

# Heterogeneous Photocatalytic Degradation of Dyes in Water/Alcohol Solution Used by the Brazilian Agate Industry

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## Abstract

The agate dyeing industry has been commonly seen as a high-pollution industry. Dyeing wastewater treatment is considered one of the most important categories for water-pollution control, because of its intense colour and the high concentration of organic contaminants. Most dyes used in the process present minimal biodegradability due to aromatic organic compounds in their structure. Using a photocatalytic reactor, experiments were carried out to study the decolorization of a water solution containing 8% ethylic alcohol and 200 mg L<sup>-1</sup> of the dye Rhodamine B (RhB), the most difficult colorant to degrade among the used by the agate industry. The best conditions were further applied to treat the same agate water/ethyl alcohol solution containing a mixture of 200 mg L<sup>-1</sup> of Rhodamine B (RhB), Crystal Violet (CV), Brilliant Green (BG), and Blood Red (BR). All the experiments were performed in a 2 L reactor equipped with ultraviolet (UV) lamps, at a wavelength of 365 nm, with powdered TiO<sub>2</sub> or ZnO as the catalyst. The results indicated that the optimal decolorization conditions were attained with 2.5 g L<sup>-1</sup> of the catalyst at pH 10 and an irradiation time of 80 min. The process resulted in complete degradation of CV, BG and 80% - 90% degradation of RhB and BR. The catalyst ZnO presented a performance somewhat better than TiO<sub>2</sub>. It is possible to conclude that the process of heterogeneous photocatalysis is effective for decolorization of water streams from the agate industry.

## Keywords

Agate, Dye, Rhodamine B, Heterogeneous Photocatalysis, Advanced Oxidation Process

## 1. Introduction

In the state of Rio Grande do Sul, located in the southern region of Brazil, there is a great occurrence of agate which is marketed worldwide [1]. Agate is a porous gemstone, commonly dyed to increase its value in the stone market [2]-[7]. Natural and artificially coloured agate plates are shown in **Figure 1**.

Agate geodes are treated and stained to produce handmade artefacts and jewelry that greatly increases their aggregate value. Unit operations involve storage, sorting, cutting, crushing, dyeing, polishing, washing, and finishing. Organic dyes used in this process present high colour intensity, minimal biodegradability and toxic effects. Wastewater generation is inevitable and, given the growing number of small-sized companies that process the stones, environmental discharge of such wastewaters is the cause for public concern [8]. Environmental legislation in the state of Rio Grande do Sul determines that, in order to dispose an effluent, it must comply with Resolution CONSEMA 355 of 2017 that states, among other parameters, that the effluent should not alter the natural colour of the receiving water body [9].

Conventional chemical treatment used by the agate industries to treat its effluents, such as sodium hypochlorite oxidation, despite of its low cost and ease of operation, performs poorly at it. Organic dyes are not completely oxidised by NaClO and many degraded compounds were found in the treated effluent, including organochlorides [10]. Other oxidation process is being suggested as an alternative to increase the treatment performance, such as ozonisation [11] and the Fenton's Reaction [12].

Like the Fenton's Reaction, heterogeneous photocatalytic decolorization is an advanced oxidation process (AOP) based in the generation of the hydroxyl radical ( $\bullet\text{OH}$ ), a chemical component with powerful oxidising potential. Heterogeneous photocatalysis is attractive since the process can be conducted using a low cost catalyst, such as  $\text{TiO}_2$  and  $\text{ZnO}$  along with UV radiation that could be furnished by a renewable energy source [13] [14] [15]. In this study, heterogeneous photocatalysis was tested to degrade the dyes present in a water/ethyl alcohol solution. Initially, the studies were conducted with Rhodamine B, considered the most difficult colorant to degrade among the used by the agate industry. The



**Figure 1.** Raw agate and dyed agate plates in many colours.

main operational variables studied were pH, concentration of catalyst (TiO<sub>2</sub> and ZnO) and UV irradiation time. Established the best condition, the treatment was applied to a water/alcohol solution containing a mixture of the colorants Rhodamine B, Crystal Violet, Brilliant Green and Blood Red combined.

