Technologies for Pollution Control

Ozonation

KEYWORDS: Ozonation / Membranes for O_3/O_2 Separation / NETmix / Membrane Contactor / Water Treatment

New ozone (O_3)-technology solutions, offering means to its wider implementation by providing innovative cost-effective systems, including (i) customized membranes for the separation of O_3/oxygen (O_2) gas stream from the O_3 generator, enabling the recycling of the O_2 enriched gas stream back to the O_3 generator; (ii) low footprint O_3 side stream contacting train, integrating the static mixer NETmix or membrane contactor, able to enhance the O_3 mass transfer from the gas phase to the liquid phase.

Introduction

The increasing global health concerns due to the surge in urbanization, increasing water contamination, and increasing world industrialization are driving the ozone (O_3) technology market globally.

O_3 is usually produced by passing a stream of O_2 through a corona discharge system, which provides energy to convert O_2 to O_3. The reactive nature of O_3 typically limits the capability of O_3 generators to produce O_3 in concentrations greater than 15%, resulting in low yield and high O_3 production costs. High O_3 supply demands, the extended contacting time required in the reaction chamber, and the bulky size of the equipment (low gas-liquid mass transfer rates of O_3) also constitute a major impediment to the mass penetration of O_3 technology in the water treatment sector.

Our goal is to address these issues by developing disruptive O_3 technology for water treatment, including: (i) functionalized membranes for O_3/O_2 separation to obtain an O_3-enriched gas stream, enabling an O_3 generation at lower concentration while utilizing less specific power; simultaneously, the O_2 from the mixture of O_2/O_3 can be recovered and recycled back to the O_3 generator, thereby saving costs for the energy to produce O_2 and reduce the O_2 consumption; and (ii) the development of a low footprint O_3 side stream contacting train for water treatment; the integration of the O_3/O_2 separation unit with a pressurized static micro/meso-structured mixer (NETmix) or membrane contactor, enhancing the O_3 mass transfer from the gas phase to the liquid phase to 100% or very close to it, thus leading to an enriched water stream and resulting in a downstream highly compact reaction chamber.

This project brings together different academia (FEUP) and industry (SIMBIENTE, Enkrott, and AdP Valor) researchers with complementary competencies and expertise.

Current Development

Under the OZONE4WATER project (www.ozone4water.com), a gas separation setup was designed and constructed (Fig 1), comprising the following main components: (i) corona discharge O_3 generator; (ii) diaphragm pump to compress the O_3 stream; (iii) membrane modules (flat sheet or spiral-wound), incorporating the synthesized membranes; and (iv) O_3 analyzer. Various membranes with customized properties for O_2/O_3 separation are being prepared and tested, including functionalized asymmetric PVDF/PDMS flat membranes and a commercial symmetric PDMS spiral-wound membrane.

Mathematic models for the O_3/O_2 separation in two different membrane configurations and for the flow patterns that may appear in each one of the membranes (cross-flow in the SWM, and co-current, counter-current, and cross-flow in the HF membranes) were studied, allowing a better understanding of the influence of the different parameters on the efficiency of the separation. The overall analysis showed that, regardless of the membrane geometry, the effect of each parameter in the membrane performance is similar, i.e., it promotes the variation of the permeate composition in the same direction. The O_3/O_2 separation was also evaluated experimentally in the PDMS spiral wound membrane, resulting in O_3/O_2 selectivity of 1.3 %.

