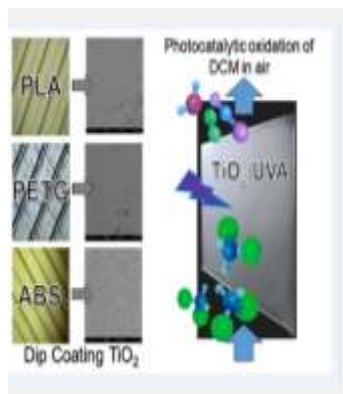


C. Passalia^{1,2}, M Flores^{2,3}, C. Dopazo^{2,3}, M.Labas^{1,2,3}, R. Brandi^{1,2,3} (1). Facultad de Ingeniería y Ciencias Hídricas, Universidad Nacional del Litoral (FICH-UNL). Ciudad Universitaria, 3000 Santa Fe, Argentina. cpassalia@gmail.com (2) Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Argentina..(3.) Instituto de Desarrollo Tecnológico para la Industria Química, INTEC (CONICET-UNL). Güemes 3450, 3000, Santa Fe, Argentina.



An experimental comparative study of three different 3D printed plastic samples as support materials for gas phase photocatalytic applications is presented. 3D printing allows precise control of the active components and expansion of the specific surface area of catalytic and photocatalytic materials. It is also capable of optimising and moulding complex substrate structures and reducing manufacturing costs. The photocatalytic oxidation of dichloromethane in air was studied using PLA, ABS and PETG in a laboratory-scale continuous reactor. The three commercial materials were investigated for catalyst loading and adherence, optical properties and catalytic activity under UVA radiation. Titanium dioxide photocatalyst was immobilised on the flat plate samples by dip coating cycles. The results indicate the feasibility of dichloromethane elimination in the three cases. The conversion of the pollutant showed an increase with the catalyst layers.

Introduction

The presence of indoor pollutants such as dichloromethane poses a significant public health challenge due to its potential adverse effects on indoor air quality [1]. Prolonged exposure to these contaminants can lead to adverse health effects, including respiratory irritation, headaches, nausea and even chronic respiratory diseases. In this sense, the concentration of indoor compounds need to be controlled. Typical technologies include filtration and adsorption, while destructive processes such as photocatalysis are also available. Photocatalytic devices can make use of 3D printing, which offers a cost-effective method for producing substrates for photocatalytic thin films of titanium dioxide (TiO₂), suggesting great potential in photocatalytic processes.

The ability of 3D printing to produce structures with specific shapes and features can lead to the optimization of photocatalytic reactors. This includes the creation of structured surfaces or composite materials that enhance the exposure of catalysts to light and increase photocatalytic activity. The aim of this study is to evaluate and compare the performance of different substrate polymers for a photocatalytic reactor using titanium dioxide (TiO₂) and near-UV radiation. The selected target pollutant for activity testing is dichloromethane (DCM).

Materials and Methods

Three printing materials, namely PLA, ABS and PETG, were selected on the basis of their market availability. Rectangular samples of each plastic were printed. Different sample sizes were used for the determination of catalyst loading, catalyst adhesion, optical properties and photocatalytic activity tests. The TiO₂ catalyst (Aeroxide P25) was immobilised on the polymeric support by a series of dip-coating cycles in a 100 g/L aqueous suspension. Catalyst loading and adherence were determined by gravimetric methods. The transmittance

and reflectance of the samples were determined in an integrating sphere spectrophotometer (Optronic OL50). For the photocatalytic activity tests, the coated samples were placed in an acrylic sandwich reactor. In order to avoid mass transfer limitations to the catalyst surfaces, the coated plastic flat plate is placed at a distance of 3 mm from each reactor window. The UVA radiation sources are two sets of actinic lamps (Sylvania F15W T12) providing a uniform flux across the reactor window. The reactor (figure 1) operates in continuous mode, in a single pass with no recycle.