## 2. Materials and Methods

### 2.1. Reagents, Materials and Effluents

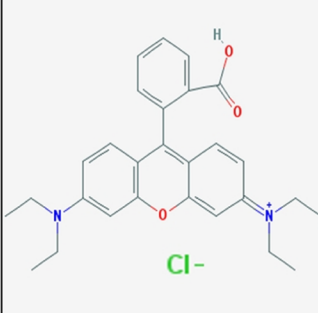
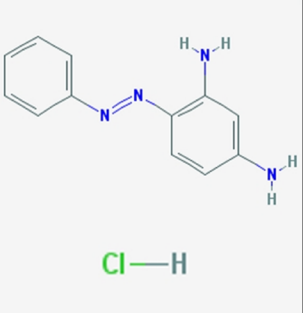
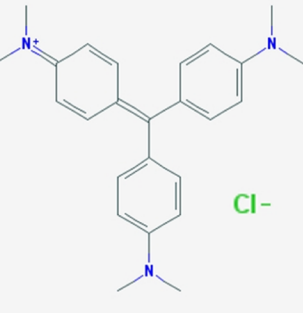
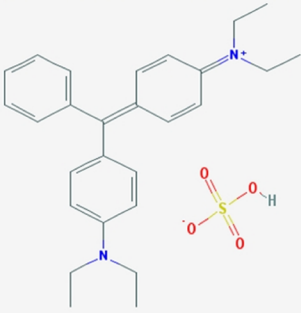
The dyes were supplied by Merck™ Brazil in order to provide the following colours: pink = Rhodamine B (RhB); purple = Crystal Violet (CV); green = Brilliant Green (BG); red (also called blood red, BR) by a composition of 30% w/w Basic Orange 2 (BO) and 70% Rhodamine B (RhB). The general characteristics of each dye are presented in **Figure 2**.

TiO<sub>2</sub> and ZnO powders were provided by Synth™ and ethyl alcohol by Nuclear™ Brazil. NaOH and H<sub>2</sub>SO<sub>4</sub>, used for pH adjustments, were provided by Sigma-Aldrich Co™. Deionized water was purified using a Milli-Q™ water ion-exchange system (1.8 × 10<sup>7</sup> Ω cm).

Synthetic effluent (SE) were prepared considering the following conditions: (a) aqueous solution containing 8% ethyl alcohol and 200 mg L<sup>-1</sup> of RhB; and (b) aqueous solution containing 8% ethyl alcohol and 200 mg L<sup>-1</sup> of RhB, 200 mg L<sup>-1</sup> CV, 200 mg L<sup>-1</sup> BG, and 200 mg L<sup>-1</sup> BR.

### 2.2. Photooxidation Experiments

All the experiments were performed in a 2 L capacity reactor equipped with UV lamps, at a wavelength of 365 nm [16]. UV radiation was provided by a 125 W HID/HPL (High Intensity Discharge/High Pressure Mercury Lamp, Philips™) in the presence of powdered TiO<sub>2</sub> or ZnO as the catalyst. The lamp's outer bulb was removed while the mercury and argon filled bulb was kept. In order to allow its

Rhodamine B	Basic Orange 2	Cristal Violet	Brilliant Green
CI nº. 45170 CAS nº. 81-88-9 Molar Mass: 479.017 Da λ <sub>max</sub> = 555 nm	CI nº. 11270 CAS nº. 532-82-1 Molar Mass: 248.714 Da λ <sub>max</sub> = 460 nm	CI nº. 42555 CAS nº. 548-62-9 Molar Mass: 407.99 Da λ <sub>max</sub> = 580 nm	CI nº. 42040 CAS nº. 633-03-4 Molar Mass: 482.64 Da λ <sub>max</sub> = 618 nm
<b>RhB</b>	<b>BR</b>	<b>CV</b>	<b>BG</b>
			

Where: CI = Color Index International; CAS = substance identification in the Chemical Abstracts Service, a division of the Chemical American Society; Da = unit of molar mass and λ<sub>max</sub> = wavelength of maximum absorption in nm (nanometer) adopted in this work.