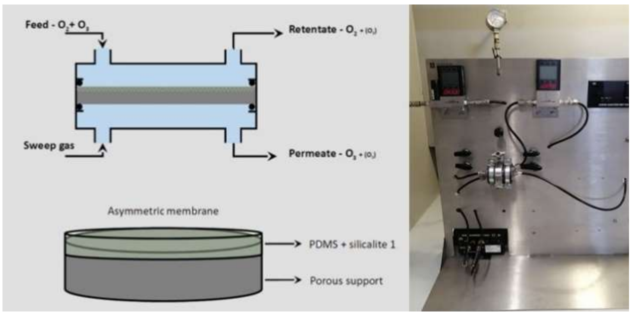
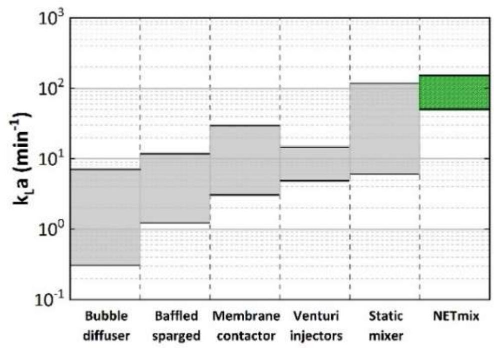
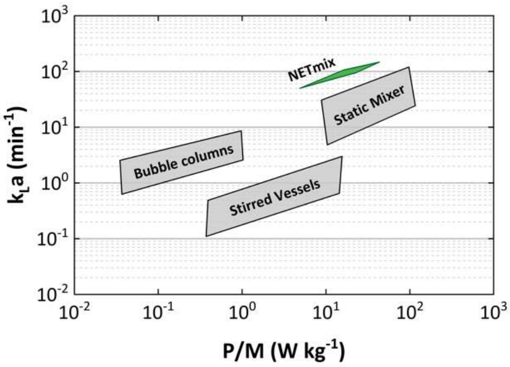


Fig 1. Scheme of flat module membrane and asymmetric membrane (left), and photograph of the gas separation setup (right).

The O_3 dissolution in the NETmix, as a function of reactor design parameters and operating conditions, was determined experimentally and validated by co compute fluid dynamics (CFD) modeling. Fig 2 shows the volumetric mass transfer coefficients (k_La) and energy consumption per mass of injected liquid (P/M) associated with a NETmix unit containing 8 columns and 29 rows of unit cells in an air-water system. The NETmix technology exhibits a high gas-liquid transfer performance whilst maintaining a low energy consumption when compared to other typical commercially available static mixers.



(a)

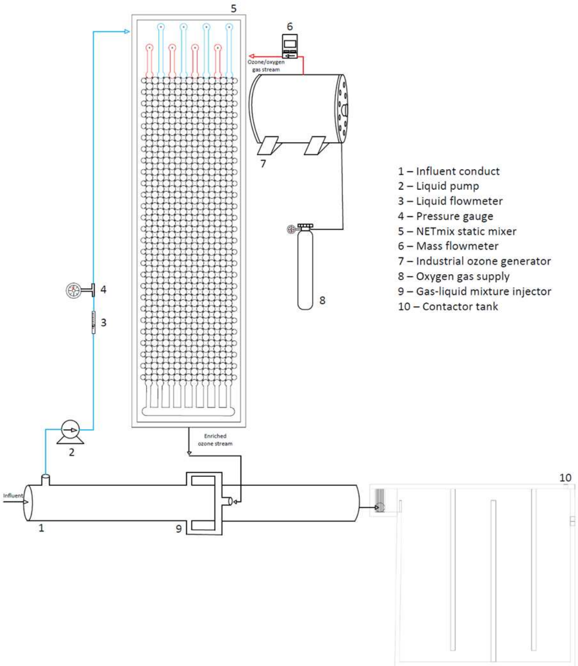


(b)

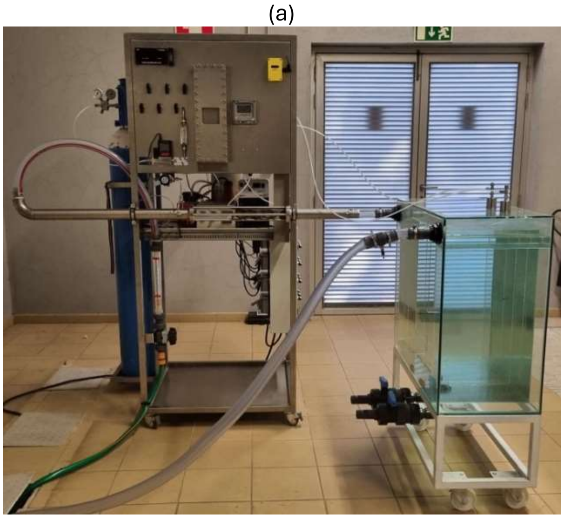
Fig 2. Measured k_La values (a) and P/M associated with the NETmix (b), in comparison with other technologies.

