



Zinc oxide immobilized on alginate beads as catalyst for photocatalytic degradation of textile dyes – an evaluation of matrix effects

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ABSTRACT

Heterogeneous photocatalysis is an attractive and efficient alternative for degradation of organic pollutants in water and wastewater. Thus, we studied photocatalytic degradation of the textile dye Orange Solimax TGL 182% (OS-TGL), using the semiconductor ZnO immobilized in alginate beads as a catalyst. The catalyst was characterized by Fourier transform infrared spectroscopy and scanning electron microscopy (MEV). The optimized photocatalytic parameters were catalyst concentration, pH, textile dye concentration, and ionic strength. Additionally, we evaluated the effect of different matrices and the presence of other textile dyes in the OS-TGL removal. The OS-TGL degradation kinetics followed a pseudo-first-order kinetic model for heterogeneous photocatalysis and photolysis processes. At optimized conditions, the heterogeneous photocatalysis promoted percentages of the OS-TGL degradation higher than 99% in 60 min of reaction time. Moreover, the proposed photocatalytic process using ZnO immobilized in alginate beads allowed recycling of the catalyst up to four times without significant loss of photocatalytic degradation efficiency.

Keywords: Textile dye; Photocatalysis; Zinc oxide; Catalyst immobilization

1. Introduction

One of the biggest problems currently faced by society is environmental pollution, which is associated with several negative phenomena on a global scale. The textile industry stands out in this context, as it uses a large volume of water during the staining and finishing process, generating large volumes of effluents [1–5]. The textile effluents have a strong coloration, high biochemical oxygen demand (BOD), and chemical oxygen demand (COD). The effluents decrease the photosynthetic activity due to the reduction of light in the aquatic environment. Moreover, their degradation is difficult, causing environmental and health problems [4–8].

Several technologies have been developed to treat textile effluents [9–11]. Advanced oxidation processes (AOPs) are a promising technology to remove organic pollutants [12]. Among AOPs, heterogeneous photocatalysis (HP) is a relevant alternative and has been extensively studied for environmental applications. Heterogeneous photocatalysis has been widely used for the degradation of organic molecules, such as dyes [10,13,14], which can lead to the mineralization of most organic pollutants, without generating solid residues. This technique has other advantages such as good removal efficiency, non-toxicity, and low cost, which are important factors for large-scale application.

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The most used semiconductors in HP are TiO_2 , ZnO, and most recently Nb_2O_5 . Zinc oxide stands out among the semiconductors for its high efficiency and low cost. Additionally, ZnO has a band gap of ~ 3.3 eV, high chemical and thermal stability, as well as important electronic and structural properties in catalysis and photocatalysis processes [12,15,16]. Additionally, ZnO is a non-toxic catalyst, which has been used successfully in the photocatalytic degradation of organic pollutants [7,17].

The application of photocatalysts can be carried out with catalyst in suspension or immobilized forms. However, the use of catalysts in the immobilized form is more advantageous because it is easy to remove at the end of the process, which makes the catalyst easier to use and reuse. The catalyst can be immobilized with supports, such as glass, carbon nanotubes, and polymers [10,17]. Among the supports currently studied, sodium alginate has shown promise in the immobilization of the catalysts. Alginate has several advantages because it is non-toxic, biodegradable, water soluble, and non-immunogenic. In the presence of divalent cations, alginate can form stable hydrogels with the formation of a three-dimensional network, which can be used to immobilize simply and easily the semiconductor [18,19].

In our study, the degradation of the orange textile dye Orange Solimax TGL 182% (OS-TGL) was evaluated using HP and ZnO immobilized on calcium alginate beads as catalyst. We characterized the ZnO–alginate beads and evaluated the effect of different matrices and the presence of other textile dyes in the OS-TGL removal.

2. Experiment

2.1. Reagents and solutions

All the reagents used were of analytical grade. Ultrapure water with $18 \text{ M}\Omega \text{ cm}$ resistivity was purified in a purifier Master All 2000 (GEHAKA, Brazil). Orange Solimax TGL 182% (OS-TGL) textile dye solution was prepared for the photocatalytic process. Zinc oxide (Dinâmica, Brazil), Nb_2O_5 (Brazilian Mining and Metallurgy Company – CBMM), and TiO_2 in anatase form (Sigma-Aldrich, Germany) were evaluated as catalysts. Sodium alginate (Sigma-Aldrich, Germany) and CaCl_2 (Dinâmica) were used to immobilize the catalysts. Potassium chloride (Dynamics) was used to evaluate the effect of the ionic strength, while the Solimax Yellow and Solimax Blue dyes were employed to verify the influence of other dyes in the process. The pH was adjusted with HNO_3 (Dinâmica) and NaOH (Dinâmica) solutions. All solutions and standards were prepared using ultrapure water.