**Figure 2.** Properties of the 4 dyes and representation of its chemical structures.

immersion aiming total exposure of the samples to the radiation, the lamp was conditioned in a quartz tube (Figure 3).

The reaction time of the heterogeneous catalysis was 100 minutes, assisted by UV radiation the entire time. Samples were retrieved at 5 minutes intervals; the solid catalysts were withdrawn from the reactor by filtration using TPP™ polystyrene vacuum system with 0.22  $\mu\text{m}$  polyester sulfone membrane and the effluent was adequately diluted and evaluated in an UV-Vis spectrophotometer. The system was maintained at 30°C by means of a thermostatic bath and such temperature was kept throughout all the experiments. These procedures were applied to evaluate the effect of pH and catalyst concentrations. pH adjustment was carried out with solutions of sodium hydroxide and sulfuric acid. The concentration of  $\text{TiO}_2$  or  $\text{ZnO}$  applied were 0.0  $\text{g L}^{-1}$  (control), 1  $\text{g L}^{-1}$ , 2.5  $\text{g L}^{-1}$  and 5.0  $\text{g L}^{-1}$ .

The absorbance in the maximum wavelength ( $\lambda_{\text{max}}$ ) was measured using a UV-Vis spectrophotometer (Shimadzu™ UV 1800), each dye being determined at a specific maximum wavelength in the same analysis, (RhB = 555; CV = 580; BG = 618 and OB = 460 nm). The absorption spectrum for the dye solutions ranging between 300 and 700 nm is shown in Figure 4. Calibration curves were performed in a concentration range of 0 to 20  $\text{mg L}^{-1}$  for the dyes in an aqueous solution and its parameters are expressed in Figure 5.

### 3. Results and Discussion

The oxidation rates and efficiency of the photocatalytic system UV/ $\text{TiO}_2$  and UV/ $\text{ZnO}$  depend highly on the number operation parameters that govern the kinetics of the discoloration. Some of these parameters are temperature, pH, concentration of the solid semiconductor, and light incidence time. These parameters either raise or reduce the reaction rate depending on the pollutant's structural complexity and hydrophobic tendencies [17]. It has been reported that minor incremental changes in temperature do not significantly affect the rate of

