3D-Printed Carbon Nanotubes-based Catalysts and their Stability for Oxalic Acid Ozonation

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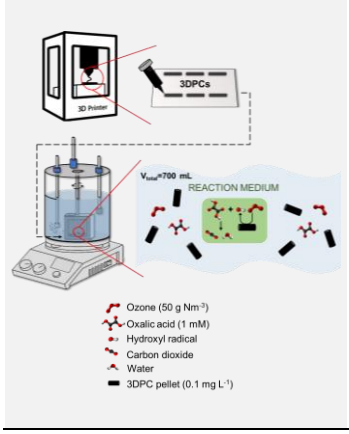

In recent years, various emerging organic pollutants, which are difficult to remove by traditional water treatment methods, have been identified in watercourses at concerning concentrations. Although catalytic ozonation processes have shown promising results in addressing this issue, most exploited catalysts are in powder form. The challenges of scaling up and handling these materials hinder their introduction into the industry. To overcome these limitations, additive manufacturing, also known as 3D-printing, emerges as a viable solution. This study focuses on the development of macrostructured carbon-based catalysts through Direct ink writing (DIW), and the evaluation of catalytic activity and stability of the obtained 3D printed catalysts (3DPCs). Multiwalled carbon nanotubes (MWCNT) combined with 20 wt.% of sodium carboxymethyl cellulose (CMC, binder) stand out as the most promising 3DPC, achieving 95 ± 1.0% of oxalic acid (OxAc) removal. Furthermore, this 3DPC maintained high catalytic activity after 5 cycles of reaction (93% removal of oxalic acid).

Introduction

Water pollution is a persistent issue demanding solutions for mitigation. Organic pollutants (OPs) pose a significant challenge to conventional water treatment methods because they show incapacity to remove them [1]. Advanced techniques like ozonation offer better results but struggle with refractory compounds like oxalic acid, a byproduct of OP degradation. Heterogeneous catalytic ozonation, particularly with carbon catalysts, shows promise in enhancing removal efficiency [2,3]. However, traditional powder catalysts face scalability and handling issues in industrial settings. 3D printing offers a solution by transforming powder catalysts into macrostructured forms, adaptable to various conditions [4]. This study focuses on developing macrostructured carbon-based catalysts through Direct Ink Writing (DIW). By incorporating pseudo-plastic behaviour into the ink through binder compounds like CMC and sodium alginate (ALG), which are environmentally friendly compounds, gel-like structures can be formed in the presence of water. The catalytic performance of 3DPCs MWCNT-based catalysts was assessed in a semi-batch reactor for OxAc catalytic ozonation in the liquid phase.

Material and Methods

Commercial MWCNT were used as catalysts, CMC and ALG were used as binders and deionized water was used as a solvent to prepare the printing inks. Firstly, MWCNT were mixed with each binder at different mass ratios (5:1 and 1:1) through mechanical stirring for 30 min for 5:1 samples and 60 min for 1:1 samples. Then, the resulting mixtures were wetted drop by drop and stirred until a workable rheology for printing was obtained (printing ink). 3DPCs pellets were developed by DIW (Ultimaker 2+ 3D-printer with an extrusion system, Discov3ry), putting the prepared inks into a syringe, and the printing process was carried out by applying controlled pressure. The 3DPCs were named with the following code: MWCNT_XY, wherein X corresponds to the mass fraction of binder (20 or 50 wt.%) and Y is CMC or ALG.

N_2 physisorption at -196 °C, scanning electronic microscopy (SEM) and elemental analysis were performed to characterise the 3DPCs, and ionic chromatography (IC) to evaluate the stability of 3DPCs after ozonation.

The catalytic performance was evaluated in a semi-batch reactor for OxAc catalytic ozonation, as schematized in the graphical abstract, and the concentration of OxAc was monitored by HPLC with a UV–Vis detector.

Results and Discussion

All the established 3DPCs were successfully printed varying the type and amount of binder. Textural properties determined by N_2 physisorption at -196 ºC revealed binder obstruction in inner cavities of MWCNT, reducing specific surface area. SEM analysis confirmed the obstruction effect provoked by the binder due to the formed gel-like structures. In **Figure 1**, it is possible to see a huge difference between pristine MWCNT and MWCNT_20CMC

which shows a kind of filling between the voids of nanotubes.

