Photocatalytic degradation of methylene blue using TiO₂ supported in ceramic material

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ABSTRACT: The present work evaluates the use of ceramic material, produced with the aid of industrial waste through the Gel-Casting method, as a support for catalysts in the photocatalytic degradation of Methylene Blue. The analysis was carried out in a reactor containing UVC lamps through batch processing. The results show that the reaction of photocatalytic degradation of the dye presents pseudo-first order kinetics, with values of degradation between 60 and 70 %. The study evaluated the deactivation of the catalysts synthesized and supported in the ceramic material. In this case, it was observed that the larger the mass of deposited catalyst on the ceramic support, the longer the lifespan of the sample, since a larger mass takes longer to deactivate.
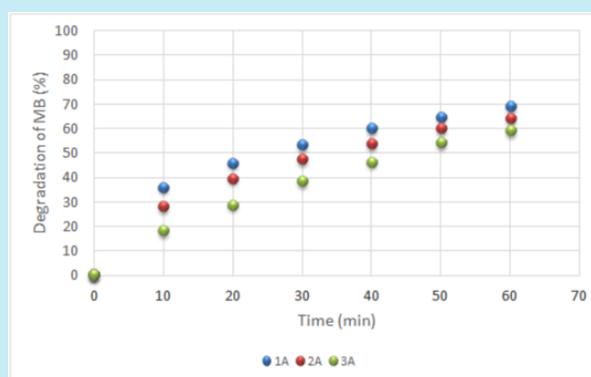
1. Introduction

In the midst of a wide range of pollutants and contaminants from a large variety of sources, there is a need for the development of effluent remediation systems, whether liquid or gaseous. Among these pollutants are dyes, which are widely used in the textile, rubber, paper, plastic, and cosmetic industries. Dyes provide a significant share of environmental contamination, since they alter the natural coloration of the ecosystem to which they are released[1]. About 30 % of the synthetic dyes used in industry are discarded in the form of residues[2]. It is also estimated that 280,000 tons of textile dyes are discharged as industrial effluents worldwide each year[3]. Effluents containing dyes are commonly characterized as having high quantities of salts and organic matter and high toxicity, and a low potential for biodegradation[4].

Different techniques have been developed for the removal of dyes, including chemical precipitation, chemical oxidation, adsorption, and membrane-based biological treatment techniques[5]. However, these techniques mostly result in environmental liabilities when the dye is inadequately disposed of, therefore generating

damages to the environment. One promising alternative for the treatment of water and industrial effluents, which is especially useful for compounds resistant to conventional technologies, are advanced oxidative processes (AOPs). AOPs are based on the generation of hydroxyl radicals, which are a highly oxidizing and low selective species. Several AOPs have been used for dye degradation, among them heterogeneous photocatalysis.

The heterogeneous photocatalytic processes occur when a light energy falls on a semiconductor, with a wavelength equal to or greater than the band-gap energy of this semiconductor. This generates electron pairs that can undergo subsequent oxidation and reduction reactions with some species. These species can then be adsorbed on the semiconductor surface, generating the necessary products[6].

Titanium Dioxide (TiO_2) has attracted a great deal of attention because of its semiconductor properties, since it is a non-toxic, stable photo, with high photocatalytic ability to decompose organic compounds present in air or water[7]. For the TiO_2 fixation, ceramic supports are widely used, due to their properties of mechanical resistance, high surface area, and other properties that favor their use[8].

In this context, this work aims to produce a porous ceramic material, with the aid of industrial waste, impregnated with TiO_2 and applied in the photocatalytic degradation of dye. Methylene blue was used as a model molecule, as it shows similarities with industrial wastewater and is widely used for analysis in bench tests, aiming to observe the behavior and efficiency of photocatalytic systems[9]. Furthermore, the deactivation of the synthesized catalysts was evaluated.

2. Materials and methods

2.1 Synthesis of the ceramic material and impregnation of TiO_2

The TiO_2 catalyst was prepared by the Sol-Gel method using titanium tetraisopropoxide/IV-TIPT (Sigma-Alrdrich), as titanium precursor material, and isopropanol PA (Nuclear), which were mixed in a 2:1 ratio and kept under stirring at 60 °C for 1 h on a hotplate (78 HW-1, Biomixer). After, deionized water was added and the mixture was stirred until dry at a temperature of 100 °C.