2.2. Catalytic immobilization

Solutions containing 2% (w/v) sodium alginate and 2% CaCl_2 (w/v) were prepared with ultrapure water to immobilize the ZnO, Nb_2O_5 , and TiO_2 catalysts in calcium alginate beads. In the sodium alginate solution, catalysts were added at different concentrations (1, 5, 10, and 20 g L^{-1}). The solution was stirred until complete homogenization. Subsequently, the suspension was dripped into the CaCl_2 solution with the aid of a peristaltic pump (Watson Marlow, United Kingdom). The beads were left in the CaCl_2 solution for 12 h for complete

stabilization. Subsequently, the beads were washed with ultrapure water to remove excess CaCl_2 . They were dried in an oven at $60^\circ\text{C} \pm 5^\circ\text{C}$ for 4 h, then the prepared ZnO–alginate beads were stored for future use.

2.3. Photocatalytic process

For the textile dye degradation process, a photocatalytic reactor containing mercury vapor lamp (250 W – wavelength 254 nm) was used without the protective glass bulb and positioned horizontally on a jacketed beaker with a capacity of 250 mL. Ultra-thermostatic bath, SOLAB 152, (SOLAB, Brazil) at $10^\circ\text{C} \pm 5^\circ\text{C}$ was used to cool the system. Aliquots of 200 mL of the OS-TGL dye solution were placed in the reactor and 0.5 g of the pre-dried beads, containing the immobilized ZnO at different concentrations, was added to it. The solution was stirred for 90 min and at time intervals, aliquots were collected and then analyzed in the UV-Vis spectrophotometer, 800 XI, (FEMTO, Brazil) at 405.0 nm. We evaluated the following parameters: pH of the solution, concentration of the catalyst, and concentration of dye in the solution. In addition, the influence of the matrix effect, ionic strength, reuse of the beads and the presence of other textile dyes in the photocatalytic process were evaluated. With the exception of the pH test, all analyses were performed at pH 7.0. The photocatalytic process performed in triplicate showed a standard deviation of less than 4%.

2.4. Material characterization

Before and after the degradation process of the OS-TGL dye by HP, the ZnO–alginate beads were characterized by Fourier transform infrared spectroscopy (FTIR) using a spectrometer (PerkinElmer Frontier model) and by scanning electron microscopy, Vega 3 LMU, (Tescan, Czech Republic) coupled with energy-dispersive X-Ray spectroscopy (EDS), AZTec Energy X-Act, (Oxford, United Kingdom). Additionally, TiO_2 (anatase form), ZnO, and Nb_2O_5 also characterized by photo-acoustic spectroscopy (PAS), X-ray diffraction (XRD) and the data are presented in a previous work [20].

3. Results and discussion

3.1. Evaluation of catalysts

The performance of the catalysts TiO_2 (anatase form), ZnO, and Nb_2O_5 in the photocatalytic degradation of the dye was evaluated, and the results are presented in Fig. 1. No significant difference was observed in the rate of degradation of the dye using Nb_2O_5 and TiO_2 (anatase form) as catalysts. However, ZnO promotes faster degradation, reaching a $>99\%$ in 60 min, while Nb_2O_5 and TiO_2 (anatase form) presented only 77% degradation in the same time interval. Researchers have also reported a greater ability of ZnO than TiO_2 to degrade dyes [21–23]. Bansal and Sud [22] obtained a greater photocatalytic efficiency using ZnO in the degradation of the textile dye PBH at pH 7.0 than with TiO_2 , which is one of the most used catalysts for HP. Tian et al. [23] also observed a more rapid degradation of methyl orange dye using ZnO than with P-25. Consequently, the following experiments were performed using ZnO as a catalyst.