Based on CFD modeling, a new NETmix unit was designed and constructed comprising two innovative injection cones for the separate distribution of the entrance fluids at the mixer's inlet: each cone has a circular entrance and an elliptical base. Therefore, both liquid and gas phases are injected separately into four cylindrical chambers. Hence, the two phases interact solely at the micro/meso-structured network of unit cells characteristic of the NETmix technology. At the outlet, the exiting gas-liquid mixture is collected by an identical cone.

A prototype for water treatment using an O_3 side stream contacting train was designed and constructed (Fig 3). A portion of the main water flow (1) is split off into a side stream. Compressed O_3 gas and water (side stream) are injected in the NETmix pressurized reactor (1-5 bar), boosting O_3 dissolution. The supersaturated O_3-enriched water stream leaves the NETmix and is rapidly blended into the main water flow (9), providing the stable dissolved O_3 required to obtain the oxidation/disinfection credits in the contact/reaction chamber (10).



(a)



(b)

Fig 3. Scheme (a) and photograph (b) of the prototype.

Under the NOR-WATER project, a membrane O_3 contactor, operated under continuous mode, was developed and tested for the tertiary treatment of urban wastewater (UWW), targeting the removal of contaminants of emerging concern (CECs), bacterial disinfection, and toxicity reduction. This system relies on the homogeneous radial distribution of O_3 in the reaction zone by "titration" through a microfiltration tubular membrane, while the UWW swirls around the membrane and drags the O_3 microbubbles generated in the membrane shell-side. The ozonation tests were carried out with secondary-treated UWW collected in different seasons (winter and summer) and spiked with a mix of 19 CECs (10 µg L^{-1} each). For an O_3 dose of 18 g m^{-3}, removals above 80% or concentrations below the limit of quantification were obtained for up to 13 of the 19 CECs and reductions up to 5 log units for total heterotrophs and below the limit of detection for enterobacteria and enterococci. After ozonation, the abundance of antibiotic-resistant bacteria was reduced but not eliminated, and microbial regrowth after 3-day storage was observed. No toxic effect was detected on zebrafish embryos using a dilution factor of 4 for the ozonized UWW, and when granular activated carbon adsorption was subsequently applied, the dilution factor decreased to 2.

Future Perspectives

OZONE4WATER project: Validation of the ozonation prototype for the pre-oxidation of freshwater and tertiary treatment of urban wastewater, thereby allowing for access to safe and affordable drinking water and production of irrigation-grade treated urban wastewater, safe for reuse in agriculture; Environmental, economic, and social impacts of the technology.

NEWater project, supported by the Water4All program: Integration of ozonation, biofiltration, and membrane filtration for the treatment of secondary municipal wastewater, enabling the production of a high-quality permeate for electrolysis.

Related Sustainable Development Goals

Outputs

PhD Theses

[1] Pedro Henrique Presumido, Membrane processes for tertiary treatment of urban wastewaters: photocatalytic membrane reactor and ozone membrane reactor, PDEA, FEUP, 2023

Master Dissertations

[1] Cristiana Andreia Vieira Gomes, Intensification of ozonation processes for water treatment: ozone/oxygen separation by membrane, MIEQ, FEUP, 2019

[2] Paulo Henrique Marrocos de Oliveira, A low footprint ozone mixer based on the NETmix technology: CFD modelling and experimental validation, MIEQ, FEUP, 2021

Selected Publications

[1] P.H. Presumido et al., J. Environ. Chem. Eng. 10, 108671 (2022)

[2] P.H. Presumido et al., Sci. Total. Environ. 892, 164492 (2023)

[3] M.M. Pituco et al., Chem. Eng. Process.: Process Intensif. 194, 109566 (2023)

Team

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