the most

13   used configurations. Flat sheet membranes have a low fouling tendency and are easy to

14   clean, but they have a low packing density (<100-400 m^2 m^{-3}). On the contrary, hollow

15   fibre membranes have a very high packing density (>30000 m^2 m^{-3}), but have a very

16   high fouling tendency besides being difficult to clean properly[16]. Flat sheet membranes

17   have been widely studied for the gas waste abatement, although capillary membranes

18   could be a good alternative with a better performance[17]. Capillary membranes come to

19   be a balance between those two, they can afford higher packing density than flat sheet

20   avoiding the fouling problems that occurs in a hollow fibres bioreactor.

21   Despite MBR have been widely investigated for waste water treatment, it has

22   been sparsely studied in gas waste treatment. Therefore, unlike water treatment, the

23   implementation of the membranes for gas treatment at industrial scale needs much more

24   investigation to approach its implementation at industrial scale[18]. To the best of our

4

1 knowledge, this is the first report on the hydrophobic VOCs long term operation by a

2 commercial capillary membrane, for both individual and mixture of VOCs.

3 In this work the biodegradation of three hydrophobic VOCs (toluene, iso-octane

4 and hexane) by a MBR was investigated. The MBR used is a commercial capillary

5 microporous polypropylene membrane module commonly used for wastewater

6 treatment. Toluene, n-hexane and iso-octane were selected according to their different

7 hydrophobicity in order to evaluate the influence of that factor. Their octanol-water

8 partition coefficients (Log Kow) are 2,7, 4,0 and 5,2 respectively. The effectiveness of

9 the system was studied under different operational conditions of empty bed residence

10 times, liquid velocities and inlet concentration. Moreover, experiments were performed

11 for both individual compounds and mixtures of different VOCs to emulate industrial

12 emissions, which usually contain more than one compound. The MBR adsorption

13 capability and the flow resistance were also investigated to evaluate the permeability

14 and feasibility for the biological technique.

15

16 **2. EXPERIMENTAL**

17 **2.1. Membrane**

18 A commercial module (Microdyn, Germany) consisting of 40 microporous

19 membrane capillaries, usually used for the treatment of wastewater, was tested. The

20 hydrophobic material of the membrane was polypropylene (PP) with an average pore

21 size of 0.2 μm. The capillaries had an inner diameter of 1.8 mm and a length of 420 mm

22 with total air volume 43. The capillaries were sealed in a polyurethane module with an

23 external diameter of 25 mm and a calculated shell volume of 206 cm^3.

24 **2.2. Mineral medium and inoculum**

1   Mineral medium composition (per litre of water) was KH_2PO_4 (1 g), K_2HPO_4 (1

2   g), NH_4Cl (1 g), NaCl (1 g), $MgSO_4$ (0.02 g), $CaCl_2$ (0.02 g) and trace elements (1 cm^3);

3   the trace elements concentration was described elsewhere[19]. Activated sludge obtained

4   from an urban wastewater treatment plant (Salelles, Spain) was used for the inoculation

5   of the MBR, which was carried out by recirculating 1 dm^3 of the activated sludge, with

6   a biomass concentration of 4 $g \cdot m^{-3}$ (TSS), across the outer side of the membrane during

7   72 h. In this period biomass attachment was confirmed due to the decreasing of the

8   biomass concentration in the recirculation (2 $g \cdot m^{-3}$) (TSS).

9   **2.3. MBR set up**

10   Figure A.1 found in the supplementary data (appendix A) shows and schematic

11   of the plant constructed for the present study. The nutrients solution tank was placed in

12   a thermostatic bath at 30 ºC under continuous stirring. The recirculation liquid flow rate

13   was adjusted to $1.20 \cdot 10^{-4}$ $m^3 \cdot h^{-1}$ by a peristaltic pump (Cole Palmer, USA),

14   corresponding to a hydraulic retention time of 17 h. The liquid phase was replaced

15   periodically with fresh solution to replenish nutrients and avoid accumulation of toxics

16   by-products.

17   The contaminated air stream was prepared by bubbling clean air in an impinger

18   filled with the target VOC. This stream was mixed with a secondary clean air stream in

19   a mixer camber to obtain the desired concentration in the final stream, which was

20   introduced to the reactor. Clean air flowrate was controlled by a flowmeter (Cole

21   Parmer, USA). The system had two sampling ports (inlet and outlet) that allowed

22   monitoring the inlet concentration (C_{in}) and the outlet concentration, (C_{out}). This data

23   was further used to calculate parameters such as the inlet load, IL ($g \cdot m^{-3} \cdot h^{-1}$);

24   elimination capacity, EC ($g \cdot m^{-3} \cdot h^{-1}$); and removal efficiency, RE (%). The outlet stream

1　of the reactor was passed through a carbon filter to adsorb possible remaining pollutants

2　not biodegraded in the bioreactor.

3　**2.4. Analytical techniques**

4　　　　Toluene, iso-octane and hexane concentrations were monitored by gas

5　chromatography with a Perkin Elmer Clarus 400, USA instrument equipped with a

6　flame ionization detector (FID) and a capillary column (N65110C0, PerkinElmer,

7　USA). The gas carrier was helium at a flow rate of 1 mL·min^{-1}. The injector and

8　detector temperature were 250ºC and oven temperature was 200°C. For gas mixtures,

9　the oven temperature set-up was 5 min at 50ºC, 10ºC·min^{-1} until 100ºC and 5 min at

10　100ºC. The injection volume was 5 cm^3 and was taken using a 5 cm^3 syringe (Pressure-

11　Lok, USA). Oxygen and carbon dioxide concentrations were measured with an infrared

12　(IR) gas analyser (Maihak S710, Germany). Pressure drop was measured with a

13　differential pressure transmitter (Testo 506, Spain) for the gas phase and for the liquid

14　phase (Testo 512, Spain). In the liquid phase the dissolved oxygen (Oxical, Germany)

15　was adjusted at 7.5 g·m^{-3} by a constant air flow bubbling in the nutrient tank and the pH

16　(Basic 20, Spain) at 6.5 by periodical addition of NaOH to offset the acidification of the

17　medium due to microorganisms activity. The biomass activity can be related with the

18　CO_2 production inside the bioreactor, thus, an increase of the CO_2 value in the outlet

19　steam indicates that the biomass was active and the biodegradation of the pollutant was

20　taking place.