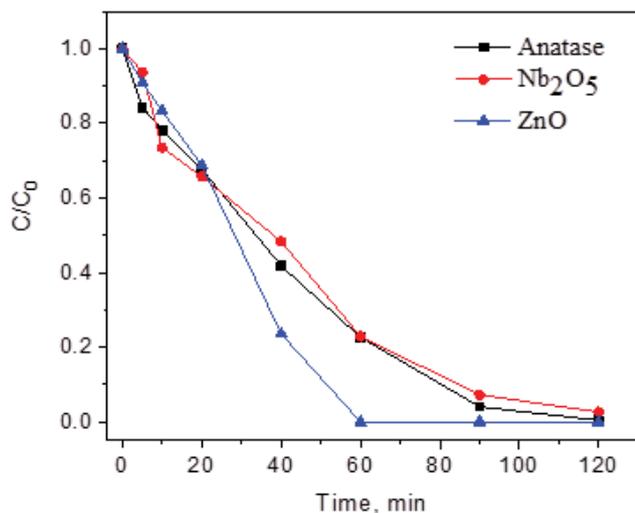


Fig. 1. Evaluation of different photocatalysts in the degradation of OS-TGL dye by heterogeneous photocatalysis. Conditions: 200 mL of OS-TGL at 20 mg L⁻¹, 0.5 g of dried beads prepared with 20 g L⁻¹ of each catalysts, and pH 7.0.

3.2. Characterization of ZnO–alginate beads

In a previous work [20], the catalysts TiO₂ (anatase form), ZnO, and Nb₂O₅ were characterized, in their powder form, by PAS and XRD. The XRD patterns of the photocatalyst displayed characteristic crystalline structures for all the catalysts. The obtained bandgap values were 3.10, 3.12, and 3.84 eV, respectively, for TiO₂ (anatase form), ZnO and Nb₂O₅, which are very close to the values reported in the literature [20]. However, considering the performance of the evaluated catalysts in the photodegradation of OS-TGL, presented in item 2.1, the following characterization analysis were performed for ZnO, which demonstrated the best efficiency.

The FTIR spectra of ZnO-containing alginate beads before and after photocatalysis are provided in Fig. 2. The spectra contain a broad band at 3,400 cm⁻¹ corresponding to the –OH groups. A small band at 2,925 cm⁻¹ is attributed to the symmetrical and asymmetrical stretching of the –CH₂ and –CH₃ groups. Intensive bands in the region of 1,600 cm⁻¹ and 1,020 cm⁻¹ correspond to the stretching of the C=O and C–O groups, respectively. The FTIR spectra before and after the photocatalytic process of new bands did not appear, suggesting that the polymer structure did not change. Only a small suppression of the signal in the spectrum occurred after photocatalysis. This may be related to loss of the polymer chains during the process since the alginate beads are sensitive to the reaction medium, in which mass loss may occur. The decrease in the signal in the region of about 500 cm⁻¹, attributed to ZnO, may be due to the loss of catalyst, which may have occurred due to loss of alginate mass.

Figs. 2a–d show the micrographs obtained by scanning electron microscopy. The ZnO–alginate beads have a uniform size distribution, both before and after the HP process, presenting some irregularities that may arise from the drying process of the beads. The surface of the beads has small whitish protrusions possibly formed due to the presence of

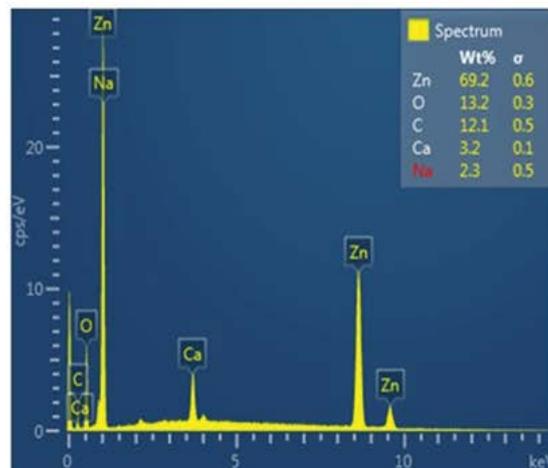
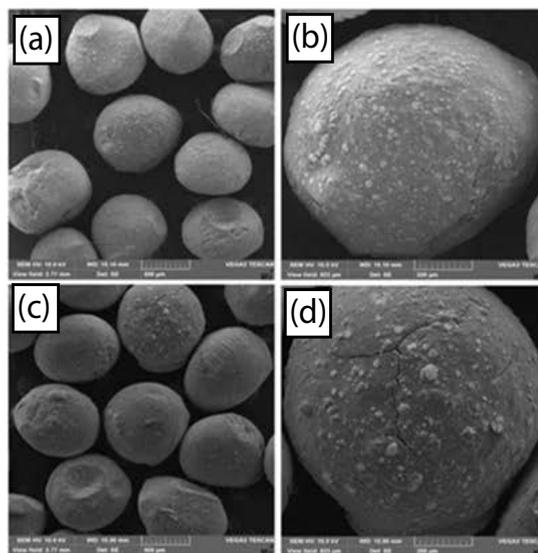


