

Enhanced adsorptive removal of rhodamine B by MnO₂ and Zn-modified MnO₂: decoupling adsorption and photocatalysis

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Abstract

There is significant interest in adsorption and photodegradation studies due to the growing need to remove dyes and organic pollutants from water sources efficiently. This study investigated the removal of Rhodamine B (RhB) from aqueous solutions using MnO₂ and Zn-modified MnO₂ as adsorbents and photocatalysts. The materials were synthesized and characterized using XRD and FTIR. Their RhB removal and photodegradation efficiencies were evaluated under UV-Vis irradiation from an Osram ultra-vitalux 300 W 230 V AC lamp (emitting UVA and UVB radiation). Results indicated that light radiation did not influence the removal process for both Mn-based materials. While MnO₂ removed only about 10% of RhB, Zn-modified MnO₂ exhibited exceptional adsorption capacity, achieving over 98% RhB removal within 15 minutes. Therefore, our findings indicate that adsorption is the primary mechanism for RhB removal by MnO₂-Zn, rather than photocatalysis. These data highlight adsorption's crucial, yet often overlooked, role in photodegradation studies. Furthermore, this work underscores the importance of developing efficient adsorbents for the remediation of dyes and organic pollutants in water treatment processes.

Keywords: Manganese oxides, wastewater, zinc doping.

1. Introduction

The removal of organic pollutants from aqueous solutions has been extensively studied, focusing on adsorption and photodegradation methods. Adsorption, renowned for its efficiency and simplicity, captures many contaminants, including dyes like Rhodamine B [1,2]. Conversely, photodegradation harnesses light energy to mineralize pollutants through redox reactions catalyzed by suitable materials. [3].

Although often portrayed as an independent process, adsorption is critical in photodegradation [4]. Adsorption can act as a necessary initial step, where the pollutant is concentrated on the surface of the photocatalyst before degradation occurs [5]. This step, however, is only sometimes fully understood or adequately considered in many photodegradation studies, which can lead to misleading interpretations of the processes'

efficiency [6].

Manganese oxides (MnO₂) have attracted significant attention for their potential as both adsorbents and photocatalysts, offering a promising future for water treatment processes [7,8].

Their structural versatility and redox properties facilitate contaminant capture and potential degradation. Modifying MnO₂ with metals such as zinc can further enhance these capabilities, promising improved pollutant removal. However, a comprehensive understanding of the relative contributions of adsorption and photocatalysis is crucial for accurate evaluation and understanding of the interactions between pollutants and the materials employed [9].

This study aims to elucidate the efficiency of MnO₂ and Zn-modified MnO₂ in removing Rhodamine B (Rh-B) from aqueous solutions at pH 5.5, focusing on the adsorption mechanism.

By characterizing the materials and assessing their performance as adsorbents and photocatalysts, we seek to decouple the adsorption and photodegradation processes to gain deeper insights into the underlying mechanisms.

2. Experimental

2.1 Materials

Analytical-grade commercial reagents were used as received, and distilled water was employed for solution preparation. The reagents included potassium permanganate (Merck), manganese sulfate monohydrate (Merck), 65% nitric acid (Merck), zinc chloride (Merck), rhodamine B (CAS 81-88-9, IBQSFAR).

2.2 Synthesis and characterization of MnO₂ and MnO₂-Zn (15%)

MnO₂ was synthesized by reacting an aqueous solution of potassium permanganate (0.037 M, 0.0037 mol) with manganese sulfate monohydrate (0.0555 M, 0.001665 mol) in the presence of nitric acid (3 mL) [10,11].

For the Zn-modified MnO₂, a 0.01 mol L⁻¹ (0.00133 mol) zinc chloride solution was added to the manganese sulfate solution prior to the reaction, achieving a 15% Zn modification. The mixture was refluxed at 100°C for 24 hours, followed by filtration, washing, and drying to obtain the final Zn-modified MnO₂ material. The dried materials were then characterized by X-ray diffraction (XRD) and FTIR spectroscopy, using KBr pellets.

2.3 Adsorption and Photodegradation methodologies

The removal of Rhodamine B using MnO₂ and MnO₂-Zn(15%) was investigated through three experimental setups: photolysis, adsorption, and photodegradation. For each experiment, 60 mL of a 1.25×10^{-5} M Rhodamine B solution was used.

In the photolysis experiment, the dye solution was exposed to Uv-vis irradiation, using an Osram ultra - vitalux 300 W 230 V AC (280 – 400 nm). For adsorption, 50 mg of each manganese oxide was added to the dye solution, and the mixture

was kept in the dark. The photodegradation experiment followed the same procedure as adsorption, but under light irradiation.

All experiments were performed in duplicate. Samples were collected at 5, 10, 15, 20, 30, 40, 50, 60, and 90 minutes, filtered through pre-cleaned PVDF syringe filters (13 mm diameter, 0.22 μm pore size) to remove particulates, and analyzed via UV-Vis spectrophotometry to determine dye concentration. A calibration curve was constructed using Rhodamine B standard solutions.