21　**2.5 MBR abiotic characterization**

22　　　　In order to determine the abiotic parameters of the MBR, mass transfer, sorption

23　capacity and oxygen mass transfer were evaluated before inoculation. Sorption capacity

24　was determined by frontal analysis methodology using toluene measurements at the

7

1   inlet (tube side) and outlet (shell side) of the reactor as described elsewhere[20]. To adapt

2   this technique at the MBR characteristics, the polluted stream was introduced inside the

3   capillary. The outlet of the capillary module was sealed tightly. Thus, the total amount

4   of polluted gas was forced to pass through the membrane.

5   The total amount of toluene transferred through the membrane was another

6   abiotic parameter studied. To evaluate the toluene mass transfer between gas and liquid

7   phases a test without biomass was carried out. For this purpose, the polluted stream

8   circulated inside the capillary membrane while water circulated along the shell side.

9   During this experiment several gas flows (0.1-0.8 $m^3 \cdot h^{-1}$), pollutant concentration (0.05-

10 0.45 $g \cdot m^{-3}$) and water flows ($1.4 \cdot 10^{-2}$-$7 \cdot 10^{-4}$ $m^3 \cdot h^{-1}$) were tested. The co-current and

11 counter-current gas and liquid flows configurations were also tested.

12   Finally, to determine the oxygen overall volumetric mass transfer coefficient

13 ($K_L a$), a clean gas flow was circulated inside the capillary membrane while a

14 deoxygenated water stream was circulated along the shell side. In order to deoxygenate

15 the water a nitrogen flux was bubbled in the nutrient tank. The experiment was kept on

16 until the equilibrium between the air and liquid phases was reached. To monitor the

17 increase in dissolved oxygen concentration an oxygen sensor was put inside the nutrient

18 tank. A dynamic mass balance for the liquid phase (Equation 1) allows to calculate the

19 $K_L a$ value.

$$\frac{dS_{O_2}}{dt} = K_L a \cdot (S_{O_2}^* - S_{O_2}(t)) \tag{1}$$

20 Where $dS_{O_2} \cdot dt^{-1}$ is the dissolved oxygen (DO) rate, $S_{O_2}^*$ is the DO saturation

21 concentration and $S_{O_2}(t)$ is the DO concentration at the instant 't'. A numerical solution

22 algorithm based on Runge–Kutta methods was applied to compute the parameters in Eq.

23 (1). All computations were performed in MATLAB R2016 using a curve fitting of

8

1   experimental data. Parameters were estimated by minimizing the difference between the

2   experimental and predicted DO concentrations according to the following objective

3   function (2):

$$F = \sqrt{\sum_{i=1}^{n}(DO_{exp} - DO_{model})} \qquad (2)$$

4

5   Where F is the objective function to minimize, n is the number of experimental

6   measurements, DO_{model} is the simulated oxygen concentration (g/dm^3) and DO_{exp} is the

7   experimentally measured oxygen concentration (g/dm^3).

8   **2.6 MBR performance tests**

9   After abiotic tests, inoculation of the system was conducted. Table I summarizes

10 the tests performed with the MBR throughout the period studied. The membrane

11 bioreactor was operated for 7 months and experiments were divided into three stages.

12 The first stage experiment was started using toluene as unique pollutant. Elimination

13 capacity (EC) and the relationship with EBRT and efficiency percentage (RE%) were

14 analysed over 70 days. Afterwards, the second stage was started using, firstly iso-octane

15 as unique pollutant and later, a mixture of toluene and iso-octane. When the second

16 stage was finished, the MBR was thoroughly washed, in order to remove the pollutants

17 previously adsorbed on the membrane, and inoculated again. Subsequently, the third

18 stage was started, firstly only with hexane over eighty days, the EC and the relationship

19 between RE% and EBRT was determined and, then, the mixture performance of

20 hexane-toluene and hexane-methanol was tested.

1   **3. RESULTS AND DISCUSSION**

2   **3.1 MBR abiotic characterization**

3   **3.1.1 Adsorption capacity**

4   Adsorption capacity represents the amount of pollutant retained by the

5   membrane. This parameter has been well established in several water treatment by

6   MBR studies[13,14]. However, the adsorption capacity of MBR for waste gas treatment

7   remains unstudied. To determinate the adsorption capacity, the polluted stream was

8   introduced inside the capillary while the outlet of the capillary module was sealed

9   tightly. Therefore, the total amount of polluted gas was forced to pass through the

10   membrane. The amount of pollutant adsorbed on the membrane was calculated by

11   frontal analysis methodology.

12   <FIGURE 1>

13   Fig 1 shows the amount of toluene adsorbed as a function of the inlet toluene

14   concentration. As it can be seen, the amount of toluene adsorbed was linearly correlated

15   with the toluene concentration in the inlet stream up to 1.5 $g \cdot m^{-3}$. However, beyond 1.7

16   $g \cdot m^{-3}$, the toluene adsorption remains almost constant regardless toluene inlet

17   concentration. The maximum amount of toluene adsorbed on the membrane was 1.13

18   $g \cdot m^{-2}$. This value is quite similar to the value previously reported (1.47 $g \cdot m^{-2}$) by Juang

19   et al.[13]. This type of isotherm curve is characteristic of interactions between a non-ionic

20   aromatic solvent (toluene) and a hydrophobic polymer (polypropylene). This behavior

21   could be for the high affinity of toluene for the membrane matrix, and the ability of the

22   pollutant to diffuse into the crystalline regions of the polymer[21].

