

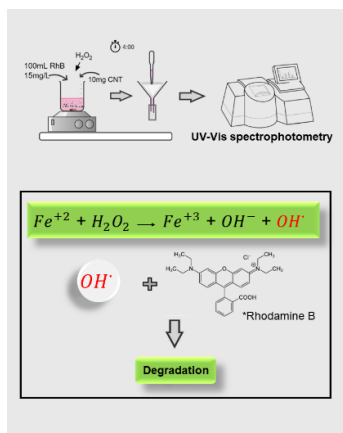
Iron Oxide Catalyst Supported on Carbon Nanotubes for the Degradation of a Persistent Pollutant.

POSTER

Ph.D. Student: N

Journal: NONE

V. Drügg¹, G. Saboia¹, F. M. Mayer¹, M. C. Rangel¹, M.C. Alves¹, G. Chacón², M. Vasconcellos³, J. Morais³. (1) Institute of Chemistry, Federal University of Rio Grande do Sul, Porto Alegre, Brazil. vitdrugg@gmail.com. (2) Instituto of Chemical Technology, Valencia, Spain. (3) Institute of Physics, Federal University of Rio Grande do Sul, Porto Alegre, Brazil.



Due to the global demand for recycling water, there is a need to develop effective methods for the degradation of pollutants, especially those persistent, such dyes. For this purpose, carbon nanotube supported-iron oxide (1, 4 and 8% Fe) catalysts were prepared by wet impregnation, characterized by various techniques and evaluated in promoting the Fenton reaction to degrade Rhodamine B (RhB), an organic and recalcitrant pollutant. The removal efficiency was quantified using UV-Vis spectroscopy and the degradation was evaluated by analyzing the products by UHPLC-QTOF-MS system. The catalysts were efficient to remove the pollutant, achieving a maximum removal of 90,1% when the 10% iron catalyst was employed. However, the catalyst with 5% Fe led to a close removal (88.3%) and is the most economic one.

Introduction

In the current pollution scenario, there is a great concern for the environment protection. In this context, Rhodamine B (RhB), a red dye widely used in the textile industry and in microscopic labeling applications [1], is a concerning pollutant due to its carcinogenic properties and resistance to conventional water treatment methods [2]. Advanced oxidation methods are effective in degrading organic pollutants, among which the Fenton method stands out as one of the simplest and most efficient one. The process uses ferrous ions to decompose hydrogen peroxide to generate hydroxyl radicals able of oxidizing organic matter [3]. Aiming to find alternative catalysts for degrading Rhodamine B, carbon nanotube-supported iron oxide catalysts were studied in this work. Carbon nanotubes (CNTs) are promising materials due to the high specific surface area, which can be functionalized to increase the amount of active sites and facilitate the formation of small iron oxide particles [4]. Furthermore, the use of support makes the removal of the catalyst from the treated effluent easier.

Material and Methods

Iron oxide catalysts supported on carbon nanotubes were obtained by wet impregnation of commercial CNTs, using iron nitrate solution. Samples with 1, 5 and 10 wt% Fe were obtained and named as CNT1,

CNT5, CNT10.

The samples were characterized by flame atomic absorption spectrometry, thermogravimetry, nitrogen physisorption, X-ray diffraction, Mössbauer spectroscopy, Raman spectroscopy, X-ray photoelectron spectroscopy, and scanning electron microscopy.

The degradation experiments were performed using a RhB (15 mg/L) solution, acidified to pH 4 with sulfuric acid solution (0.1 mol/L). The Fenton reaction was carried out in a beaker (250 mL) containing 100 mL of the RhB solution (15 mg/L, pH 4) and 10 mg of catalyst. Hydrogen peroxide (1000 μ L) was added after 60 min of reaction to initiate the Fenton reaction. The reaction takes 180 min at room temperature. The identification of the degradation products was performed using an ultra-performance liquid chromatograph coupled to a time-of-flight mass spectrometer (UHPLC-QTOF-MS)

Results and Discussion

The amount of iron on the CNT1, CNT5, and CNT10 catalysts was 1.01%, 4.03%, and 8.00%, respectively. The specific surface area and pore volume of the CNTs decreased after impregnation, probably due to pore obstruction by iron particles. X-ray diffraction patterns showed a peak at 25.6°, corresponding to the (002) reflection plane of the hexagonal graphite lattice. The formation of hematite and magnetite phases was detected for all

catalysts. Iron oxide particles appeared as superparamagnetic for the CNT1 and CNT5 samples, indicating sizes smaller than 10 nm, while the CNT10 sample the particles were bigger. Scanning electron microscopy shows that the materials are arranged in large packs of nanotubes and exhibit fibrous/tubular structures.