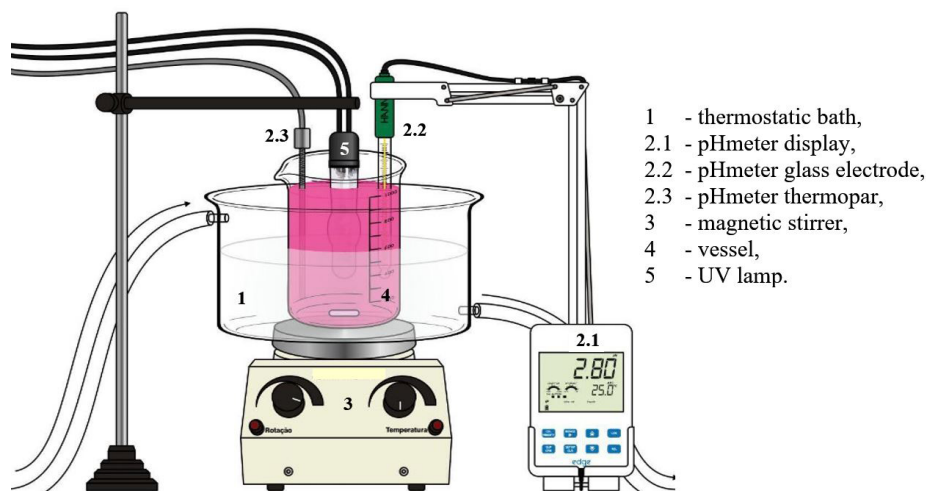
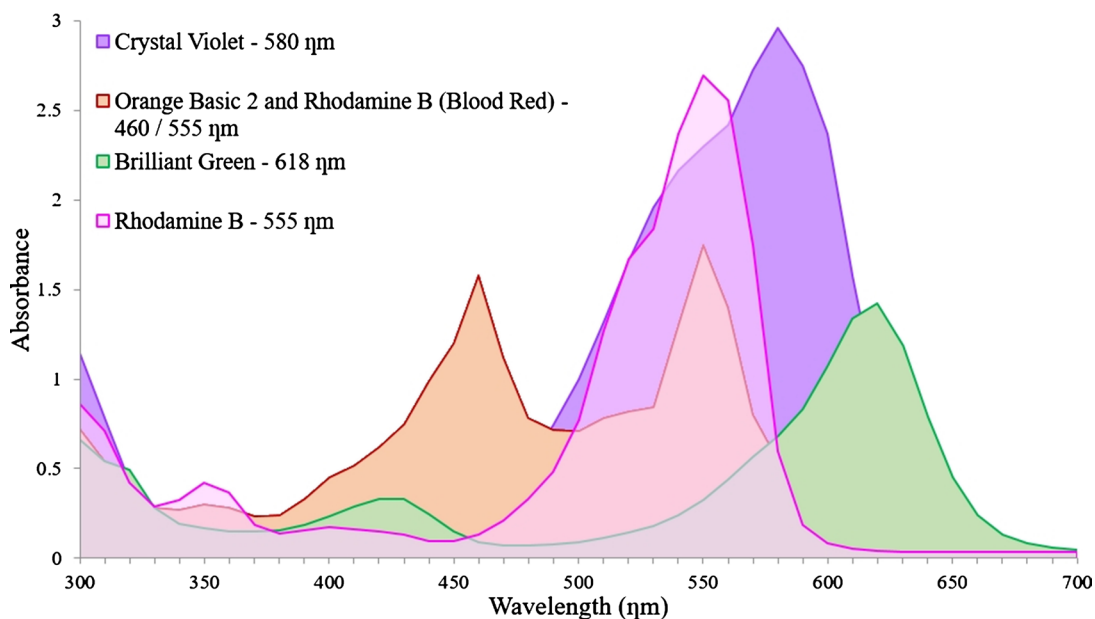
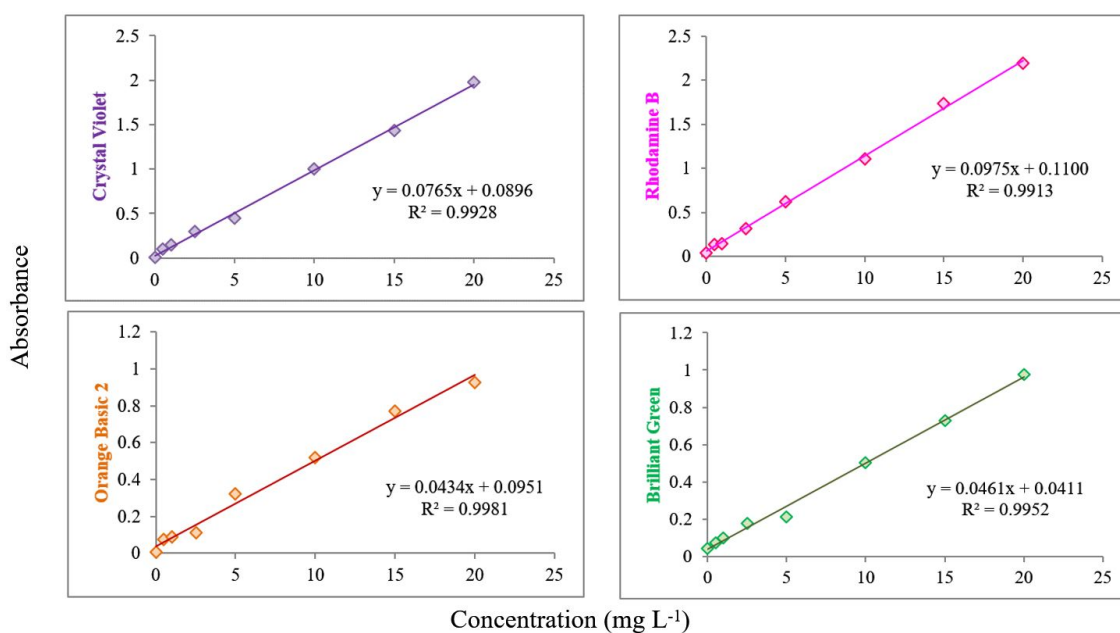


Figure 3. Schematics of a heterogeneous photocatalysis reactor.