23   A good adsorption capacity is a key parameter which can improve the robustness

24   of the system when industrial emissions are treated. As an example, the system would

1   be capable to adsorb toluene during ~12 h under an IL 220 $g·m^{-3}·h^{-1}$ (0.1 $g·m^{-2}·h^{-1}$). The

2   microorganisms can use this retained pollutant as a secondary source of substrate. So

3   the negative effects of starvation periods can be eliminated or reduced. It also can avoid

4   concentration fluctuations in the inlet stream that normally can be found in the

5   exhausted air from industrial facilities due to their daily and weekly rotation in the

6   production. Therefore, the membrane can be used as a buffer when fluctuations in the

7   gas inlet occurred and avoid starvation periods[12,22] .

8   ### 3.1.2 Mass transfer characterization

9   In order to determine the maximum amount of pollutant that the system was

10   capable to transfer from the gas side to the liquid side, a set of experiments using

11   toluene as pollutant were carried out at several EBRT, IL and water flows. The polluted

12   stream at different flows ($1·10^{-2}$-$8·10^{-2}$ $m^3·h^{-1}$) and different concentrations ($5·10^{-2}$-

13   $4.5·10^{-1}$ $g·m^{-3}$) was forced to circulate inside the capillary membrane while water flow

14   ($7·10^{-4}$-$1.4·10^{-2}$ $m^3·h^{-1}$) circulated along the shell side. Those configurations correspond

15   to a gas linear velocity of 100-800 $m·h^{-1}$ (tube side) and a water linear velocity of 35-

16   1.75 $m·h^{-1}$ (shell side).

17   The maximum mass transfer, 226 $g·m^{-3}·h^{-1}$ (RE 26%), (0.1 $g·m^{-2}h^{-1}$), was

18   obtained when the gas flow was $8·10^{-2}$ $m^3·h^{-1}$ and the liquid flow was counter-current

19   pumped at 1.4 10^{-2} $m^3·h^{-1}$. Working under the same conditions, except for the water

20   flow rate which was reduced to $7·10^{-4}$ $m^3·h^{-1}$, the RE slightly decreases (23%). This

21   indicates that, in the range studied in the present work, the liquid flow rate has little

22   influence on the system performance, when the reactor works at counter-current flows

23   set-up. On the other hand, when the same operation conditions were tested using co-

24   current flow an important reduction of the RE% was observed. RE% values decrease

1   from 23% to 14% when liquid flowrates of $1.4 \ 10^{-2}$ $m^3 \cdot h^{-1}$ and $7 \cdot 10^{-4}$ $m^3 \cdot h^{-1}$ were used,

2   respectively. Modelsky et al.[23] also observed an important reduction of the mass

3   transfer, between the gas side to the liquid side, when the liquid velocity was decreased

4   in a polypropylene capillary reactor working under co-current flows. Based on these

5   results co-current operation and a liquid flow rate of $7 \cdot 10^{-4}$ $m^3 \cdot h^{-1}$ were used in the

6   biotics experiments to evaluate the performance of the MBR working at the more

7   unfavorable conditions and, thus, to evaluate the system improvement when the

8   bioreactor was inoculated.

9   **3.1.3 Determination of oxygen mass transfer**

10   In the MBR, VOCs are degraded aerobically; this means that O_2 concentration in

11   the liquid medium is a key parameter for proper operation of the system. To evaluate the

12   membrane capability to supply O_2, the volumetric mass transfer coefficient, $K_L a$, was

13   calculated. In order to determine the $K_L a$ a clean gas flow was circulated inside the

14   capillary membrane while a deoxygenated water stream was circulated along the shell

15   side. The experiment was kept on until equilibrium between the air and liquid phases

16   was reached. $K_L a$ values determined for the experiments were found to be in the range

17   2.75-3.25 h^{-1}. These values are significantly lower than those reported in the literature

18   for other kind of reactors (3.6–180 h^{-1} for a perforated plate, 360–1800 h^{-1} for a jet-

19   venturi and 54–108 h^{-1} for a venturi ejector[24]. However, one advantage when a MBR is

20   used it is possible to create a bubbleless aeration system[25]. The absence of bubbles in

21   the liquid side might improve the biomass grow.

22   In order to calculate the amount of oxygen transferred from the gas side to the

23   liquid side through the membrane, the standard oxygen transfer rate (SOTR, kg O_2 h^{-1})

24   was calculated according to equation 3:

$$SOTR = K_L a \cdot S_{O_2}^* \cdot V_M \qquad (3)$$

Where $K_L a$ is the mass transfer coefficient h^{-1}, $S_{O_2}^*$ is the dissolved oxygen concentration at saturation, $kg \cdot m^{-3}$ and V_M is the volume of the membrane, m^3. In the present work, a SOTR value of $1.2 \cdot 10^{-3}$ $g \cdot h^{-1}$ was obtained for a $K_L a$ of 3.25 h^{-1} (the most favourable $K_L a$ value obtained). Equation 4 shows the theoretical complete biodegradation (mineralization) of toluene. Taking into account the reaction stoichiometry, it has been estimated that an oxygen rate of $1.3 \cdot 10^{-2}$ $g \cdot h^{-1}$ would be necessary to degrade an IL of 100 $g \cdot m^{-3} \cdot h^{-1}$. Therefore, the maximum amount of O_2 $(1.2 \cdot 10^{-3} g \cdot h^{-1})$ that the system is capable to supply is ten times lower that the theoretical O_2 amount needed. In order to improve the total amount of dissolved oxygen, a secondary diffuser was introduced into the nutrient tank when the biotic tests were carried out. Actually, this behaviour is similar to the observation reported by Kumar et al.[26] who observed an improvement of toluene rate consumption when oxygen is supplied through both the membrane and the liquid phase.