Subsequently, the material was ground in a mortar and placed in an oven (MB150/6, Marte) at 100 °C for 1 h, and finally calcined at 500 °C for 2 h.

The ceramic materials that served as support for the synthesized TiO_2 catalyst were produced from the Gel-Casting method, a process developed by the Oak Ridge National Laboratory[10]. Green sand (5.5 % w/w), clay (27.5 % w/w), corn starch (16.5 % w/w), tobacco powder, 75 % w/w), sunflower stem (0.44 % w/w) and water (47.3 % w/w) were used for the synthesis of the ceramic material. Also, residues were used in the manner in which they were available. It should be noted that green sand, tobacco powder, and sunflower stem are considered waste in industrial processes, originating from the foundry industry, tobacco industry, and biodiesel production, respectively. However, when added to the ceramic support composition, the amount of clay (raw material) used decreases, mitigating the environmental impacts from the extraction and transport of the same concomitant to the aggregation of the value of the waste generated by the industries.

The materials were mixed in a mechanical mixer (Q-250M2, Quimis), poured into molds (62 x 62 x 16 mm) and passed through the greenhouse gelling processes (MB150/6, Marte) to 80 °C for 24 h and quenched in a muffle type oven (9813, Jung Ltda.) at 1175 °C for 2 h. After the heat treatment process, the synthesized ceramic samples were sanded with a file, in order to reveal the porosity of the material and, consequently, to increase the surface area. Finally, the ceramic material was weighed and divided into 3 groups of approximately 50 g each.

For impregnation of the TiO_2 in the ceramic supports, a solution containing 5 g of TiO_2 in 100 mL of deionized water was prepared. For the impregnation of the catalyst in the ceramic material a Dip-Coating device was used. The ceramic samples (50 g) were immersed several times in the TiO_2 solution, for 1 min, in order to standardize the thickness and amount of catalyst adhered to the porous surface of the ceramic materials. After impregnation, the samples were calcined in a muffle type oven (9813, Jung Ltda.) at a temperature of 600 ºC for 1 h.

Water absorption (WA) tests were performed by immersing the ceramic samples in water for 24 h. The masses were analyzed before immersion, after immersion and still saturated, with the mass measurement of the sample immersed in water. For this analysis, Equation 1 was used:

$$WA\ (\%) = \left(\frac{M_u - M_s}{M_s}\right) * 100 \qquad \text{(Eq. 1)}$$

where M_u (g) is the mass of the sample saturated with water and M_s (g) is the mass of the sample after drying.

For the apparent porosity (AP) tests, the same mass measurements were used that were performed in the water absorption analysis for the samples. The analysis is done based on Equation 2:

$$AP\ (\%) = \left(\frac{M_u - M_s}{M_u - M_i}\right) * 100 \qquad \text{(Eq. 2)}$$

where M_u (g) is the mass of the sample saturated in water, M_s (g) is the mass of the sample after drying and M_i (g) is the mass of the sample immersed in water.

2.2 Photocatalytic degradation tests of dye

The tests were carried out in a vertical batch reactor irradiated with a 254 nm ultraviolet lamp (UVC) arranged in the center of the reactor in order to obtain better use of the irradiation area by the dye solution to be tested. A peristaltic pump (AWG 4000, Provitec) was used to inject air into the reactor, which is necessary for a photocatalytic reaction and keeps the dye solution under stirring. Figure 1 shows a schematic of the assembly system used for the degradation assays. The vertical reactor was covered with aluminum foil.

For the reactions of photocatalytic degradation, 3 ceramic samples supported with a photocatalyst were used, labeled samples 1A, 2A, and 3A. These samples were placed in the vertical reactor and added to 300 mL of 5 mg L^{-1} aqueous methylene blue solution. The analysis of each of the samples lasted 60 minutes and, every ten minutes, aliquots of the material containing the dye were collected using a syringe and analyzed in a spectrophotometer (V1200, Pró-Análise) through measurements of absorbance, at the wavelength of 665 nm (maximum absorbance of methylene blue). In addition, the deactivation of the synthesized catalysts was evaluated, for which 3 subsequent reactions were carried out with the same catalyst.