RhB degradation can be observed in Fig. 1(a), which shows the removal as a function of time. Before the addition of hydrogen peroxide ($t = 0$ min), the CNT, CNT1, CNT5, and CNT10 catalysts removed 53.7%, 64.5%, 66.2%, and 66.5% of the pollutant, respectively, indicating high RhB adsorption capacity of all catalysts. The addition of hydrogen peroxide did not significantly alter the pollutant removal over the iron-free catalyst (CNT), while for the CNT1, CNT5, and CNT10 samples, the removal increased to 78.4%, 88.3%, and 90.1%, respectively. This indicates that the pollutant was oxidized by the Fenton reaction. The catalysts with the highest iron content (CNT10) removed the most amount of pollutant, as shown in Fig. 1(b). However, the CNT5 sample demonstrated the highest cost/benefit ratio, as it achieved removal close to that of CNT10, but with lower iron content, resulting in savings during the catalysts production.

The aliquots collected at different reaction times ($t = 0, 60, 90,$ and 180 min) were analyzed by UHPLC-

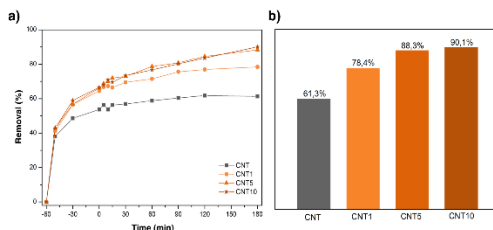


Figure 1. (a) Performance of the catalysts in removing RhB; (b) Total removal of RhB after 240 min.

QTOF-MS, and the degradation products of RhB were identified. The intermediates of the decomposition of RhB (m/z 443) with m/z values of 459, 415, 387 were found. The 415 and 387 were identified as N, N-diethyl-N'-ethyl rhodamine and N, N-diethyl rhodamine, respectively. These intermediates are formed in the first stage of degradation of RhB through a stepwise N-deethylation pathway [5]. The central carbon of RhB was also attacked by $\text{HO}\cdot$ radicals to form the hydroxylated product ($m/z = 459$) via the additive reaction [5]. Evaluating acute and chronic toxicities of by-products towards Fish, Daphnia, and Green Algae indicates that the toxicity of by-products with $m/z > 223$ is high [6].

Conclusions

The catalysts with different iron contents showed a decrease in specific surface area and pore size, attributed to the blockage of iron oxide particles. Hematite and magnetite phases were formed for all samples. The iron oxide particles in the CNT1 and CNT5 samples exhibited superparamagnetic properties, indicating average sizes smaller than 10 nm. RhB degradation experiments demonstrated high initial adsorption capacity for all samples. The catalysts with the highest iron content showed the greatest efficiency in the RhB removal, being the CNT10 catalyst the most effective. However, the CNT5 catalyst offered the best balance between removal efficiency and iron content, suggesting cost savings in the catalyst production. The main degradation products identified have high molecular mass and still present high toxicity.

Acknowledgments

We would like to thank the National Petroleum Agency (ANP) and the National Council for Scientific and Technological Development (CNPq).

References

- [1] Al-Buriahi, A.K. et al. Elimination of rhodamine B from textile wastewater using nanoparticle photocatalysts: a review for sustainable approaches. *Chemosphere* 287, 132162, 2022.
- [2] Opeyemi, T.O.; Oyewo, O.A.; Onwudiwe, D. C. Adsorption and photocatalytic removal of Rhodamine B from wastewater using carbon-based materials. *FlatChem* 28, 100277, 2021.
- [3] Deng, Y.; Zhao, R. Advanced Oxidation Processes (AOPs) in Wastewater Treatment. *Current Pollution Reports* 1, 167-176, 2015.
- [4] Zhang, J. et al. Recent progress on carbon-nanotube-based material for photocatalytic applications: a review. *Solar RRL* 6(9), 2200243, 2022.
- [5] Zhou, C. et al. Kinetic and Mechanistic Study of Rhodamine B Degradation by H_2O_2 and $\text{Cu}/\text{Al}_2\text{O}_3/\text{g-C}_3\text{N}_4$ Composite. *Catalyst* 10, 317, 2020.
- [6] Mohod, A.V. et al. Degradation of Rhodamine dyes by Advanced Oxidation Processes (AOPs) – Focus on cavitation and photocatalysis - A critical review. *Water Resources and Industry* 30, 100220, 2023.