$$C_7H_8 + 9O_2 \rightarrow 7CO_2 + 8H_2O \qquad (4)$$

3.2 Biotic performance

3.2.1 Study of toluene abatement

After the abiotic experiments, the MBR was inoculated with a mixed consortium. During the first 50 days of this research, only toluene was fed into the MBR at an inlet concentration ranging from 200 to 5000 ppm_v at an EBRT of 60 s which corresponded to IL from 43 $g \cdot m^{-3} \cdot h^{-1}$ ($2 \cdot 10^{-2}$ $g \cdot m^{-2} \cdot h^{-1}$) to 1600 $g \cdot m^{-3} \cdot h^{-1}$ ($7 \cdot 10^{-1}$ $g \cdot m^{-2} \cdot h^{-1}$), respectively. This concentration could be highest that the typically values found in industrial gas waste, however the aim of this work was studied the maximum performance of the system. The performance of the reactor was determined by

13

1   measuring the inlet and outlet toluene concentrations to calculate EC and RE. After day

2   50, the inlet concentration was gradually decreased to 1000 ppm_v, moment at which the

3   tests to determinate the relationship between the RE and EBRT was started (from day

4   60 to 70).

5   <FIGURE 2>

6   Fig 2 shows the EC and the RE of the system along the first 70 days. As can be

7   seen the start-up period was quick, the RE quickly increased to around 90% after 72 h

8   of operation. This behaviour is similar to the observation reported by Dorado et al.[27],

9   who had used activated sludge obtained from the same urban wastewater treatment plant

10 that was used in the present work. As can be also observed, the maximum EC was 1300

11 $g \cdot m^{-3} \cdot h^{-1}$ ($6 \cdot 10^{-1}$ $g \cdot m^{-2} \cdot h^{-1}$) and values of RE obtained were always higher than 95% and

12 sometimes even 100% in the inlet loading rate between 43 $g \cdot m^{-3} \cdot h^{-1}$ - 1300 $g \cdot m^{-3} \cdot h^{-1}$.

13 But, when the IL was higher than 1300 $g \cdot m^{-3} \cdot h^{-1}$ a RE drop down to 80% was observed.

14 On the other hand, when the relationship between EBRT and RE was studied an

15 important decrease on the overall system performance at low EBRT was observed (from

16 day 60 to 70).

17   <FIGURE 3A and 3B>

18   EC values as function of IL are shown in Fig. 3A. In this figure, it is observed

19 that values of RE obtained for inlet loading rate between 43 and 1200 $g \cdot m^{-3} \cdot h^{-1}$ were

20 higher than 95% and sometimes, 100%. Over this IL value, the efficiency of the system

21 decreased to 80%. However, the EC remained almost constant and close to 1300 $g \cdot m^{-}$

22 $^{3} \cdot h^{-1}$ (0.6 $g \cdot m^{-2} \cdot h^{-1}$) regardless the increasing inlet concentration. This indicates that this

23 value is the maximum EC that the system was capable to eliminate at an EBRT of 60s.

24 It's noteworthy that these EC values found in the present work are quite superior to

25 those reported by some authors working under similar condition but with different

14

1   configurations of bioreactors. For example, Zilli et al.[28] reached an EC of 242 $g \cdot m^{-3} \cdot h^{-1}$

2   (RE 24%) when a biofilter was fed with an IL of 1000 $g \cdot m^{-3} \cdot h^{-1}$ at EBRT of 28s.

3   Whereas Aizpuru et al.[4] studied the biofilter performance at EBRT of 90s and an IL of

4   1700 $g \cdot m^{-3} \cdot h^{-1}$, obtaining an EC of 290 $g \cdot m^{-3} \cdot h^{-1}$ (RE 17%). These promising results

5   obtained in the present study shown that MBR has a very high potential to be used for

6   the treatment of poorly soluble pollutants at very high loads. The higher EC obtained

7   here compared to traditional biofiltres configuration could be due to the fact that the

8   membrane constitutes a physical separation between the gas and the liquid phases.

9   Thus, the pollutant diffuses directly from the membrane to biofilm avoiding the

10 diffusion through water, limited step when hydrophobic compounds are treated.

11   To evaluate the relationship between RE and EBRT a constant inlet

12 concentration of 1000 ppm_v was used while the EBRT was decreased. The results

13 obtained during this stage are plotted in Fig 3B. The maximum RE of the system was

14 99% at the EBRT of 60s, but when the EBRT was decreased to 5s the RE dropped to

15 23%. This could indicate that the time that the pollutant was inside the capillaries was

16 not long enough to allow that the whole pollutant passes through the membrane,

17 indicating mass transport limitation, and only a little part of toluene was available for

18 the microorganisms. Anyway, it should be noted that despite the reduction in the

19 efficiency of system when EBRT was halved (30 s), the RE of 79% (EC of 551 $g \cdot m^{-3} \cdot h^{-1}$

20 ^{1} or 0.2 $g \cdot m^{-2} \cdot h^{-1}$) is still higher compared to classic biological configurations. In the

21 light of these results, a range between 30 and 60 s could be considered as the optimum

22 work range.

23 **3.2.2 Study of iso-octane abatement**

24   After proving the efficiency of the MBR in treating gas streams contaminated

25 with a common model compound (toluene), the performance of the bioreactor was

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1   evaluated using a more hydrophobic pollutant (iso-octane). Iso-octane is almost two

2   times more hydrophobic than toluene, apart of being a very recalcitrant pollutant due to

3   its quaternary carbon. The study was carried out for 22 days at EBRT of 60 s and an

4   average inlet concentration of 175 ppm_v.