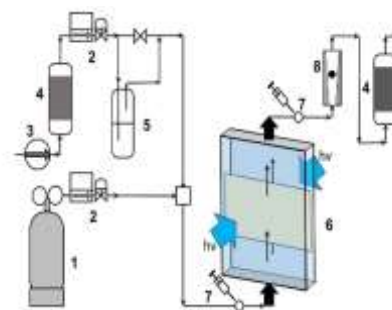


Figure 1: experimental device setup. 1) cylinder with DCM in air mixture; 2) mass flow controller; 3) air compressor; 4) air filter with activated carbon and silica gel; 5) humidifier; 6) photo-reactor; 7) sample port; 8) rotameter

A continuous stream of air is fed into the reactor with a known concentration of dichloromethane and relative humidity. The dichloromethane gas was supplied on-line from a custom-built pressurised gas cylinder. The desired concentration of dichloromethane at the reactor inlet is achieved by appropriate regulation of the mass flow controllers. A series of experiments were carried out by

varying the substrate material and the number of catalyst coating cycles (4,8,12 cycles). To make the results comparable, all operating variables were kept constant: inlet dichloromethane concentration (52.6 ± 3.4 ppmv), total flow rate 1 L min^{-1} , radiation level 28 W m^{-2} and relative humidity $15,1 \pm 2 \%$.

Results and Discussion

In all three plastic materials similar results were achieved concerning the mass of TiO_2 per unit area. PLA showed the highest load per unit area. PETG, however, had a lower capacity for adding catalysts.

To assess the degradation of DCM within the reaction device, a series of blank tests were conducted. An analytical screening of the air supplied by the purification system revealed no peaks in the chromatogram, indicating the absence of unwanted substances. Subsequently, a blank test for photolysis was executed by circulating the DCM mixture in the reactor with an uncoated plate (lacking catalyst) and subjecting it to maximum irradiation power. Finally, a test was conducted using TiO_2 -coated samples in the reactor with the lamps turned off.

The photo oxidation tests performed with dichloromethane showed the feasibility of organic removal from air (table 1). Table 1 shows that increasing the number of coating cycles results in higher conversions, but the intrinsic performance does not follow the same trend. According with the results these thermoplastic materials, have great potential in the reactor design and optimization in the field of environmental and chemical engineering in general, for the elimination of chemical pollutants by advanced oxidation processes.

Table 1. DCM conversion

| Material | coating cycles | DCM conversion (%) | TiO2 mass, (mg) |
|----------|----------------|--------------------|-----------------|
| ABS | 4 | 8.7 ± 1.4 | 189 |
| | 8 | 15.7 ± 1.6 | 501 |
| | 12 | 25.3 ± 4.5 | 1008 |
| PETG | 4 | 8.9 ± 1.3 | 228 |
| | 8 | 14.2 ± 2.0 | 459 |
| | 12 | 18.5 ± 3.5 | 873 |
| PLA | 4 | 14.8 ± 3.1 | 285 |
| | 8 | 17.3 ± 2.4 | 867 |
| | 12 | 23.3 ± 2.7 | 1395 |

Conclusions

In this investigation, which focuses on gas-phase pollution control, three distinct polymers (PLA, ABS, and PETG) were tested as potential substrates for immobilizing photocatalysts. PLA emerged as the most promising candidate, exhibiting superior characteristics in terms of load capacity, photocatalytic efficiency, and also it is biodegradable. This study provides a foundation and a method for upscaling the photocatalytic reactor to treat larger air volumes using functionalized 3D printed components. The findings are significant because they demonstrate a straightforward and effective process for functionalizing plastics, eliminating the need for complex methodologies involving the dispersibility of TiO_2 filler within the PLA matrix.

Acknowledgments

The authors would like to thank the Agencia Nacional de Investigaciones Científicas y Técnicas, Consejo Nacional de Investigaciones Científicas y Técnicas and the Universidad Nacional del Litoral for their financial support.

References

- [1] JE. Lee , SO Yong , D Tsang, HY Song, S Jung , YP Park YP (2020) *Sci Total Environ* 719:137405. doi: 10.1016/j.scitotenv.2020.137405 (2020).
- [2]M Srivastava, S Rathee S. *Prog Addit Manuf* (2022) 7:261–287. doi: 10.1007/s40964-021-00229-8