

# N-Deethylation Process of Rhodamine B in Aluminum Polyphosphate Gel: Theoretical and Experimental Study

Sheila C. S. Costa, Paula A. Jaramillo, Rodrigo J. Oliveira & Marcos S. Amaral

## Introduction

Rhodamine B (RhB) is a xanthene dye, whose optical properties depend of several factors, such as solvents, concentration, pH, etc. The carboxyl group present on structure participates in acid-base balance, giving rise to acidic and basic structural forms [1]. This compound is widely used in textile industries, ink and cosmetics, among others [2]. However, it was proved experimentally the carcinogenicity of Rhodamine B and its high toxicity[3], such as most of non-biodegradable coloring agents [4], the RhB remain in waste waters of industrial handling, and an improper discharge of these wastes in urban storm water systems can cause adverse effects, harmful to the aquatic ecosystem and to human life. Several techniques have been employed for the removal of dyes from wastewater [5]. Currently, a great interest has been concentrated on the incorporation of organic dyes in solid matrices using the sol-gel technique as a photocatalyst of noxious compounds to the environment [6]. The Rhodamine B may suffer several degradation pathways, one such process is the de-N-ethylation under irradiation of visible light [7]. With this end, we propose the entrapment of Rhodamine B in Aluminum Polyphosphate Gel (APP/Gel) as a photocatalytic precursor and we associate theoretical simulation to investigate the type of degradation process that occurs with the RhB within

the APP/Gel [8]. We used a combination of sequential Monte Carlo/quantum mechanics (MC/QM) to describe the absorption bands of two forms of Rhodamine B (RhB<sup>+</sup>) and Rh<sup>+</sup> (Figure 1). Time-dependent density-functional theory (TD-DFT) [9] using three functional (B3LYP, CAM-B3LYP, BP86) [9] was also used in the theoretical description. All calculations were carried out using Gaussian 09 suite program [9] and DICE [10].

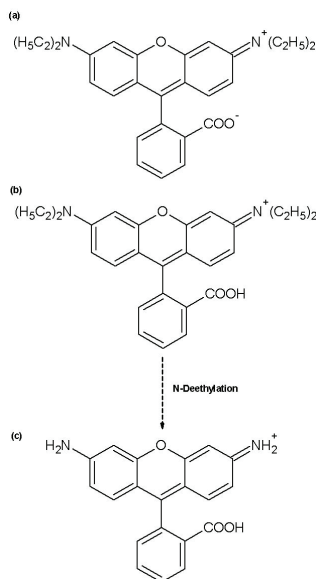
## Methods

In experimental procedure, the synthesis of the Aluminum Polyphosphate/RhB (APP/RhB) was prepared using  $2.0 \text{ mol} \times \text{L}^{-1}$  of sodium polyphosphate and  $1.0 \text{ mol} \times \text{L}^{-1}$  of aluminum nitrate in aqueous solution[8]. An aqueous solution of RhB using  $1.0 \times 10^{-3} \text{ mol} \times \text{L}^{-1}$  was prepared and added in the sodium polyphosphate solution and mixed at room temperature ( $\sim 25 \text{ }^\circ\text{C}$ ) under mechanical stirring. From of the experimental absorption data of the (APP/RhB), we simulate the N-Deethylation process of Rhodamine B. We optimized the structures of RhB<sup>+</sup> in cationic form (Figure 1-a), and Rh<sup>+</sup> (Figure 1-c) using DFT (B3LYP, CAM-B3LYP, PB86) methods and [6-311+(d,p)] basis set. sequentially, was used the Monte Carlo method to simulate both RhB<sup>+</sup> and Rh<sup>+</sup> molecules plus 1500 water molecules in the NPT ensemble in a cube box of lengths of

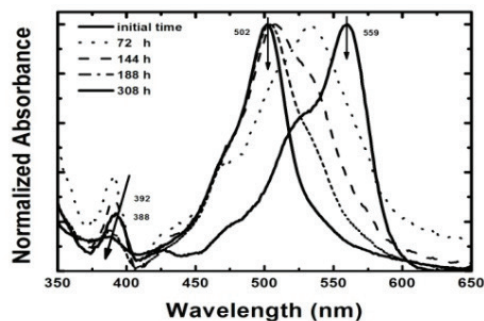
35.7 (Å). The average calculated density was 1.024 g/cm<sup>3</sup> and average specific molar heat was 0.02130 kcal/mol·K. After calculating the statistical correlation interval [11], a total of 75 uncorrelated configurations were selected with less than 15% of statistical correlation, for both Rhodamine B systems. TDDFT (B3LYP, BP86)//6-31+G(d, p) in PCM [9] level, were performed on each solute-solvent structure selected, which included the molecules of water explicit in hydrogen bond (HB).