Fig. 2. FTIR spectra and scanning electron microscopy (SEM) of the ZnO–alginate beads before and after heterogeneous photocatalysis (HP). SEM micrographs before (a and b) and after (c and d) HP. The EDS spectra from the surface of the ZnO–alginate bead before HP (Micrography B).

the catalyst on their surface. After HP, we verified that no significant change occurred in the structure and size of the beads. The EDS spectra of ZnO–alginate beads confirmed the presence of Zn, O, Ca, and C, which are the main components of the evaluated beads. The sodium peak is from residual sodium alginate solution used for the ZnO immobilization.

Kosera et al. [17] proposed a triclosan degradation by HP using ZnO immobilized in biopolymer as catalyst and performed the characterization of the free and immobilized ZnO. They found that the catalyst is available in a uniform way under the surface of the alginate spheres and the PAS analysis of spheres showed a bandgap of 3.08 eV, which is very close to the value found for ZnO in free form. Based on this result, we can assume that even when the ZnO is immobilized in alginate, the necessary energy for its activation remains almost the same as in its free form.

3.3. Effect of catalyst concentration

The evaluation of the concentration of catalyst present in the beads is very important to determine the adequate amount to obtain the best performance in the photocatalysis process and to avoid the unnecessary use of catalyst. The amount of ZnO used to prepare the beads was evaluated at concentrations of 1, 5, 10, and 20 g L⁻¹. No significant improvement in the degradation of the dye compared with photolysis was obtained by using the beads prepared with 1 g L⁻¹ of ZnO. At concentrations of 5 and 10 g L⁻¹, 87% and 95% degradation, respectively were obtained at the same reaction time. The best performance was obtained for beads prepared with 20 g L⁻¹ of ZnO, which showed degradation of the OS-TGL dye higher than 99% in 60 min. Therefore, by increasing the amount of catalyst, the number of active sites on the ZnO–alginate beads surface is also higher, making its photodegradation performance more efficient.

3.4. Photocatalysis, photolysis, and adsorption

Adsorption and photolysis tests were also performed to verify their efficiency in dye removal (Fig. 3). The experiments to investigate the adsorption capacity of the dye were performed with beads containing 20 g L⁻¹ of ZnO. The beads present a low ability to adsorb dye, less than 6% in 120 min. Sudrajat and Babel [21] also observed that ZnO has a low ability to adsorb dye molecules. Those researchers obtained less than 6% adsorption of the yellow and methylene blue dyes after 2 h of contact with a suspension of ZnO [21]. A photolysis, on the other hand, was efficient but with slower degradation of the dye (74% in 60 min) than the photocatalysis (>99% in 60 min).

According to the literature, the photocatalytic degradation of dyes can be described by Langmuir–Hinshelwood (L-H) kinetic model [24–30], which is represented by Eq. (1):

$$-\frac{dC}{dt} = \frac{kKC}{1+KC} \quad (1)$$

where C is the given dye concentration (mg L⁻¹), k represents the kinetic constant of the reaction (mg L⁻¹ min⁻¹), and K is the adsorption constant (L mg⁻¹). Considering that low

