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BAC filtration to mitigate micropollutants and EfOM content in reclamation reverse osmosis brines

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HIGHLIGHTS

- BAC filtration alone only improved some water quality parameters of the RO brine.
- The highest EfOM removals were achieved by the combination of ozone and BAC.
- To ensure the total removal of pharmaceuticals was necessary the integration of an AOP with BAC.
- ATP analyses and FISH technique allow the assessment of the BAC filters biomass.
- β-Proteobacteria was the main bacteria phylum identified in the three biofilters.

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ABSTRACT

The effluent organic matter (EfOM) including micropollutants present in the concentrate streams generated from reverse osmosis (RO) based municipal wastewater reclamation processes entails environmental and health risks on its disposal to the receiving environment. The suitability of a biological activated carbon (BAC) process to treat municipal wastewater RO concentrate was evaluated at lab scale during 320 days of operation. BAC alone and combined UV/H_2O_2–BAC and ozone–BAC were performed. The combination of both advanced oxidation processes with the BAC filter improved considerably the water quality parameters. Overall eliminations for dissolved organic carbon, chemical oxygen demand and ultraviolet absorbance at 254 nm ranged between 50–66%, 48–66% and 73–87%, respectively, improving considerably the removals obtained without pretreatment step (28%, 19% and 37%, respectively). Moreover, although some pharmaceuticals were partially removed by the BAC filter, the integration of the UV/H_2O_2 or the ozone step was necessary to achieve the total removal of those micropollutants. Finally, biomass assessment techniques allowed determining the diversity of different BAC filter scenarios.

1. Introduction

It is generally assumed that not all polluting agents are removed through conventional wastewater treatment plants (WWTP). These persistent compounds include the emerging pollutants group, constituted by chemicals of very diverse origin. They are characterized by their high production and consumption volumes, which entails their continuous presence in the environment even at low concentrations [1]. Whereas their occurrence is fairly well-established, their long-term effects and environmental consequences are not clearly identified [2]. Thus, additional advanced treatment steps should be considered to reduce their discharge into receiving waters.

In recent years, reverse osmosis (RO) has been applied to further treatment of the secondary effluents of wastewater treatment plants [3]. The resultant permeate is usually used for irrigation or aquifer recharge. Despite the high quality effluent generated, salts, biological constituents and organics, including micropollutants, coming from secondary effluent, are concentrated in the rejected effluent [4]. Consequently, one of the major drawbacks of RO is the need to dispose this concentrate. These waste effluents are usually discharged to surface waters, oceans or groundwaters. Although their discharge is currently not regulated, safe environmental practices would suggest their treatment before its release and dilution into the environment [3,5].

Advanced oxidation processes (AOPs) have been applied to treat RO retentates in order to reduce their high concentration in

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recalcitrant micropollutants [4,6–12]. AOPs are those processes which involve *in situ* generation of hydroxyl radicals (HO•) and their reaction with organics converting them into simpler compounds or even leading to their total mineralization. The HO• radical is a powerful oxidant species with a reduction potential of 2.80 V. Its non-selectivity is also remarkable [13]. Furthermore, taking advantage of the biodegradability enhancement achieved by AOPs, the use of a subsequent biological step has also been previously suggested to minimize even further the organic load of the target effluent [14].

Granular activated carbon (GAC) filters have been used for long time to remove by adsorption undesirable organic compounds including biodegradable organic matter, micropollutants, halogenated hydrocarbons and taste and odor compounds [15]. GAC offers an effective mean to remove organic compounds due to its irregular creviced, porous particle shape and affinity for attaching to itself most organics even at low concentrations [16,17]. However, one of the major limitations of GAC is saturation which implies the need to regenerate it, with the economic costs it entails. On the other hand, crevices and macropores of activated carbon are also an excellent support material for the development of microbial biofilms as they provide protection from shear stress to microorganisms colonies [15–18]. Such colonized filters are referred in the literature as biological activated carbon (BAC) filters. When the GAC media particles start becoming exhausted for adsorption, the rough porous surfaces are amenable to indigenous microbial communities establishment. This transition from GAC to BAC filter is a time-dependent process where simultaneous adsorption and biodegradation processes can coexist [15,16,19]. Precisely, biodegradation mechanism consists on a first adsorption of organic matter, removed from water into macropores, where it is detained long enough to promote its slow biodegradation by attached bacteria [16]. Extending GAC service life and decreasing backwash frequency are the main benefits of BAC filters [17]. Pre-oxidation of high recalcitrant effluents prior to BAC filtration is a commonly used combination. It results in an increase of the biodegradability of the inlet effluent, therefore promotes biological activity of the biofilm and consequently extends GAC media life [17,20–22].