3. Results

3.1 Characterization of Mn-oxides

X-ray diffraction (XRD) patterns of both MnO₂ and Zn-doped MnO₂ were collected (Fig. 1). The diffraction patterns of both samples exhibit characteristic peaks of α-MnO₂, indicating the preservation of the crystal structure after Zn doping. The XRD diffractograms of the samples can be indexed to the tetragonal crystalline phase structure of α-MnO₂ (JCPDS #44-141). The diffraction peaks observed at 2θ values of 12.8°, 17.6°, 28.5°, 37.5°, 41.0°, 41.9°, 49.9°, 56.1°, 62.2°, 69.4°, and 73.0° correspond to the (110), (200), (310), (211), (420), (301), (411), (600), (002), (514), and (312) planes, respectively. As can be seen, a reduction of approximately 11% in the peak intensity at 2θ = 37.5° was observed in the Zn-doped sample compared to pure MnO₂. This decrease in intensity can be attributed to factors such as a reduction in crystallite size, the presence of crystal defects, or the non-uniform distribution of Zn within the structure. Although the peak intensity was affected, the maintenance of the main diffraction peaks indicates that the overall crystal structure of MnO₂ was preserved, suggesting a partial substitution of Mn by Zn in the lattice without the formation of new crystalline phases detectable by XRD.

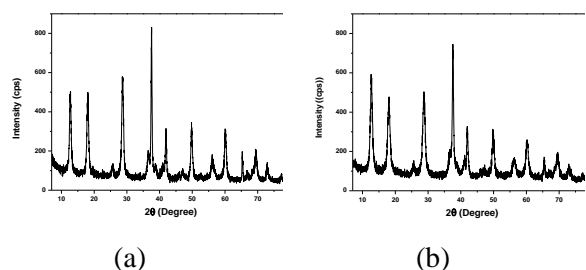


Fig. 1. X-ray diffractograms of (a) MnO_2 and (b) MnO_2 -Zn samples.

The FTIR spectra of both MnO_2 and Zn-modified MnO_2 (Fig. 2) exhibit characteristic vibrational bands at 3442 cm^{-1} , 1626 cm^{-1} , 519 cm^{-1} , and 457 cm^{-1} . The broad band at 3442 cm^{-1} is attributed to O-H stretching vibrations from adsorbed water or hydroxyl groups, while the peak at 1626 cm^{-1} corresponds to the bending mode of water molecules. The bands at 519 and 457 cm^{-1} are assigned to Mn-O stretching vibrations, indicative of the MnO_2 structure, which appears largely preserved in the Zn-modified sample. A significant spectral difference is observed at 708 cm^{-1} , where MnO_2 shows a well-defined peak while the Zn-modified sample presents a less prominent shoulder. This modification suggests alterations in the Mn-O-Mn vibrational environment due to Zn incorporation. The weakened intensity of the 708 cm^{-1} band implies potential changes in bond lengths or angles within the MnO_2 lattice, consistent with the XRD results indicating minor structural modifications.

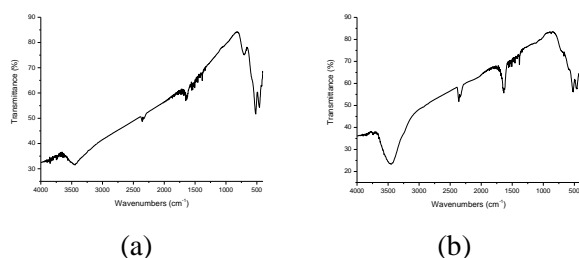


Fig. 2. FTIR spectra of (a) MnO_2 and (b) MnO_2 -Zn samples.

3.2 Degradation/Adsorption of Rh-B

Figures 3 and 4 depict the photolysis, adsorption, and photodegradation of Rhodamine

B (RhB) in the presence of MnO_2 and Zn-modified MnO_2 . The results indicate that the employed radiation was ineffective in photodegrading RhB due to the dye's stability. MnO_2 exhibited minimal RhB removal (approximately 10%) under both light and dark conditions, confirming its limited efficiency as a photocatalyst or adsorbent for RhB. Conversely, Zn-modified MnO_2 demonstrated exceptional adsorption capabilities, removing over 98% of RhB within 15 minutes under dark conditions. Spectral analysis provided no evidence of direct photocatalytic degradation, suggesting that adsorption is the predominant mechanism for RhB removal by Zn-modified MnO_2 . Furthermore, the absence of a significant influence of UV light on the removal process reinforces this conclusion.