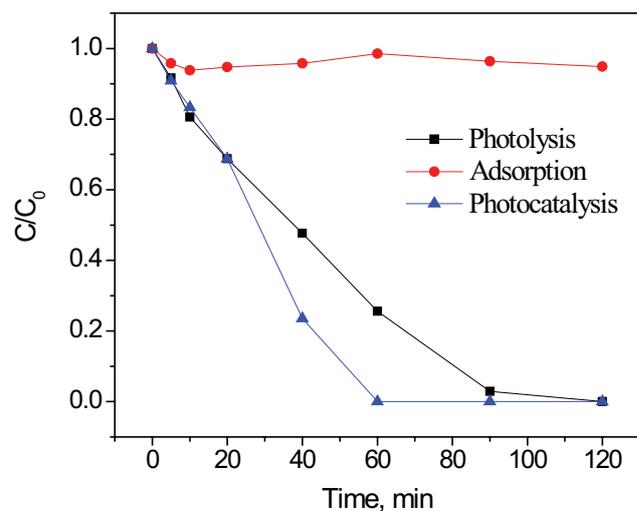


Fig. 3. Comparison of adsorption, photolysis, and photocatalysis processes. The adsorption and photocatalysis tests were performed using ZnO–alginate beads. Conditions: 200 mL of OS-TGL at 20 mg L⁻¹, 0.5 g of dried beads prepared with 20 g L⁻¹ of ZnO, and pH 7.0.

concentrations of dye are used, the term KC can be considered negligible, thus Eq. (1) can be simplified to:

$$-\frac{dC}{dt} = kKC = k'C \quad (2)$$

In this equation, k' represents the apparent constant of pseudo-first-order, thus the photocatalytic degradation of dye can be described by a pseudo-first-order kinetic model [24]. As observed in Fig. 3, the adsorption of the dye in the beads is negligible and the presence of radiation is required for dye removal as described by a pseudo-first order kinetic model. The linear fitting between $\ln(C_0/C)$ and reaction time showed that the photocatalytic degradation as well as photolysis degradation follows a pseudo-first-order kinetic model. The kinetic data obtained for the degradation of OS-TGL under photolysis and photocatalysis are provided in Table 1.

As observed, apparent reaction rate constant and half-life obtained under photolysis and photocatalysis degradation were similar. However, the total degradation of the evaluated dye is slightly faster under photocatalysis conditions, as can be observed in Fig. 3. Although, the difference between the photolysis and photocatalysis processes is very small, the process applying photocatalysis promotes the dye degradation in shorter time, which is an advantage in terms of economy and treatment efficiency in case of real application.

3.5. Influence of pH

The characteristics of textile wastewater are highly dependent on the textile and the chemical process used. Thus, the quantities of suspended and dissolved solids, BOD, COD, and chemicals can vary significantly in textile

Table 1

Linear regression of a pseudo-first kinetic model obtained for the degradation of OS-TGL under photolysis and photocatalysis

| | Parameters | Values |
|----------------|---|--------|
| Photolysis | Apparent reaction rate constant (min^{-1}) | 0.0185 |
| | R^2 | 0.9976 |
| | Half-life (min) | 37.5 |
| Photocatalysis | Apparent reaction rate constant (min^{-1}) | 0.0187 |
| | R^2 | 0.9996 |
| | Half-life (min) | 37.1 |

effluent. Consequently, the wastewater containing textile dyes may be discharged at a wide pH range, generally the pH range varies from 6.0 to 10.0 [25]. Therefore, the pH is an important parameter to consider in photocatalytic degradation of textile dyes employing metal oxide semiconductors as catalysts [26]. Considering the range of pH that the textile effluent are discharged, the influence of pH of the solution on the photocatalytic degradation of OS-TGL was evaluated at pH values of 5.0, 7.0, and 9.0 using a dye concentration of 20 mg L^{-1} and 0.5 g of dried beads prepared with 20 g L^{-1} of ZnO as catalyst (Fig. 4). A wide pH range using highly acidic or basic solutions was not evaluated to avoid the degradation of ZnO–alginate beads under these pH conditions. Additionally, acid conditions can promote the dissolution of the ZnO, which was observed by Behnajady et al. [26], during the photocatalytic degradation of C.I. Acid Yellow 23 by using ZnO photocatalyst.

No significant difference was found in the evaluated pH in the photodegradation of OS-TGL. The zero-charge point (pzc) is one of several factors that can influence the effect of pH on photodegradation of dyes. Considering that the pzc of ZnO is 9.0 ± 0.3 , the catalyst surface is positively charged at $\text{pH} < 9.0$ [22,27].

Consequently, in the evaluated pHs, the surface charge of ZnO did not change and remained positively charged; the electrostatic interactions between the positive charged catalyst surface and the anionic molecules of OS-TGL dye are favorable.