Active biomass characterization is important during BAC filter processes in order to stablish connections between the degradation process and the biomass involved. Various methods have been used by different authors to assess the biomass activity. These include heterotrophic plate counts (HPC) [23], phospholipid extraction method [24], adenosine tri-phosphate (ATP) analyses [15,20,25] and respirometric measurements [19,26] among others. Likewise, determination of microbial communities is also essential information for a better understanding of BAC filters performance. Few studies have been conducted using culture-dependent methods on drinking water BAC applications [25,27,28]. However, only a very small fraction of microorganisms in the environment is cultivable on the commonly applied media. Culture-independent molecular methods are therefore preferred above culture-dependent in most sorts of microbiological investigations in wastewater treatments [28,29]. Within them, 16S ribosomal ribonucleic acid (rRNA) gene clone library analysis [25,28,30,31] and fluorescence *in situ* hybridization (FISH) [32,33], with rRNA-targeted, probes are known to be very powerful tools for the identification of microorganisms in microbial biofilms.

This study aims to evaluate the performance of biologically enhanced granular activated carbon filtration in minimizing the environmental impacts associated to the direct discharge of reclaimed RO brine coming from a WWTP located in Catalonia (Spain). The BAC filter performance on the removal of micropollutants and dissolved organic carbon (DOC) was compared with the performance of two integrated systems which consist of UV/H_2O_2 or ozonation coupled with a BAC filtration. This work focused on the biological step of the three proposed treatments since the occurrence of different micropollutants in reclamation RO retentates and their mitigation by both AOPs was already assessed in previous studies [11,12]. ATP analyses and FISH technique were applied to ensure and assess the biological activity in GAC filters.

2. Materials and methods

2.1. Experimental devices

The photo-oxidation pretreatment was carried out in 2 L jacketed reactor at 25 °C. Three low pressure mercury lamps (Philips TUV 8W, G8T5) emitting at a wavelength of 254 nm were placed inside the UV/H_2O_2 reactor. The photon flow measured with uranyl-oxalate actinometry was $1.7 \cdot 10^{-5}$ Einstein s^{-1} [34]. Reaction time depended on the matrix organic load and the average reaction time was 98 min. 30 mgH_2O_2 L^{-1} were added at the beginning of the reactions and they were considered ended when an average dose of 0.82 mgH_2O_2 mgDOC^{-1} was reached. Catalase enzyme was added to quench the excess of H_2O_2 prior feeding the BAC filter.

In the ozonation pretreatment, ozone-containing stream was injected into the effluent (2 L and 25 °C) through diffusers at a flow rate of 133.5 L h^{-1} with an ozone concentration of 10 gO_3 Nm^{-3}. The average transferred ozone dose achieved was 2.2 mgO_3 mgDOC^{-1}. In this case, reaction time was also dependent from the ozone demand of the different matrices (average reaction time: 19 min). The complete ozonation set-up is described elsewhere [35].

Three biological filters were operated. Two of them were fed with the resultant effluent from each assayed AOP and the other one was fed with RO raw brine. Filtrasorb® 400 agglomerated coal based granular activated carbon (Chemviron Carbon, Belgium) was used as a filter media. Its effective size was between 0.6 and 0.7 mm and its mean particle diameter was 1.0 mm. The set-up consisted of 3 cm inner-diameter glass columns packed with approximately 5 cm of GAC. All columns were protected from the light to minimize the potential effects of photodegradation and were run under aerobic conditions by aerating the feeding solution (until saturation) just before its entry into the columns. The columns were fed at an average flow rate of 0.79 mL min^{-1}. Contact time resulted 13.4 min (empty bed contact time (EBCT): 44.7 min). Since this study was focused on biodegradation as a removal mechanism, GAC was soaked during few days in the WWTP RO brine tank to be close to its saturation state before being packed into the columns. After that, columns were initially inoculated with secondary sewage sludge in order to accelerate the colonization process. The startup strategy is detailed elsewhere [36].

2.2. Analytical methods

Samples were withdrawn during both AOPs and also at the inlet and outlet of each biofilter to monitor the following parameters: DOC (previously filtered through 0.45 μm polyethersulfone (PES)), chemical oxygen demand (COD), ultraviolet absorbance at 254 nm (UV_{254}), turbidity and pH. DOC was measured by means of a Simadzu TOC-VCSN analyzer. To measure the COD, procedure 5220D from Standard Methods [37] was followed. Absorbance was determined by Perkin Elmer UV–Vis spectrophotometer with *Lambda 20* software. The turbidity was determined using a Hach 2100P turbidimeter. Other parameters like alkalinity were also analyzed, which was quantified by titration with HCl as described in 2320B Standard Methods procedure [37]. For the evaluation of the biological oxygen demand at 5 days (BOD_5), the WTW