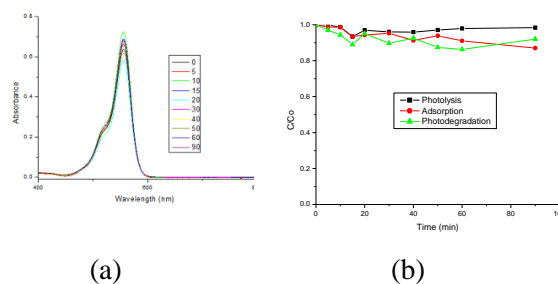


Fig. 3. UV/Vis Spectra and C/C_0 trends of rhodamine b under different experimental conditions: (a) UV/Vis spectra of Rh-B solution at different contact times with MnO_2 (adsorption); (b) C/C_0 as a function of time for photolysis, adsorption, and adsorption under light exposure.

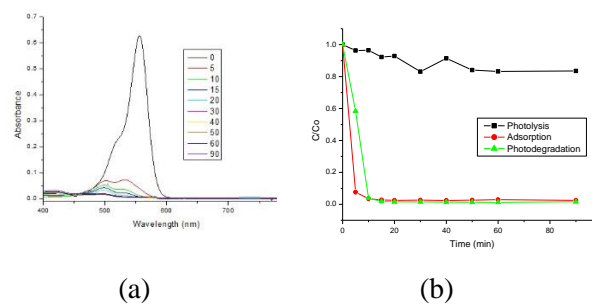


Fig. 4. UV/Vis Spectra and C/C_0 trends of rhodamine b under different experimental conditions: (a) UV/Vis spectra of Rh-B solution at different contact times with MnO_2 -Zn (adsorption); (b) C/C_0 as a function of time for photolysis, adsorption, and adsorption under light

exposure.

4. Conclusion

The present study showed an effective synthesis methodology for MnO₂ and Zn-modified MnO₂ materials. XRD and FTIR analyses suggest the incorporation of Zn into the MnO₂ structure. Regarding their potential as adsorbents for Rhodamine B removal, MnO₂ exhibited limited removal capacity, Zn-modified MnO₂ achieve more than 98% dye removal in 15 minutes. These results highlight the potential of Zn-modified MnO₂ as a promising adsorbent for Rhodamine B removal in aqueous solutions.

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References

- [1] A. Boretti, L. Rosa, Reassessing the projections of the World Water Development Report, *NPJ Clean Water* 2 (2019).
- [2] Gusmão, L. L., Tratamento de efluentes de indústria têxtil pelo processo de adsorção-fotooxidação empregando-se o compósito magnético quitosana-tio₂- óxido de ferro, Dissertação de Mestrado, Universidade Federal de Viçosa, 2014.
- [3] Lopes, P. R. M., Degradação fotocatalítica de efluente simulado de refinaria de petróleo e monitoramento de sua toxicidade com microrganismos, Dissertação de Mestrado, Universidade Estadual Paulista, 2009.
- [4] Oliveira, L. C. A., Fabris, J. D., Pereira, M. C., Óxidos de ferro e suas aplicações em processos catalíticos: uma revisão, *Química Nova* 36(1) (2013).
- [5] Canellas, L. P., Santos, G. A., *Humosfera: Tratado preliminar sobre a química das substâncias húmicas*, Campos dos Goytacazes, 2005.
- [6] Araújo, K. S. De, Antonelli, R., Gaydeczka, B., *Processos oxidativos avançados: uma revisão de fundamentos e aplicações no tratamento de águas residuais urbanas e efluentes industriais*, *Ambiente e Água* 11 (2016) 387-401.
- [7] Boas, N. V., *Síntese e Caracterização de Óxidos de Manganês Puros e Dopados com Cátions Metálicos Utilizados Como Materiais Aplicados em Dispositivos Eletroquímicos de Conversão de Energia*, Tese de Doutorado, Instituto de Química de São Carlos, Universidade de São Paulo, 2017.
- [8] Bruna, F., Celis, R., Real, M., Cornejo, J., *Organo/LDH nanocomposite as an adsorbent of polycyclic aromatic hydrocarbons in water and soil-water systems*, *J. Hazard. Mater.* 225-226 (2012) 74-80.
- [9] Vilas Bôas, Naiza, *Síntese e caracterização de óxidos de manganês puros e dopados com cátions metálicos utilizados como materiais aplicados em dispositivos eletroquímicos de conversão de energia*, Tese de Doutorado, Instituto de Química de São Carlos, Universidade de São Paulo, 2017.
- [10] Deguzman, E. C., Hong, S. B., Kim, J. H., KIM, H. J., SUIB, S. L., Shen YF, Neth EJ, Suib LS, O'Young C, Levine S, Newsam JM., *Synthesis and Characterization of Octahedral Molecular Sieves (OMS-2) Having the Hollandite Structure*, *Chemistry of Materials* 6(6) (1994) 815-820. DOI: 10.1021/cm00040a001.
- [11] Zou, J., Wu K., Wu, H., Guo, J., Zhang, L., *Synthesis of heterostructure d-MnO₂/h-MoO₃ nanocomposite and the enhanced photodegradation activity of methyl orange in aqueous solutions*, *J. Mater. Sci.* 55 (2020) 3329-3346.