Integration of UV/H_2O_2 with Membrane Bioreactor for Ethinylestradiol Removal

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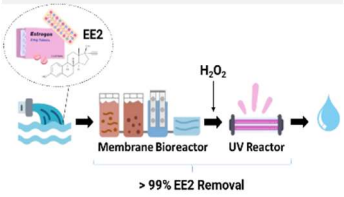

Effluent treatment containing the hormone 17α-ethinylestradiol (EE2) was conducted in a system composed of a membrane bioreactor (MBR) followed by an advanced oxidation process (UV/H_2O_2). During MBR operation, Chemical Oxygen Demand (COD), suspended solids, and turbidity analyses were performed to verify process performance. The biological reactor proved to be stable over 111 days of operation, with an average COD removal of 98.73 ± 1.15%. The combined process achieved an EE2 removal greater than 99%, something that has not yet occurred in most current treatment plants. This study can help in the discussion of micropollutant removal feasibility for future municipal wastewater treatment plants, considering that countries tend to adopt more restrictive measures and create laws that require higher percentages of EE2 removal in the near future.

Introduction

Endocrine disruptors are organic pollutants that can interfere with the endocrine system and affect hormonal function in animals and humans, even at very low concentrations (ng/L to µg/L). Among these disruptors, 17α-ethinylestradiol (EE2), a synthetic hormone found in oral contraceptives, is one of the most active estrogens in municipal wastewater [1]. The main reason for the ubiquitous presence of EE2 in water is its incomplete removal by conventional biological processes. For large-scale applications, membrane bioreactors (MBR), which consist of a combination of biological and membrane separation processes, enable greater estrogen removal than conventional activated sludge (CAS) processes [2]. Despite this possible improvement, the MBR cannot be viewed as an absolute barrier to EE2. Thus, it is necessary to integrate biological processes with membrane separation or advanced oxidation processes (AOPs) to achieve greater EE2 removal. Given this context, the aim of this study was to evaluate the application of advanced treatment processes, including a membrane bioreactor and UV/H_2O_2, for the treatment of effluent containing estrogen EE2.

Material and Methods

The MBR was operated continuously for 111 days to obtain the following operational parameters: Hydraulic Retention Time (HRT) required to operate the process with stability, MBR permeate flow, and EE2 removal. For start-up, the bioreactor was inoculated with sludge from a local municipal wastewater treatment plant, and the synthetic effluent was prepared as shown in Table 1 (Step 1). The bioreactor was operated for 48 days with an HRT of 14 h and complete sludge retention. On Day 49, EE2 was solubilized in ethanol and added to the feed according to the composition shown in Table 1 (Step 2). It was decided to work with EE2 at a higher concentration than that found in the environmental matrix, with the aim of saturating the possible sludge adsorption sites and evaluating removal by biodegradation. Subsequent long-term operation was performed with the HRT that provided the greatest stability to the reactor. The laboratory-scale MBR system used hollow fiber membranes made of polyetherimide, with an average pore size of 0.4 µm and total area of 0.032 m^2, operated at 25°C and 0.4 bar. The filtration and backwashing times were set at 15 min and 30 s, respectively. Backwashing was performed at a counterpressure of 0.4 bar.

The UV/H_2O_2 system consists of a closed chamber containing a low-pressure (20 W) UV lamp of 6.8 W/m^2 fluence. A concentration of 10 mg/L H_2O_2 and UV dose of 73.44 kJ/m^2 were used. EE2 quantification was evaluated by high-performance liquid chromatography, according to the methodology described by the authors [3].

Results and Discussion

Membrane bioreactor operation

In Figure 1, it can be seen that in the first seven days of CAS operation, a period of acclimatization of the sludge with synthetic sewage, COD removal increased until it reached approximately 90%. From the 49th day onwards, EE2 was added to the feed, and an increase in the input COD was observed owing to the presence of the solvent ethanol, used as a carbon source, and with the aim of solubilizing EE2. Even with the addition of the pollutant, the removal of organic matter remained high, with an average value of 94.31 ± 10.63%. The presence of the microfiltration membrane in the system improved

the efficiency of the process, achieving an average COD removal of 98.73 ± 1.15%, which can be attributed to the complete retention of particulate matter by the membrane.

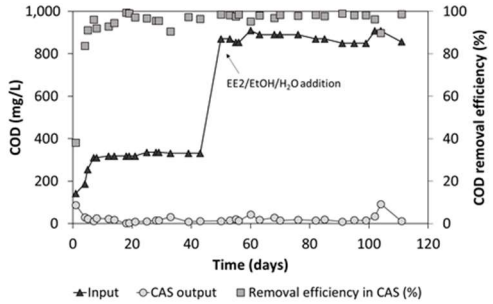

Figure 1. COD removal for conventional activated sludge (CAS).

Settleability was affected by the introduction of EE2, as evidenced by the flotation and dragging of the sludge. The biomass was stable in the short term only at the highest HRT (44 h). The use of a longer HRT did not influence the permeate flow of the MBR, which in all cases started at approximately 150 L/(h.m²) and dropped to approximately 50 L/(h.m²) after 20 min, stabilizing at this value.

EE2 removal

Table 2 presents the results of EE2 removal in the MBR operating with HRT of 14, 28, and 44 h, and in the UV/H_2O_2 treatment. Because microfiltration membranes are not considered effective for removing EE2, the reduction achieved in MBR can be attributed to the possible presence of microorganisms capable of removing estrogen, as well as the adsorption of EE2 into the biomass. Although the results achieved are satisfactory, EE2 has adverse effects on individuals, even at low concentrations, and requires post-treatment. The results of EE2 removal after UV/H_2O_2 (> 99%) confirmed the high efficiency of the advanced oxidative process in destroying organic substances that are difficult to degrade and, often, in low concentrations.

Table 1. Synthetic effluent composition.

Step 1: feed without EE2 [a]		**Step 2: feed with EE2 [b]**	
Components	Concentration (mg/L)	Components	Concentration (mg/L)
Glucose	100	Ethanol	394.5
Casein peptone	100	Casein peptone	100
Urea	35	Urea	35
Sodium acetate	225	Sodium acetate	225
Magnesium sulfate	17.5	Magnesium sulfate	17.5
Potassium fosfate	17.5	Potassium fosfate	17.5
Ferrous sulfate	10	Ferrous sulfate	10
		EE2	1

(a) COD = 324 ± 10 mg/L; (b) COD = 875 ± 22 mg/L.

Table 2. EE2 percentage removal.

HRT (h)	**EE2 after MBR (mg/L)**	**EE2 removal in MBR (%)**	**EE2 after UV/H_2O_2 (µg/L)**	**EE2 removal in UV/H_2O_2 (%)**	**EE2 removal in MBR- UV/H_2O_2 (%)**
14	0.183	82 ± 2	0.82	> 99	> 99
28	0.114	89 ± 2	0.46	> 99	> 99
44	0.096	90 ± 2	0.07	> 99	> 99

UV dose = 73.44 kJ/m2; H_2O_2 dose = 10 mg/L.

Conclusions

At the highest HRT evaluated in this study (44 h), an EE2 removal of 90 ± 2% was achieved. However, the residual concentration of EE2 at the exit of the MBR remains a concern from an environmental perspective, and post-treatment with UV/H_2O_2 has proven to be an efficient technology (EE2 removal above 99%) for safe disposal in lotic environments. This study can help in the discussion of micropollutant removal feasibility for future municipal wastewater treatment plants, considering that countries tend to adopt more restrictive measures and create laws that require higher percentages of EE2 removal in the near future.

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