3.6. Influence of initial concentration of OS-TGL dye

The influence of the initial concentration of OS-TGL dye ($10, 20, \text{ and } 40 \text{ mg L}^{-1}$) on the solution was also investigated, and the results are in Fig. 5. The degradation efficiency of OS-TGL dye decreased as the concentration of dye in the solution increases. By increasing the concentration of dye in the solution, the dye molecules occupy more active sites of the photocatalyst, which led to a decrease in photo-generated reactive radicals, reducing the efficiency of degradation [10,32]. Therefore, the greater the dye quantity, the slower the process.

The photodegradation of OS-TGL at evaluated concentrations can be described by a pseudo-first-order kinetic model. The obtained correlation coefficients were 0.9951, 0.9996, and 0.9725, respectively, for concentration of 10, 20, and 40 mg L^{-1} . Considering these concentrations, the apparent reaction rate constants calculated were 0.0745, 0.0187, and 0.0111 min^{-1} , respectively. The apparent reaction rate

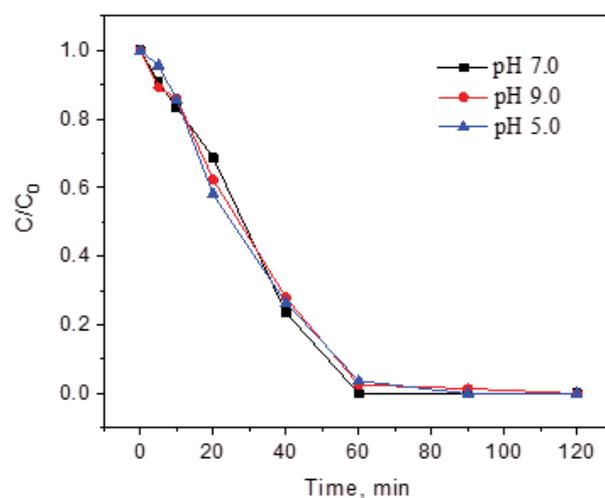


Fig. 4. Effect of pH on photocatalytic degradation of dye. Conditions: 200 mL of OS-TGL at 20 mg L^{-1} , 0.5 g of dried beads prepared with 20 g L^{-1} of ZnO.

constant decreased as the OS-TGL concentration increased. This is because the catalyst radiation absorption tends to be lower in solutions with high dye concentrations, reducing the efficiency of hydroxyl radical formation. Consequently, as the $-\text{OH}$ radicals are the main oxidants, the dye degradation is also reduced [24–31].

3.7. Effect of ionic strength and matrix influence

The influence of ions present in the solution during the photocatalysis process must be investigated, because the residual waters of dyes contain high concentration of ions, such as Na^+ and Cl^- , in their composition. This increase in ionic strength may reduce the efficiency of dye degradation [21]. In addition, the sample and/or effluent matrix can also affect this process due to the presence of other organic and inorganic compounds. The influence of ionic strength and matrix was verified, and the results are presented in Fig. 6.

The presence of salt at different concentrations affected the rate of degradation of the dye, making the process slower (Fig. 6a). Cl^- ions can compete with the dye molecules on the surface of the catalyst leading to deactivation of active catalyst sites, which result in reduced degradation of OS-TGL dye [21]. The degradation of the OS-TGL dye in

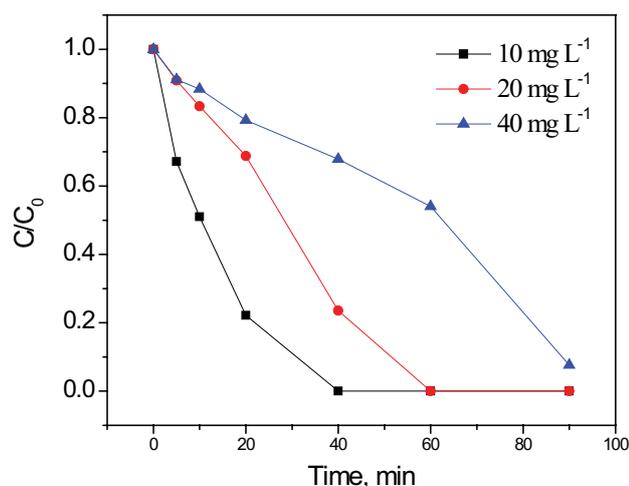


Fig. 5. Effect of the initial concentration on the OS-TGL photodegradation. Conditions: 200 mL of OS-TGL at different concentrations, 0.5 g of dried beads prepared with 20 g L⁻¹ of ZnO, and pH 7.0.

different matrices is slightly different in Fig. 6b, but after 90 min, in all matrices, the degradation was greater than 99%.