Regarding the catalytic performance, it was observed that MWCNT_50CMC was unstable in the presence of ozone and with the vigorous forces of stirring because this 3DPC crumbled into powder over the reaction, and that permitted to exclude this catalyst for future tests. The other catalysts showed better mechanical stability. **Figure 2 a)** presents the removal efficiency of OxAc through a heterogeneous catalytic ozonation reaction using stable 3DPCs. Furthermore, single ozonation (as non-catalytic) experiment was performed for comparison. MWCNT_50ALG demonstrated weak catalytic activity (worse than single ozonation) and that can be related to some active sites blockage by the increase of binder amount to 50 wt.%, which permitted the formation of too many gel-like structures. Considering the 3DPCs with 20 wt.% of binder, using ALG instead CMC as a binder, negatively affects the catalytic activity once MWCNT_20ALG demonstrated similar removal efficiency as single ozonation process and MWCNT_20CMC achieved 95 ± 1.0% after 180 min of reaction. This last 3DPC demonstrated to be the most promising to carry out reproducibility and reutilization tests. **Figure 2 b)** shows the removal efficiency of OxAc in 5 cycles of MWCNT_20CMC reutilization.

Promising results during cyclic experiments were obtained, which can be explained by evaluating the stability of MWCNT_20CMC. For that, elemental analysis was carried out to determine the amount of carbon, hydrogen, nitrogen, sulphur and oxygen before and after the reaction and the obtained results showed slight differences. IC analyses were performed to determine the amount of Na^+ that could be leached from the binders, indicating some degradation phenomena. The obtained results showed no presence of Na^+ (below the LOD=0.1 ppm) after 5 min and 180 min of reaction. These characterizations proved the physical and chemical stability of this catalyst.

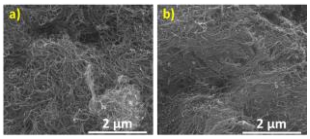

Figure 1. SEM Micrographs of a) pristine MWCNT and b) MWCNT_20CMC

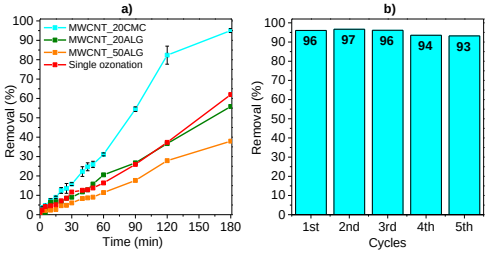

Figure 2. Removal of oxalic acid through heterogeneous catalytic ozonation using stable 3DPCs a) and catalytic performance of MWCNT_20CMC after 5 cycles of oxalic acid ozonation

Conclusions

Advances in the development of macrostructured catalysts for water treatment were obtained in this study using commercial MWCNT and two environmentally friendly binders for OxAc heterogeneous catalytic ozonation. TGA validated the synthesis method of 3DPCs, and SEM analysis showed the important role of a binder in gathering the MWCNT particles to obtain mechanically stable 3D structures. Although the presence of the binder decreased the specific surface area, CMC showed that it affects the availability of active sites less than ALG. MWCNT_20CMC achieved promising removal efficiency of OxAc with reproducible results (95 ± 1.0% after 180 min) and catalytic stability after 5 cycles of reutilization.

Acknowledgements

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References

[1] Ana M. Gorito, Ana R. Ribeiro, C. M. R. Almeida, and Adrián M. T. Silva, *Environmental Pollution* 227 (2017) 428.

[2] O. S. G. P. Soares, A. G. Gonçalves, J. J. Delgado, J. J. M. Órfão, and M. F. R. Pereira, *Catalysis Today* 2492015 (2015) 199.

[3] J. Restivo, O. S. G. P. Soares, and M. F. R. Pereira, in *From Nano- to Macrostructured Carbon Catalysts for Water and Wastewater Treatment*, M. Piumetti and S. Bensaid, (Eds.), Switzerland, Springer, 2021, 273.

[4] J. Zhu, P. Wu, Y. Chao, J. Yu, W. Zhu, Z. Liu, and C. Xu, *Chemical Engineering Journal* 134341 (2021).

[5] M. J. Regufe, A. F. P. Ferreira, J. M. Loureiro, A. Rodrigues and A. M. Ribeiro, *Microporous and Mesoporous Materials* 278 (2019) 403.