**Figure 4.** Visible absorption spectrum of the aqueous solution containing 20 mg L<sup>-1</sup> for each dye.



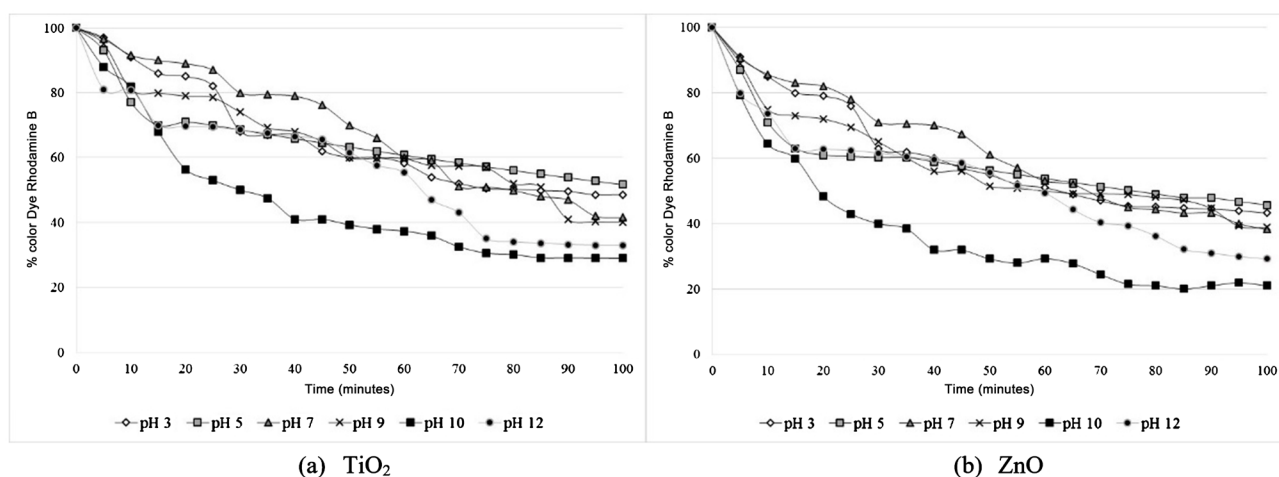
**Figure 5.** Graphical representation of the concentration (mg L<sup>-1</sup>) versus absorbance. ( $y = ax + b$ ) linear correlation for the aqueous solutions of the dyes Crystal Violet, Brilliant Green, Orange Basic 2 and Rhodamine B: where  $y$  = absorbance;  $x$  = dye concentration (mg L<sup>-1</sup>);  $R^2$  = regression coefficient;  $a$  = angular coefficient;  $b$  = linear coefficient.

photocatalytic reactions and the optimum reaction temperature for photomineralization is said to be in the range of 20°C to 80°C [18] [19], therefore in this work the temperature of 30°C was established for all the experiments.