3.8. Presence of other dyes

The effluent from a textile industry may contain more than one dye. Therefore, the degradation of the OS-TGL textile dye in the presence of other textile dyes was studied. The experiments were performed initially by mixing the OS-TGL dye with the Solimax Yellow dye and then mixing the OS-TGL dye with the Solimax Blue dye, both solutions contained the dyes in the same ratio (1:1 v/v). In the study, mixing the OS-TGL and yellow Solimax dyes, the photocatalytic degradation was monitored by scanning the UV-Vis measurements, due to the proximity of the region of maximum absorbance of both dyes. The results of this evaluation are presented in Fig. 7, and although the process is slower, both dyes are completely degraded. This demonstrates that it is possible to degrade the OS-TGL dye using ZnO as a catalyst even in the presence of other textile dyes.

3.9. Reuse of the ZnO–alginate beads

The stability and reuse of photocatalysts is a very important feature for analyzing viability in a large-scale application. To evaluate the reuse of the ZnO–alginate beads, after photocatalytic degradation, the beads were removed from the solution and subsequently washed with ultrapure water. The beads were then placed in a fresh dye solution and subjected to the procedure again. This procedure was performed four consecutive times. At the end of each cycle, the concentration of OS-TGL dye present in the solution was determined, obtaining a degradation of more than 99% after each cycle as observed in Fig. 8.

The obtained results were submitted to Tukey's test, at 95% confidence level, and no significant reduction in photocatalytic efficiency was observed between the evaluated

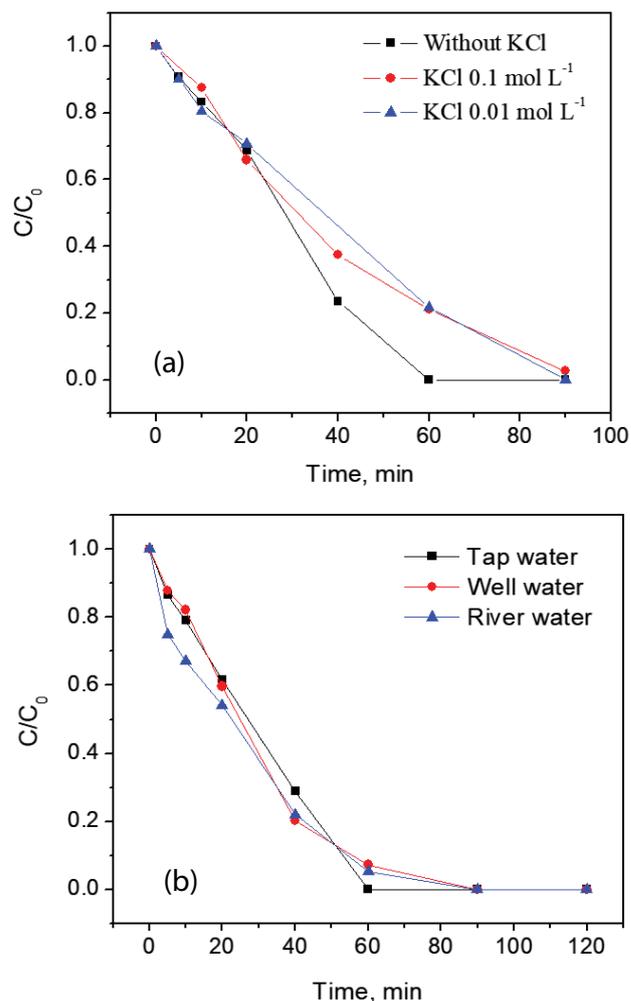


Fig. 6. Effect of ionic strength (a) and matrix (b) on the degradation of OS-TGL dye by heterogeneous photocatalysis. Conditions: 200 mL of OS-TGL at 20 mg L⁻¹, 0.5 g of dried beads prepared with 20 g L⁻¹ of ZnO, and pH 7.0.

cycles. However, after four cycles of photocatalysis a mass loss in the alginate beads is the main limiting factor for reuse of the immobilized catalyst more than four times. This demonstrates the recyclability of the ZnO–alginate beads, which can be used for several consecutive cycles without the need for treatment.