5   <FIGURA 4>

6   In Fig 4, where the EC and the RE for iso-octane along 22 days of operation is

7   shown, it can be observed that the RE for iso-octane was slightly above 80% for the first

8   9 days, indicating a rapid acclimation of the biomass to the new pollutant. However,

9   from day 79 a continuous decrease of the removal efficiency was observed up to a

10   minimum of 38% on day 85. Some authors have reported the complexity of the

11   biodegradation of this compound due to its chemical structure. In this sense, quaternary

12   carbon structures are known as highly recalcitrant. Actually, only one bacteria strain

13   (*Mycobacterium austroafricanum*) has been found to be capable to use iso-octane as

14   sole carbon and energy sources[29]. Nevertheless, Auffret et al.[30] reported better

15   degradation rates of isooctane when this compound was supplied in a mixture, rather

16   than alone. For this reason, after day 85, a mixture of toluene and iso-octane was

17   introduced in order to verify whether iso-octane degradation is improved. As can be

18   seen, from the instant that toluene was reintroduced in the MBR, a gradual increase of

19   the removal efficiency (expressed as the total VOC's at the inlet) is reached, once again,

20   with values close to 80%. The improvement in the RE%, after toluene addition might

21   indicate that the microorganisms present in the biofilm were not capable to use the iso-

22   octane as a sole carbon source and they needed a co-substrate, in this case toluene. High

23   RE values observed during the first days might be explained due to the fact that the

24   microorganisms used the toluene retained and adsorbed on the membrane as a

25   secondary source of substrate.

1   **3.2.3 Study of hexane performance**

2   According to literature, unlike iso-octane, hexane can be used as sole carbon and

3   energy sources by many bacteria and fungi[31-33]; a compound that is normally used as

4   standard of highly hydrophobic pollutant. After iso-octane experiments, the MBR was

5   thoroughly washed and dried with clean air, in order to remove any compound adsorbed

6   on the membrane and to avoid further interactions. Then, the membrane was inoculated

7   again following the same procedure explained above and after the adaptation period, the

8   MBR was fed with a single hexane stream at EBRT of 60 s and an inlet concentration

9   ranged between 6 and 6000 ppm$_v$. The bioreactor performance was again evaluated

10   based on EC and RE% values (Fig 5).

11   <FIGURE 5>

12

13   From the day 95 to 155 the maximum concentration that the system was capable

14   to treat (EC) was studied. After this period an inlet concentration of 1000 ppm$_v$ was fed

15   again, moment at which the tests to determinate the relationship between the RE and

16   EBRT were started (from day 156 to 174).

17   As can be observed in Fig 5, where the EC and the RE of the system for hexane

18   is represented, the maximum EC was 400 g·m^{-3}·h^{-1} (0.2 g·m^{-2}·h^{-1}) and the maximum

19   values of RE obtained were close 50%. However, when the relationship between EBRT

20   and RE was studied an important decrease on the overall system performance at low

21   EBRT was observed (from day 156 to 174). During this period, RE values lower than

22   10% were obtained.

23   <FIGURE 6A and 6B)

24   A maximum EC close to 400 g·m^{-3}·h^{-1} (0.2 g·m^{-2}·h^{-1}) was obtained (Fig 6A)

25   when the IL was 2600 g·m^{-3}·h^{-1} (1.1 g·m^{-2}·h^{-1}) (RE 16%). This value of EC is

17

1 significantly lower in comparison to the EC previously observed for toluene. This

2 different behavior can be partially explained by the presence of a water layer. Due to the

3 liposolubility of hexane, the presence of water in the shell might produce a decrease in

4 the diffusion of the pollutant through the membrane. The EC obtained in the present

5 study are similar to those found in the literature. For instance, Zamir et al.[34] found an

6 EC of 400 $g \cdot m^{-3} \cdot h^{-1}$ at EBRT between 78-120s when a biofilter inoculated with an

7 unidentified fungal consortium was used. The maximum EC obtained in the present

8 work is equal to the maximum EC reported previously. Therefore, the present system

9 allowed operating at low EBRT (meaning smaller reactor volume) and bacterial

10 consortium (more controllable and robust) instead of fungi. It is well-known that the use

11 of fungi instead of bacteria for degrading hexane normally achieves better performance

12 because fungi can directly transfer hexane from the gaseous phase into the aerial

13 structure of hyphae[31]. However, in this case the role of the membrane replaces this

14 advantage.

15   The relationship between RE and EBRT is plotted in Fig 6B. The maximum RE

16 of the system was close to 60% at the EBRT of 60s but when the EBRT was reduced

17 from 60 s to 50 s the RE decreased drastically from ~60% (60 s) to ~30% (50 s). The

18 RE and the EC values obtained for hexane are very low in comparison to the values

19 observed previously, in the present work, for toluene. This means that despite the fact

20 that the membrane, is used here as a mass transfer vector, in an attempt to improve the

21 mass transfer of pollutants between the contaminated pas to the liquid phase (biofilm),

22 the pollutant hydrophobicity is a key parameter that can limits the effectiveness of the

23 system. Although the polymeric material of the membrane is used as a mass transfer

24 vector, the relatively low efficiency observed for the hexane, demonstrated that the

25 pollutant hydrophobicity is a key parameter when VOC are treated. Based on these

18

1   results, the optimum EBRT working range to obtain a good abatement performance

2   when hexane was treated could be the EBRT ranged between 60 and 50 s.

3   During the last days of the experiment, the system capability to treat hexane in

4   presence of other pollutants was studied. This part of the study was motivated for two

5   reasons. The first one is that a RE improvement of iso-octane was observed when it was

6   mixed with toluene and the second one was that most of the industrial VOC gaseous

7   emissions comprise more than a unique pollutant. Thus, a more realistic scenario for the

8   hexane degradation was studied. For this purpose, two different mixtures were used in

9   this stage, hexane-toluene and hexane-methanol. When toluene was introduced as a

10   second pollutant, no effect on the hexane removal RE% was observed. Zhao et al.[11]

11   reported similar results when a mixture of hexane and toluene was treated in a hollow

12   fiber MBR. On the other hand, when the second mixture (hexane-methanol) was used a

13   decreased in hexane RE% was observed. According to literature, the addition of

14   methanol to other VOCs might have neutral, positive or negative effect depending on

15   the VOCs and their loading rates, nutrients availability, pH, and temperature[35]. Under

16   the operating conditions used in the present study, the presence of methanol in the gas

17   stream had a negative effect on the hexane removal performance, a reduction of hexane

18   RE% was observed. This reduction on the overall performance of hexane might be due

19   to the fact that methanol is a more biodegradable compound than hexane, so, the

20   microorganisms attached on the membrane had more preference to degrade methanol,

21   probably a competitive effect rather than a synergic effect occurred. These differences

22   suggested that further research is needed to understand the complex relationship

23   between co-substrates and the polypropylene capillary MBR behavior when complex

24   mixtures of compounds with different hydrophobic properties are treated.

