

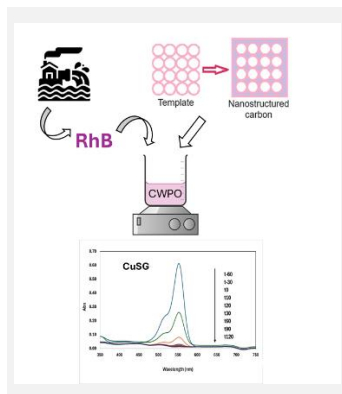
## Degradation of Rhodamine B by Advanced Oxidation Processes on Copper Supported Over Nanostructured Carbons

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**A.R. Mallmann<sup>1</sup>, O. Bomfim<sup>2</sup>, F.M. Mayer<sup>1</sup>, M.C. Rangel<sup>1,3</sup>.** (1) Institute of Chemistry, Federal University of Rio Grande do Sul, Porto Alegre, RS, Brazil, [amandamallmann000@gmail.com](mailto:amandamallmann000@gmail.com). (2) Polytechnic School, Federal University of Bahia, Salvador, Bahia, Brazil. (3) Institute of Chemistry, Federal University of Bahia, Salvador, Bahia, Brazil.



Copper supported on nanostructured carbons obtained from sucrose or glycerol were studied as new catalysts for Catalytic Wet Peroxide Oxidation (CWPO) of rhodamine (RhB), a model molecule for dyes. The supports were prepared using SBA-15 as template. All samples presented high specific surface areas, except for the copper impregnated sample prepared from sucrose. The support prepared from sucrose showed higher micropore volume compared to the template. The solids prepared from glycerol removed the highest amount of rhodamine, with the catalyst containing copper being the most efficient among the materials. All samples were able to completely remove the pollutant, except the nanostructured carbon-supported copper prepared from sucrose.

### Introduction

In the last decades, as the society developed and the population rate increased, the amount of contaminated wastewater has achieved a concerning level. The domestic, agricultural, and industrial use of water generates high volumes of pollutants that are not appropriately disposed, in most cases. A critical example is the textile industry, which generates a massive amount of toxic compounds originating from dyes. Rhodamine B (RhB), for instance, is a non-biodegradable and toxic dye widely used in the industry [1]. Among the several methods for removing such contaminants, the advanced oxidation processes (AOPs) have shown high efficiency by degrading them into less toxic organic compounds or by complete mineralization. Catalytic Wet Peroxide Oxidation (CWPO) is a combined technique of hydrogen peroxide oxidation with a heterogenous catalyst, in mild conditions. In this study, nanostructured carbons were evaluated in CWPO to remove RhB.

### Material and Methods

SBA-15, used as the template for preparing the support, was prepared according to [2]. Sucrose (SS) [3] and glycerol (SG) [4] were used as sources of carbon. The copper catalysts (10% Cu) were obtained by wet impregnation, using a copper chloride aqueous solution (CuSS and CuSG). The materials were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD) and specific surface area ( $S_{BET}$ ) and porosity

measurements.

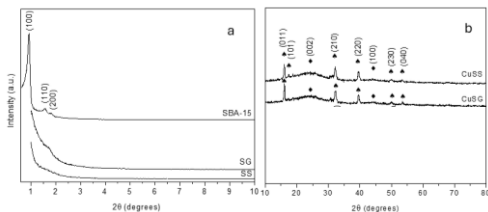
The RhB solution was prepared by dissolving 15 mg of RhB in 1.0 L of distilled water. After homogenization, the pH was lowered to 4.0 using a sulfuric acid solution ( $0.1 \text{ mol L}^{-1}$ ).

The evaluation of the catalysts in the CWPO of RhB was performed by adding 10 mg of catalyst to 100 mL of RhB solution, under stirring. After 1 h of adsorption, 1 mL of hydrogen peroxide was added, initializing the oxidation ( $t=0$ ). Throughout the reaction, 4 mL aliquots were collected at 0, 10, 20, 30, 60, 90, 120 and 180 min, while during the adsorption, aliquots were taken each 30 min. The aliquots were filtered, diluted with distilled water, and analyzed in a UV-Vis spectrometer (750-350 nm).