4. Conclusion

Photocatalytic degradation, using ZnO immobilized on alginate beads, was demonstrated to be an efficient process for the treatment of organic pollutants, such as textile dyes, with a percentage of degradation exceeding 99%. The alteration of different factors such as pH, matrices, and ionic strength did not significantly influence the process. The use of the ZnO–alginate beads for the degradation of the textile dye was highly efficient, allowing the reuse of the catalyst for several cycles without losing efficiency. The HP process proved to be an excellent alternative for the treatment of

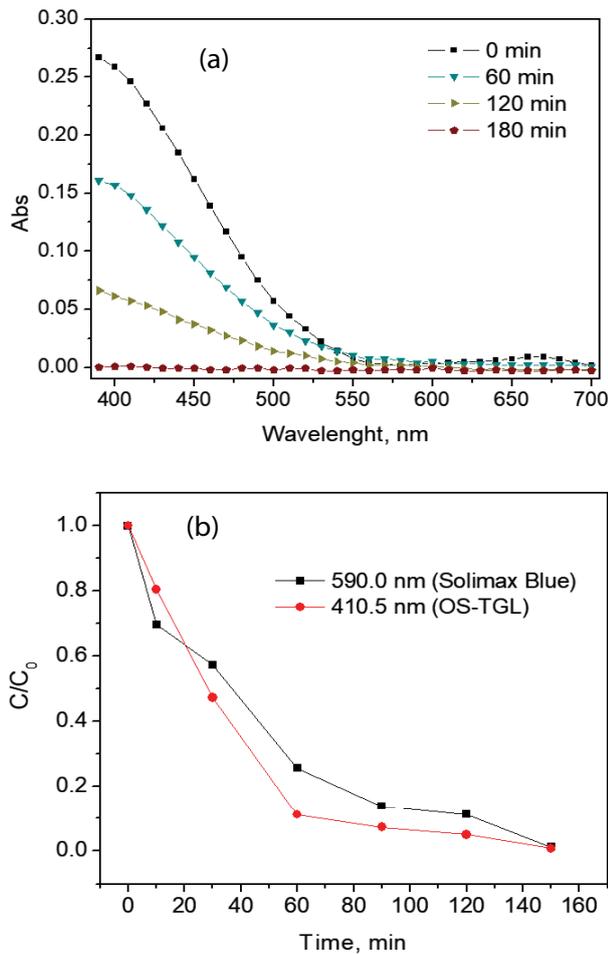


Fig. 7. Effect of the dye mixture: (a) OS-TGL (10 mg L^{-1}) and Yellow Solimax (10 mg L^{-1}), (b) OS-TGL (10 mg L^{-1}) and Solimax Blue (10 mg L^{-1}). Conditions: 200 mL of dye solution, 0.5 g of dried beads prepared with 20 g L^{-1} of ZnO, and pH 7.0.

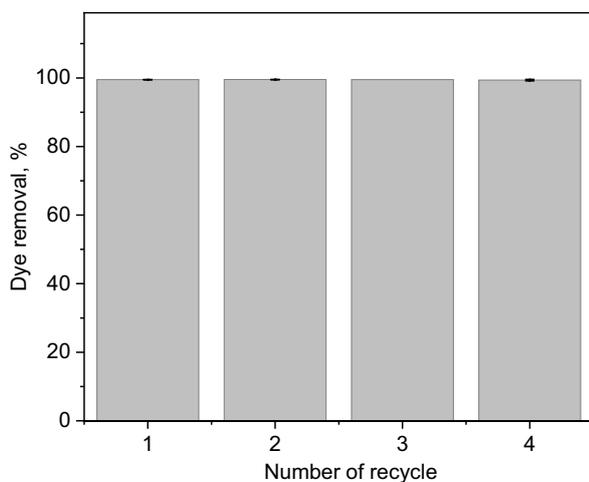


Fig. 8. Recycling efficiency of ZnO–alginate beads during photocatalytic degradation of OS-TGL. Conditions: 200 mL of OS-TGL at 20 mg L^{-1} , 0.5 g of dried beads prepared with 20 g L^{-1} of ZnO, and pH 7.0.

textile effluents, with potential application on the industrial scale.

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