19

1   It is important to highlight that during the whole MBR performance the pressure

2   drop inside the membrane (gas side) was between 2-12 mmH$_2$O/m, even when the

3   highest IL were fed. These values are lower than typically pressure drop reported by a

4   traditional biofiltration technique. Furthermore, no problems of bioclogging or

5   biofouling were observed. This is a valuable feature of MBR respect to biofiltres or

6   biotrickling filters, since biomass accumulation is one of the most critical problems that

7   need to be controlled for long-term operations. Thus, capillary MBR have the potential

8   to overcome one of the main problem of the traditional biotechniques. The excess of

9   biomass inside the bioreactor results in an increase of pressure drop, which ultimately

10 may lead to   wash out of part of the biomass from the system or to force the

11 replacement of the support media[3]. The absence of bioclogging during the whole MBR

12 performance might be produced by the fact that the sheer stress of liquid flow was

13 enough to detach the biofilm overgrow and eliminated through the purge. Thus, a thin

14 biofilm was established on the membrane surface avoiding bioclogging and channeling

15 but with enough thickness to abate satisfactorily hydrophobic pollutants.

16 **4. CONCLUSIONS**

17 Results illustrate the effective abatement of different VOC's with a commercial

18 microporous membrane adapted for waste gas treatment. Toluene was removed with

19 high efficiencies (80-99%) with a maximum EC of 1309 g·m^{-3}·h^{-1}, which improves

20 previous results for biological processes. For iso-octane, a poorer RE was observed

21 when it was fed alone as well as for hexane. Low and constant pressure drop monitored

22 during the whole experiment indicates the high stability and robustness of MBR

23 overcoming one of the main limitation of classic biofiltration. The main application of

24 this module is the treatment of moderate-small flows with high loading rates.

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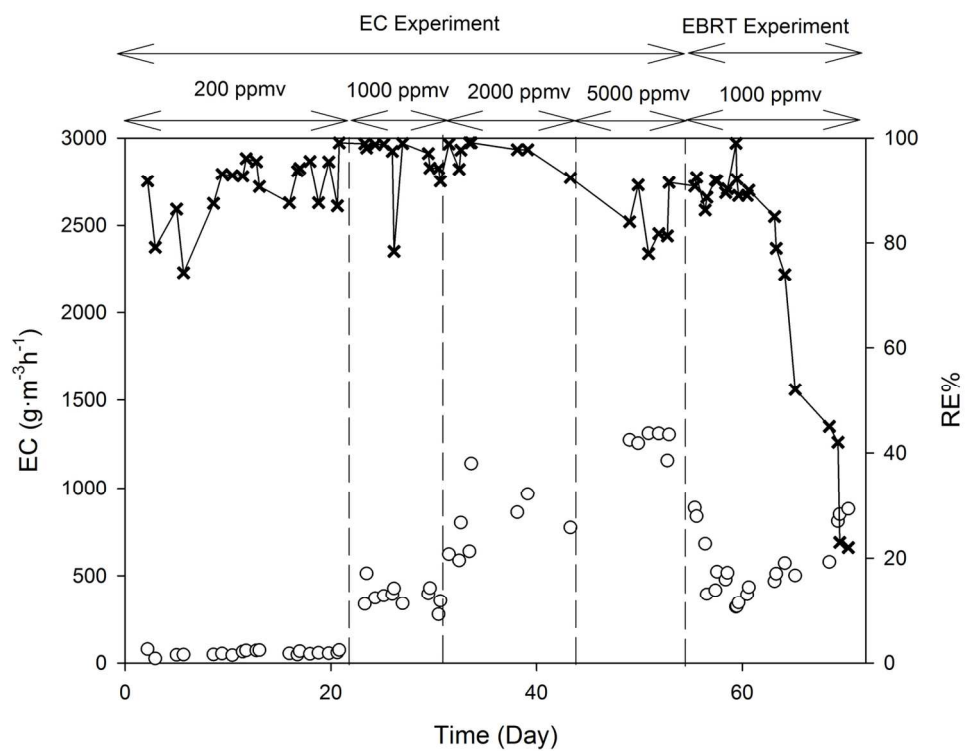
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12   ***Supplementary material***