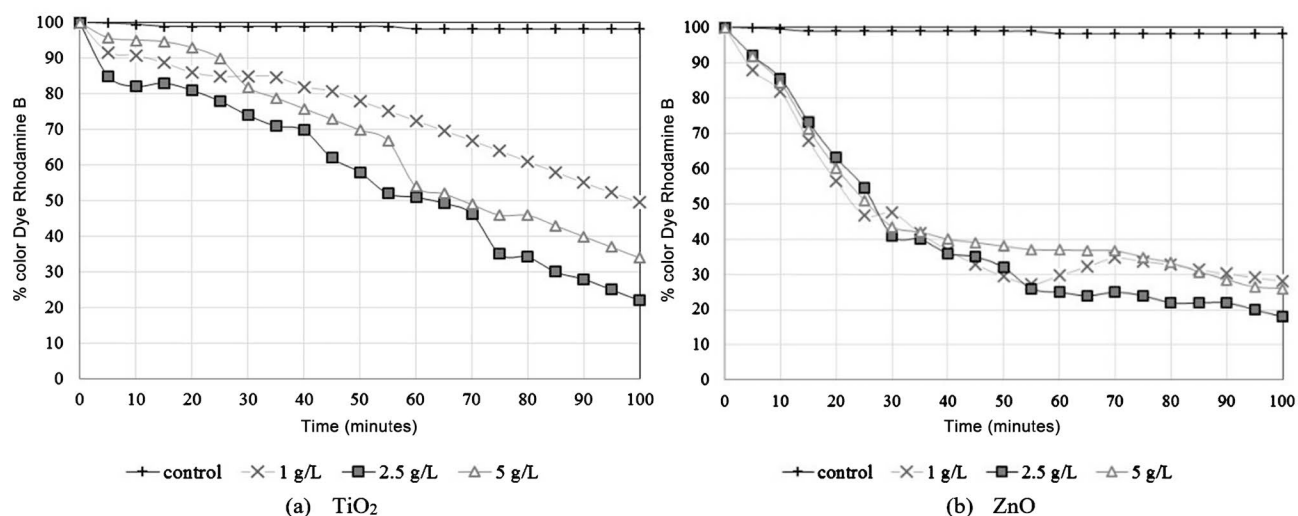
In a heterogeneous photocatalytic water system, pH is one of the most important operating parameters since the adsorption of the organic compound onto the photocatalyst surface degradation reaction depends on the surface charge of

the photocatalyst and on the ionization state of the organic compound. Hence, the adsorption of positively charged organic compounds is facilitated at a basic pH, while that of negatively charged species is favorable at an acidic pH. Therefore, it is difficult to standardize the pH conditions for the degradation of a specific class of organic compounds. It is recommended that appropriate pH control strategies be implemented at every different condition of a photocatalytic water treatment process in order to get an efficient photocatalytic reaction [14] [20]. **Figure 6** shows the effect of pH on decolorization of a 200 mg L<sup>-1</sup> Rhodamine solution. The results confirm that the best efficiency was yielded at pH 10.0 for an overall colour removal of this effluent. This is in accordance with the literature of the best decolorization performance of positively charged dyes (Rhodamine B, Basic Orange 2, Crystal violet, Brilliant Green) at basic pH [21] [22].

The concentration of the photocatalyst is another critical parameter that determines the degradation rate of any organic compound [23] as it relies upon the volume of the solution being treated and the initial concentration of the organic compound. It has been widely observed that the degradation rate increases with an increase in catalyst loading. This is due to the availability of more active catalyst sites at higher concentrations, which results in the generation of more hydroxyl species. However, when such load is increased beyond an optimum value, there is no appreciable increase in the degradation rate. This is due to fact that catalyst particles scatter light, reducing the effective light intensity reaching the bulk reaction solution. In the literature, 0.4 - 3.5 g L<sup>-1</sup> of catalyst has been used for the photocatalytic degradation of different organic compounds [24]. **Figure 7** shows the effect of catalyst concentration on decolorization of a 200 mg L<sup>-1</sup> Rhodamine solution. The results confirmed a good performance with 1 g L<sup>-1</sup>, but the best efficiency was achieved with 2.5 g L<sup>-1</sup> for both TiO<sub>2</sub> and ZnO. These results are close to those obtained by Sivalingam *et al.* [25] that observed that the



**Figure 6.** Rhodamine B remaining as a function of UV irradiation time with pH ranging from 3 to 12 in a synthetic effluent composed by 200 mg L<sup>-1</sup> RhB in and aqueous solution containing 8% ethyl alcohol (v/v), using 1 g L<sup>-1</sup> of TiO<sub>2</sub> (a) or 1 g L<sup>-1</sup> ZnO (b) as catalyst and temperature 30°C under constant stirring.