## Results and Discussion

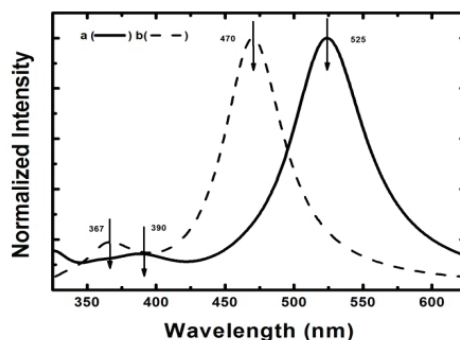
Samples of APP/RhB were monitored via UV-vis absorption (Figure 2), the normalized absorption spectra exhibited an hypsochromic shift of 57 nm between the absorption bands from APP/RhB initially formed (559 nm) up to N-deethylated product (502 nm) measured after 308 hours. The maximum absorption for initial time (just after preparing sample), is ~559 nm; after 308 hours, the maximum absorption is ~502 nm. The normalized absorption spectra for RhB<sup>+</sup> and Rh<sup>+</sup> in water (Figure 3) correspond to excited states calculated to 75 solute-solvent configurations from MC simulation. Theoretically was found a blue shift of ~ 54 nm approximately between the absorption bands of the RhB systems added in H<sub>2</sub>O with.



**Figure 1.** Schematic description of the Rhodamine B conformations. (a) Zwitterion form (RhB<sup>±</sup>), (b) Cationic form (RhB<sup>+</sup>) and (c) N-Deethylated (Rh<sup>+</sup>) product (Rhodamine-110).



**Figure 2** – Normalized UV-vis absorption spectra for Aluminum Polyphosphate and Rhodamine B (prepared from 2.0 mol×L<sup>-1</sup> of sodium polyphosphate, 1.0 mol×L<sup>-1</sup> of aluminum nitrate and 1.0×10<sup>-3</sup> mol×L<sup>-1</sup> of Rhodamine B, in aqueous solution) in room temperature (~25 oC) at different degradation instants. The maximum absorption for initial time (just after preparing sample), is centered at ~559 nm; after 308 hours, the maximum absorption band is centered at ~ 502 nm. The intermediate absorption spectra carry the hypsochromic shift signature of the main band.



**Figure 3.** Normalized absorption spectra for RhB<sup>+</sup> and Rh<sup>+</sup> in water with hydrogen bond (HB) calculated with TD-BP86/6-31+G(d,p) method. These spectra correspond to excited states calculated on 75 solute-solvent configurations from MC simulation. In the simulation of the N-deethylation process of RhB<sup>+</sup> (a) the maximum absorption peak at ~ 525 nm undergoes a blue shift of ~ 55 nm compared to Rh<sup>+</sup> (b).

## Conclusions

In this work, we propose to identify the type of degradation of Rhodamine B in the sol-gel matrix polyphosphate of aluminum. Through theoretical simulation we describe the gel of the internal environment where the Rhodamine B has been encapsulated, as well to study the occurrence of the N-ethylation process via absorption spectrum. Experimentally verified

by absorption spectra of the APP / RhB undergoes a hypsochromic shift characteristic of the process of de-N-ethylation of RhB. Considering that the theoretical and experimental results are in good agreement we propose that the matrix APP / Gel is a good fotocatalizador precursor and can be used for removal of dyes from wastewater.

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Sheila C.S. Costa<sup>a\*</sup>, Paula A. Jaramillo<sup>b</sup>, Rodrigo J. Oliveira<sup>c</sup> & Marcos S. Amaral<sup>a</sup>.

<sup>a</sup> Universidade Federal do Mato Grosso do Sul, INFI, 79070-900, Campo Grande, MS – Brasil.

<sup>b</sup> Universidade Federal da Integração Latino-Americana, ILACVN, 85867-970, Foz do Iguaçu, PR – Brasil.

<sup>c</sup> Universidade Estadual da Paraíba, DQ, 58109-790, Campina Grande, PB – Brasil.

\*E-mail: sheila.costa@ufms.br