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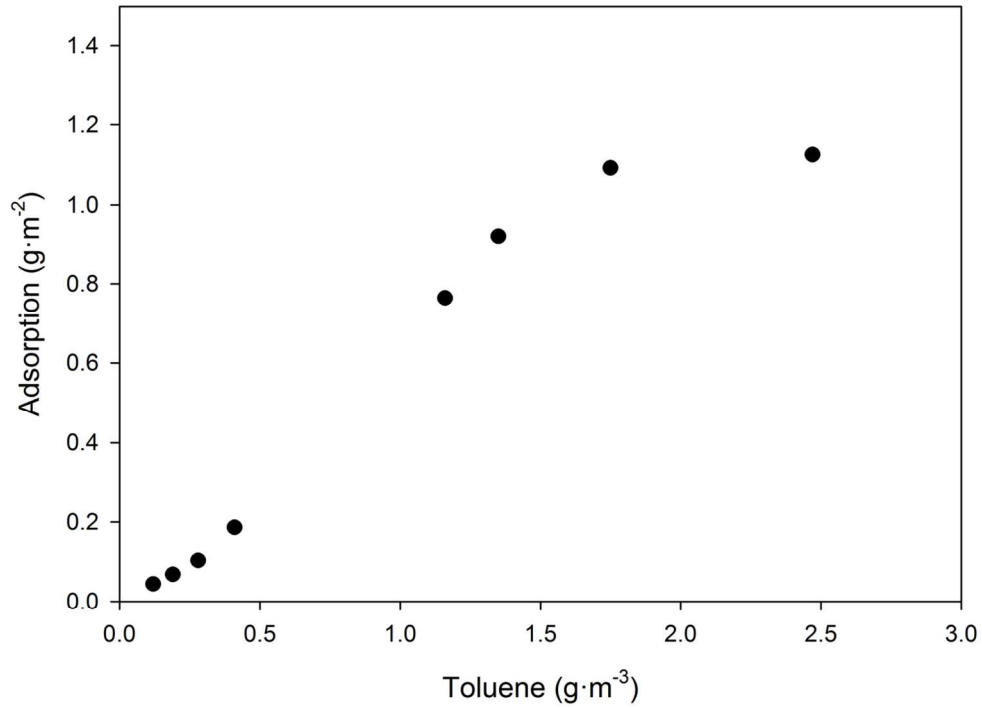
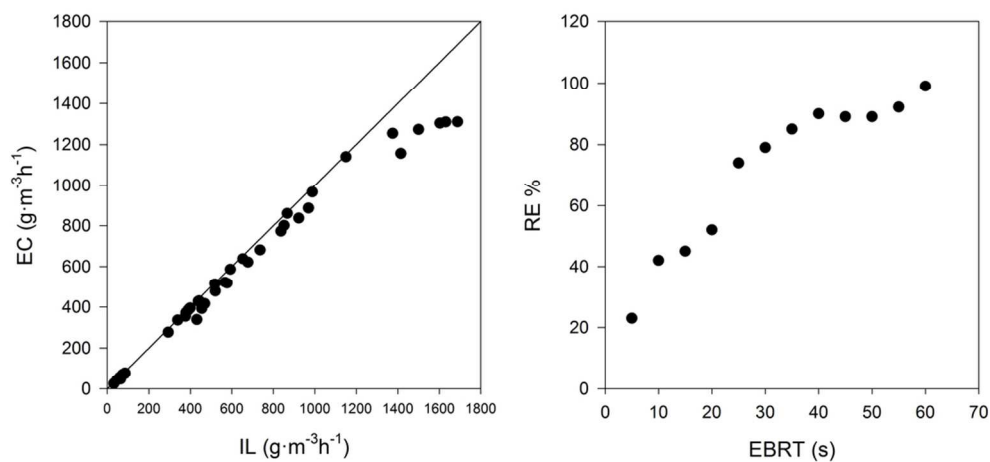Sorption capacity of toluene (●) in the membrane
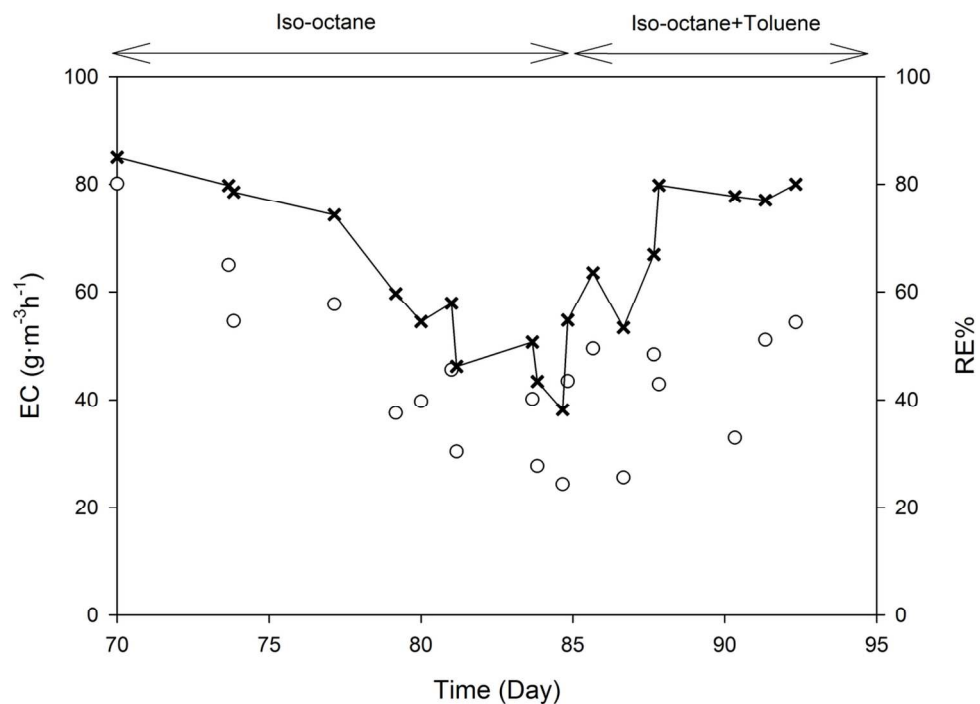
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Evolution of the RE (x, secondary axis) and EC (○) of toluene
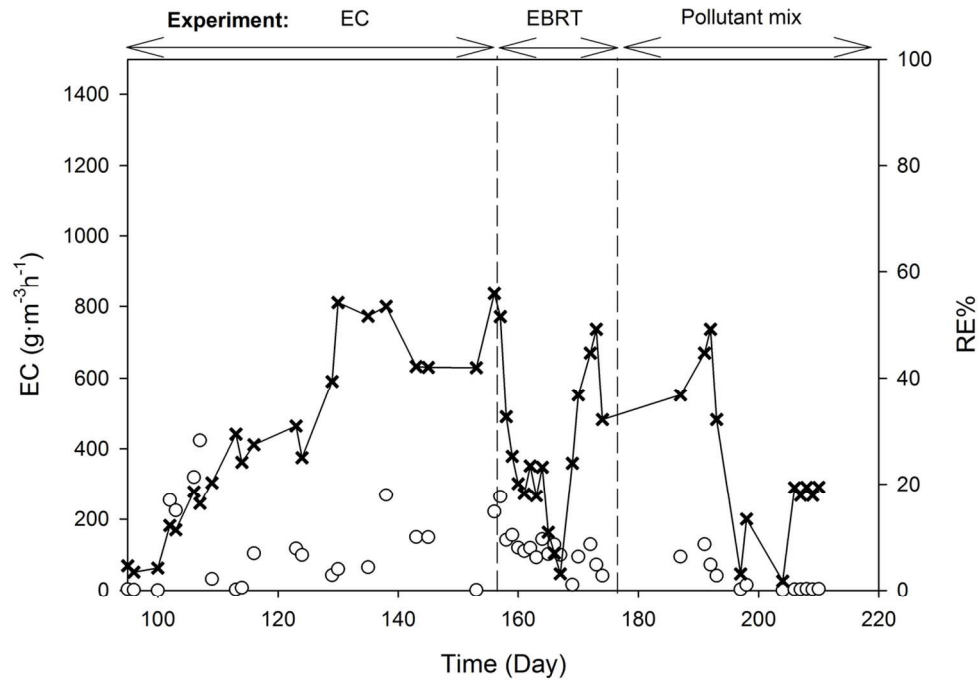
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A; Toluene variation of EC (●) with IL. B; Toluene relationship between EBRT and RE(●)