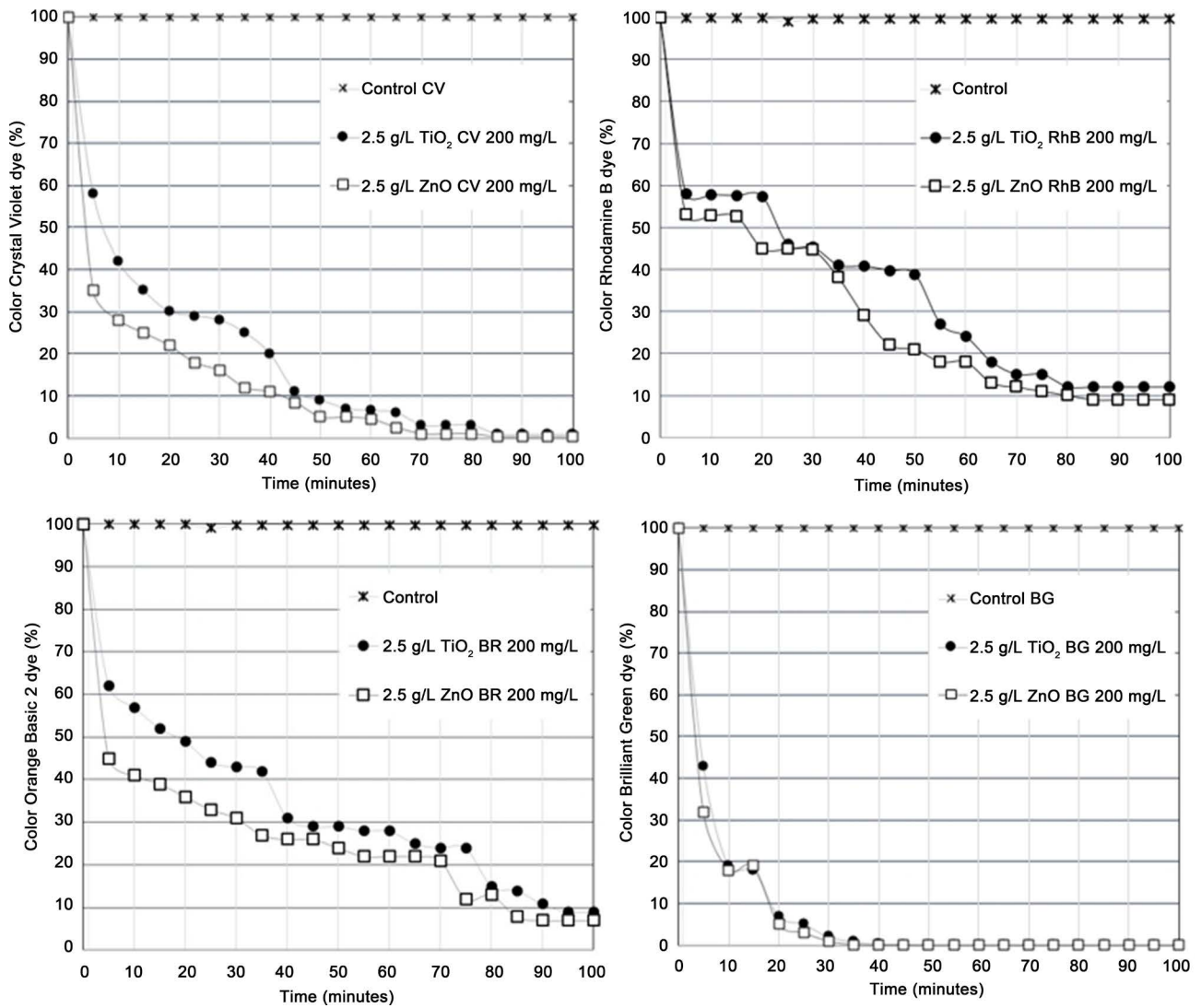


**Figure 7.** Rhodamine B remaining as a function of UV irradiation time varying the concentration of catalyst from 1 g L<sup>-1</sup> to 5 g L<sup>-1</sup> in a synthetic effluent composed by 200 mg L<sup>-1</sup> RhB in and aqueous solution containing 8% ethyl alcohol (v/v), using TiO<sub>2</sub> (a) and ZnO (b) as catalyst, at pH 10 and 30°C temperature under constant stirring.

optimum added of TiO<sub>2</sub> for the degradation of dyes is 1 g L<sup>-1</sup>. In the work of Ahmed *et al.* [15] the concentration of reactive yellow dye treated was 50 mg L<sup>-1</sup> and the best ZnO catalyst dosage was found in 3.5 g L<sup>-1</sup>.