### Results and Discussion

Figure 1a presents the diffractograms at low angles for the template (SBA-15) and for the supports. Three well resolved peaks can be identified for the SBA-15, related to (100), (110) and (200) planes. They are typical of the two-dimensional hexagonal space group  $p6mm$  and of the mesoporous silica structure. The supports only presented the (100) plane, indicating that most of the ordered pores were lost. This finding suggests the collapse of the carbon structure, leading to the creation of slit-shape pores with different diameters. Figure 1b shows the diffractograms for the catalysts. Peaks related to atacamite,  $\text{Cu}_2\text{Cl}(\text{OH})_3$ , were found for both samples. The diffractograms also show

amorphous halos around 23° and 43° related to the (002) and (100) planes respectively, characteristic of graphite.



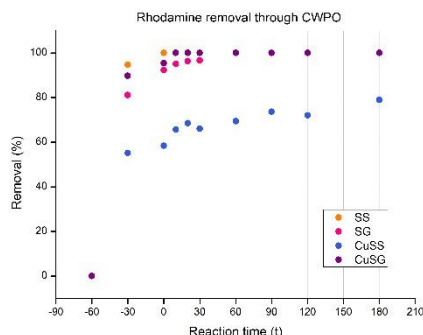
**Figure 1.** Diffractograms for the a) template (SBA-15) and for the supports at low angles ( $0.6^\circ \leq 2\theta \leq 10^\circ$ ) and for the b) catalysts ( $10^\circ \leq 2\theta \leq 80^\circ$ ), respectively.

Table 1 presents the specific surface area and pore volume and size of the template, supports and catalysts. Both SS and SG showed specific surface areas higher than the template, probably due to the porosity generated in the synthesis - specifically, the carbonization and template removal. The CuSG sample showed the same specific surface area of its support, within the error of the measurement. The CuSS sample showed the lowest specific surface area, indicating that the impregnation obstructed a large amount of pores. These results implied that the shape and size of pores impact on the copper dispersion. In comparison to the template, both SS and SG samples showed smaller pore size and volume, which is related to the contraction of the material during the carbonization of the carbon precursor, resulting in the shrinking of the porous structure and consequently, smaller pore size than the template.

**Table 1.** Specific surface areas ( $S_{BET}$ ), mesopore diameter ( $D_{meso}$ ), mesopore volume ( $V_{meso}$ ) and micropore volume ( $V_{micro}$ ) of the samples.

Sample	$S_{BET}$ ( $m^2 g^{-1}$ )	$D_{meso}$ (nm)	$V_{meso}$ ( $cm^3 g^{-1}$ )	$V_{micro}$ ( $cm^3 g^{-1}$ )
SBA-15	810	6.492	1.146	0.0352
SS	878	5.221	1.056	0.0561
SG	1106	3.870	0.574	0.00725
CuSS	404			
CuSG	1115			

Figure 2 presents the RhB removal through CWPO throughout reaction. SS sample showed the highest adsorption capacity, which can be related to the larger micropore volume of the material when compared to the SG and to the high surface area. All samples were able to completely remove the RhB in 120 min, except the CuSS sample. While the support shows as a great adsorbent, the catalyst obtained from SS presented the lowest specific surface area, thus affecting the catalyst efficiency. SG and CuSG samples exhibited exceptional adsorption capacity for the pollutant removal. The metal impregnation enhanced the removal by oxidation on copper, enabling the material to completely remove the RhB in a shorter reaction time.



**Figure 2.** Rhodamine removal through CWPO.

## Conclusions

The removal rates of the catalysts showed evident relation to the specific surface area and to copper. The CuSS sample had the lowest specific surface area, thus decreasing the catalytic activity. The CuSG sample showed the highest specific surface area, and the best performance during reaction. This study supported the hypothesis that the nanostructured carbons work as great catalysts for the effluent treatment.

## Acknowledgments

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## References

- [1] D. Vasu, et al. J. Ind. Eng. Chem. 133 (2024) 419–427.
- [2] D. Y. Zhao, et al. J. Am. Chem. Soc. 120 (1998) 6024–6036.
- [3] S. Jun, et al. J. Am. Chem. Soc. 122 (2000) 10712–10713.
- [4] M. Ignat, et al. Carbon 48 (2010) 1609–1618.