96x46mm (300 x 300 DPI)

Evolution of the RE (x, secondary axis) and EC (○) of iso-octane and iso-octane/toluene mixtures
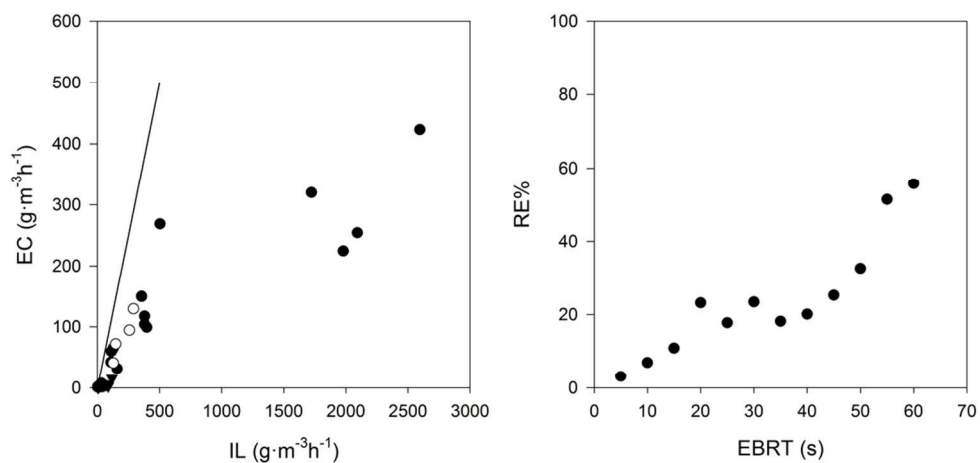
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EC (○) and RE (x, secondary axis) during hexane and hexane/toluene and hexane/methanol mixtures tests

120x87mm (300 x 300 DPI)

A; Hexane variation of EC with IL, (●) hexane, (○) hexane+toluene, (▼) hexane+methanol. B; Hexane relationship between EBRT and RE (●)

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Stage	Pollutant	Days	EBRT	Experiment
Stage 1	Toluene	2-50	60s	Maximum EC
	Toluene	60-70	5-60s	EBRT
Stage 2	Iso-octane	71-84	60s	-
	Iso-octane/Toluene	85-92	60s	Co-metabolism
Stage 3	Hexane	95-154	60s	Maximum EC
	Hexane	155-175	5-60s	EBRT
	Hexane/Toluene	176-185	60s	Pollutant mix
	Hexane/Methanol	186-190	60s	Pollutant mix

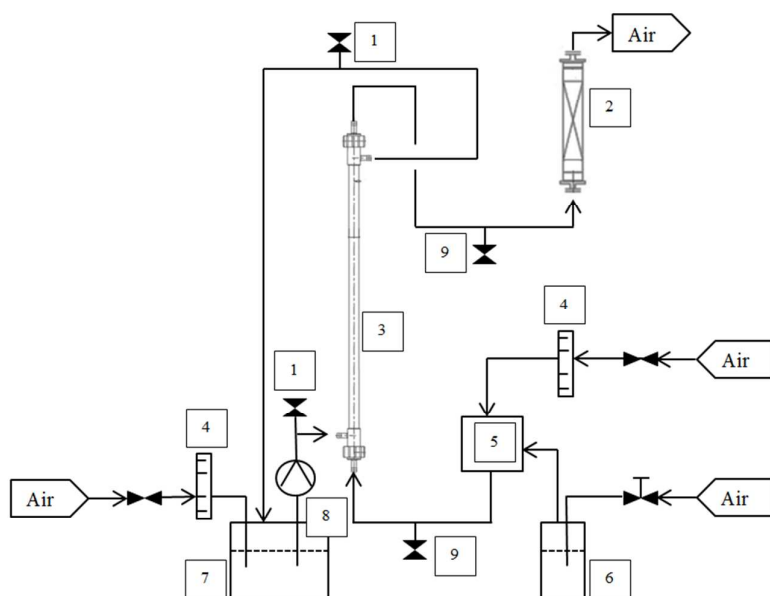Table I Summarize of operation conditions during the 3 stages

Supplementary material

Figure A.1: Schematic of the lab scale plant. 1: Liquid sampling port, 2: Carbon filter, 3: Membrane bioreactor, 4: Flowmeter, 5: Mixer chamber, 6: VOC's bottle, 7: Nutrients tank, 8: Peristaltic pump, 9: Gas sampling port