

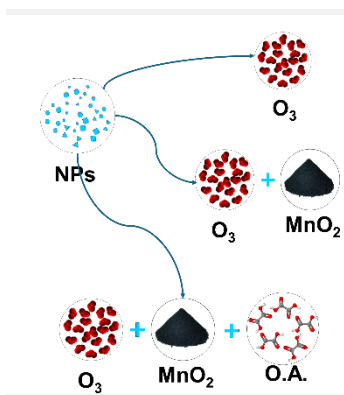
Study on assisted catalytic ozonation for the removal of nanoplastics from water

POSTER

Ph.D. Student: N

Journal: ESPR

V.F. Mello¹, J. Nieto-Sandoval², R.P. Cavalcante^{2,3}, C. Sans², M. Dezotti¹ (1) Programa de Engenharia Química/COPPE, Universidade Federal do Rio de Janeiro, Centro de Tecnologia, Cidade Universitária, Rio de Janeiro, Brasil. (2) Chemical Engineering and Analytical Chemistry Department, Faculty of Chemistry, Universitat de Barcelona, Martí i Franquès, 1, 08028 Barcelona, Spain. (3) Universidade Estadual de Campinas (UNICAMP), Faculdade de Tecnologia, Paschoal Marmo 1888, 13484332 Limeira, SP, Brazil rodrigpc@unicamp.br



Plastic pollution in the aquatic environment is an increasing concern, since micro- and nanoplastic particles have been found even in drinking water. Advanced technologies are needed to be developed to completely remove them, such as advanced oxidation processes (AOPs). Heterogeneous catalytic ozonation appears as a promising technology for that purpose and the use of common minerals such as clay, zeolites, and oxide minerals as catalysts can reduce costs associated with their application. Thus, this work aims to investigate the application of pyrolusite, as a catalyst, for polystyrene NPS removal from water. The catalytic ozonation in the presence of pyrolusite (0.5 g/L) coupled with oxalic acid (10 mg/L) resulted effective for NPs removal, achieving up to 75% of COD removal in 30 min reaction time at pH = 4.

Introduction

The occurrence of plastics in the aquatic environment represents an issue of increasing concern, as a result of the extensive consumption, associated with the incorrect disposal of plastic materials. In recent years, concern about the presence of plastics of smaller sizes, such as microplastic particles (MPs, particle size < 5 mm) and nanoplastics (NPs, particle size < 1 μm), in the aquatic environment has increased, even in drinking water [1].

In this sense, conventional processes applied in water treatment are ineffective for the completely removal of MPs and NPs. Thus, advanced technologies are needed to be developed to warrant their removal. Among these processes, ozonation has been applied for decades as disinfection step for drinking water in several European countries. However, single ozonation is not sufficient for the removal and mineralization of NPs. For such goal, the application of advanced oxidation processes (AOPs) such as heterogeneous catalytic ozonation appears as a promising technology [2].

This process consists on the application of catalysts in solid form with high stability in order to improve ozone decomposition mainly generating hydroxyl radicals, reducing operational costs and increasing the efficiency of the treatment. Furthermore, the application of heterogeneous catalysts in AOPs allows their recovery, avoiding secondary pollution generated by the homogeneous ones. In order to reduce catalysts costs based on metals, the employment of common minerals, such as clay, zeolites and oxide minerals as catalysts have been investigated.

In this context, this work aims to investigate the application of pyrolusite, consisting on MnO₂ and the most abundant manganese mineral in nature, as a catalyst in the catalytic ozonation process for the removal of polystyrene NPs from water.

Material and Methods

The ozonation experiments were conducted within a continuously stirred semi-batch reactor with initial NPs concentration fixed at 20 mg/L. Commercial polystyrene NPs of 140 nm were employed as target pollutants. The reaction occurred under ambient conditions (20°C, 1 atm) and initial pH of 4 for all the experiments. The reaction volume was fixed at 300 mL and the stirring velocity at to warrant the suspension of NPs. Pyrolusite concentration was studied in the range from 0 to 1.0 g/L. The catalyst was added to the NPs solution and left stirring for 15 min as an adsorption step before O₃ inlet. After the adsorption step, oxalic acid (OA) (0 – 10 mg/L) was introduced to the reaction from a stock OA solution of 10 g/L concentration. Ozone was continuously fed to the reactor medium through a porous stone at doses varying from 10 – 50 mg/min. Samples were collected at fixed intervals (0 – 30 min) and filtered by glass fiber membranes (0.45 μm average pore size) for the separation of the catalyst prior to TOC analyses.