Degradation efficiency obtained for the aqueous/ethyl alcohol (8%) solution containing the mixture of 200 mg L<sup>-1</sup> of RhB, 200 mg L<sup>-1</sup> CV, 200 mg L<sup>-1</sup> BR and 200 mg L<sup>-1</sup> BG at pH 10.0 with the presence of each catalyst (TiO<sub>2</sub> or ZnO) as a function of time is presented in **Figure 8**. It is possible to observe that decolorization was successfully achieved. The color promoted by the dyes brilliant green and crystal violet was completely removed in a reaction time of 80 min under constant stirring. On the other hand, given the same amount of time, the discoloration reached on Rhodamine B or the composition made of Rhodamine B and Basic Orange 2 was only about 90%. These results confirm Rhodamine B to be the most resistant to degradation dye among the colorants studied. Among the catalysts, ZnO presented a slightly better performance on all the studied dyes. **Figure 9** shows the aspect of the dye solution before and after the dye degradation procedure carried out by heterogeneous photocatalysis.

Adsorption studies on the solid catalysts were performed and the results demonstrate that the adsorption of the dyes is not significant for these solutions under these conditions, presenting results of less than 0.03%. For degradation control tests, considering the use of just the catalyst or just the UV irradiation, there was no discoloration above 0.006%. Considering such findings, it is safe to assume that the process of decolorization is just associated to the formation of hydroxyl radicals ( $\bullet\text{OH}$ ) by the UV/TiO<sub>2</sub> or UV/ZnO process. As expected, the ZnO catalyst produced better results than the TiO<sub>2</sub>, since, in comparison, it has a minor band gap energy and also is capable of providing a higher oxidation energy [20] [26] [27].



**Figure 8.** Colour remaining as a function of UV irradiation time for a synthetic solution containing 200 mg L<sup>-1</sup> of each dye (RhB, CV, BR, BG) in aqueous solution with 8% of ethyl alcohol (v / v). Treatment with 2.5 g L<sup>-1</sup> of TiO<sub>2</sub> and ZnO, at pH 10 and temperature of 30 °C under constant stirring.



**Figure 9.** Aspect of the synthetic effluent containing the 4 dyes before and after the application of the photocatalytic treatment with ZnO (2.5 g L<sup>-1</sup> in aqueous solution with 8% ethyl alcohol), UV irradiation, temperature-controlled system at 30 °C and pH 10.



Agate dyeing wastewaters always present highly recalcitrant dyes, in concentrations which can give water resources undesirable color when launched without treatment. The use of heterogeneous catalysis process is advantageous because it is built upon just energy and a catalyst without the need of any other chemical reagent and the catalyst can also be recovered after the end of each treatment process cycle and put back to use once again. The volumes of effluent produced, in the order of 0.2 m<sup>3</sup> per kg of stained stones [8], are in the order of few m<sup>3</sup> per week, which is totally suitable for oxidative processes like the heterogeneous photocatalysis. The process could be improved or associated to some other processes, such as ozonation or adsorption to improve the water quality parameters of discharge or even to allow water reuse in its own system.

#### 4. Conclusion

The aqueous/ethyl alcohol solutions of Rhodamine B and the composition of Rhodamine B, Crystal Violet, Brilliant Green, and Blood Red were decolorized by heterogeneous photocatalysis in the system UV/TiO<sub>2</sub> and UV/ZnO. The best conditions found were 2.5 and g L<sup>-1</sup> of catalyst at pH 10 and an irradiation time of 80 min. The process resulted in the complete degradation of crystal violet, brilliant green and 80% - 90% degradation of Rhodamine B and Blood Red. The proposed system can be adapted to small companies of agate processing in order to help with colour removal of dyeing wastewaters.

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#### Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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