Results and Discussion

Single ozonation experiments were conducted in order to evaluate the optimum ozone dose without the assistance of OA and MnO₂. The results obtained are summarized in Figure 1a. Single ozonation showed some potential for NPs degradation,

achieving a maximum of 35% TOC reduction in 30 min at 50 mgO₃/min. Even though the highest ozone dose studied was 5x the initial ozone dose it yielded only a 32% increase in TOC removal. This might be due to the saturation of the solution to ozone, which after a certain threshold it doesn't yield better results. Nonetheless, 50 mg/min was chosen for catalytic ozonation and assisted ozonation with oxalic acid.

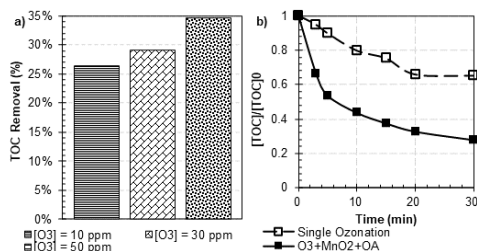


Figure 1. TOC removal during a) single ozonation experiments; b) comparison between single ozonation and assisted catalytic ozonation. [NP]₀ = 20 ppm; [O₃] = 50 mg/min; pH = 4.

Catalytic ozonation experiments were conducted in the presence of MnO₂ (0.125 - 1.0 g/L) and just a slight increase in TOC removal after 30 min reaction was achieved, being the highest removal 40% using 0.5 g/L. Moreover, the effect of OA concentration

were also studied from 1.25 mg/L to 10 mg/L, with 50 mg/min ozone dose in the absence of MnO₂. In this case, the increase in OA concentration led to a reduction in TOC removal capacity (see Table 1), due to the competition for ozone as scavenger of OA, reducing the removal efficiency. Finally, experiments were carried out for the ozonation of NPs in the presence of both MnO₂ and OA, as an assisted catalytic ozonation process. In this system, establishing the ozone dose at 50 mg/min, a higher efficiency obtained. The relation between MnO₂ and OA concentrations was studied, as described in Table 1. The application of 0.5 g/L of MnO₂ and 10 mg/L of OA led to the highest improvement in TOC removal up to 75% removal in 30 min (Figure 1b). Furthermore, an increase in the reaction time to 2 h, the mineralization grade was increased up to 80%. This synergistic effect on the catalytic ozonation with pyrolusite and oxalic acid could be attributed to the formation of a surface complex between MnO₂ and OA [3], as described by the equations below.

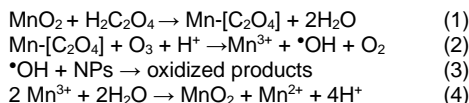


Table 1. TOC removals after 30 min of assisted catalytic ozonation varying OA and MnO₂ concentrations.

		[MnO ₂] (g/L)					
		0	0.125	0.25	0.5	0.75	1.0
[OA] (mg/L)	0	35 %	38%	38%	39%	39%	36%
	1.25	32%	63%	67%	69%	68%	63%
	2.5	31%	59%	72%	71%	65%	64%
	5.0	31%	60%	66%	72%	66%	65%
	10.0	30%	58%	59%	75%	72%	70%

Conclusions

Even though, separately, the processes of single ozonation, catalytic ozonation with pyrolusite and assisted ozonation with oxalic acid don't yield high efficiency on the removal of polystyrene NPs, a synergistic effect could be obtained from combining the processes, reaching a 75% maximum TOC removal within 30 min. The results show that the assisted catalytic ozonation process is a promising technology for the degradation of nanoplastics in water.

Acknowledgments

This research has been supported by the Spanish Ministry of Science and Innovation through the project PID2020-112674RB-I00.

This study was financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior – Brasil (CAPES) – Finance Code 001.

R.P. Cavalcante thank the financial support of the São Paulo Research Foundation (FAPESP) [grant number #2023/02506-0].

References

- [1] A. L. Andrady, Marine Pollution Bulletin, 119 (2017) 12.
- [2] Y. Li, C. Zhang, C. Shen, G. Jiang, and B. Guan, Environmental Research, 220 (2023) 115220.
- [3] H. Xiao, R. Liu, X. Zhao, and J. Qu, Journal of Molecular Catalysis A: Chemical, 286 (2008) 149.