Figure 1. Photo of the vertical reactor used in the experiments: a) peristaltic pump and b) vertical reactor containing the UVC lamp (schematic).

3. Results and discussion

3.1 Synthesized catalysts

The ceramic samples were weighed before and after impregnation with TiO_2 (Figure 2) to determine the mass of catalyst adhered to the carrier. The mass values before and after the impregnation are presented in Table 1. It can be seen that, on average, 0.4 g of TiO_2 mass was deposited in each of the samples.

Figure 2. Ceramic samples impregnated with TiO_2.

Table 1. Mass values of samples before and after impregnation

Sample	Weight of ceramic material (g)	Weight of TiO_2 (g)
Sample 1A		
Without TiO_2	50.37	
With TiO_2	50.75	0.38
Sample 2A		
Without TiO_2	50.36	
With TiO_2	50.75	0.39
Sample 3A		

Without TiO₂	50.34	
With TiO₂	50.81	0.47

The mean values of absolute porosity and water absorption for the synthesized catalysts are approximately 35.0 % and 22.5 %, respectively. Sifontes et al.[11], in his study, achieved a porosity of approximately 67 % for ceramic supports obtained from the replica method with polyurethane foam. This difference in the porosity is mainly due to the method for obtaining the samples. In the method used in the present study, the porosity is obtained by burning the loading material and also by the organization of the structure in the burning process. However, in the replicate method, the ceramic material copies the porosity already existing in the base material, thus leaving it with greater porosity. According to Menezes, Neves and Ferreira[12] the water absorption of ceramic materials, where there are ceramic flux residues, is between 5 and 18 %. The value obtained in this work is due to the fact that it contains other elements in the composition that alter its absorption property.

3.2 Photocatalytic degradation tests of methylene blue

The process of direct photolysis with ultraviolet radiation is one in which the only source capable of decomposing or dissociating the dye is light. Experiments were performed with the methylene blue only in the presence of UVC radiation, without the presence of the catalyst, to quantify the contribution of photolysis. The results are shown in Figure 3. The degradation of the methylene blue by photolysis was observed to be approximately 16 %.
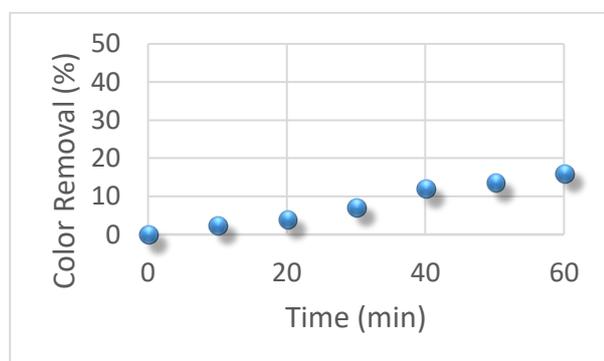
Figure 3. Percentage of color removal for methylene blue due to photolysis.

For the photocatalytic degradation reactions of methylene blue, the three ceramic material supported with synthesized catalyst TiO₂ were used, labeled 1A, 2A and 3A. Figure 4 presents the triplicate data analyzes for TiO₂ supported in ceramic material. For each one of the three analyzes were used ceramic material with TiO₂ supported without previous use, under UVC radiation. The methylene blue photocatalytic degradation values for the synthesized catalyst samples were between 60 and 70 % for 60 minutes of reaction, that is, on average 65 % of degradation. These results show a good reproducibility in the synthesis of these ceramic samples supported with TiO₂ photocatalyst.

Xu, Rangaiah and Zhao[13] also studied the photocatalytic degradation of methylene blue with a TiO₂ catalyst and obtained values of dye degradation of approximately 100 % for 65 minutes of reaction. This difference of degradation is possibly due to ultraviolet radiation used in the experiments. The results of these authors were obtained through the use of a 500 W mercury vapor lamp with a wavelength of 365 nm. According to Lan, Lu and Ren[14], the activation range of the TiO₂ catalyst is 280-400 nm and in the present work a UVC lamp with a wavelength of 254 nm was used, which probably explains the lower degradation obtained, on average 65 %.
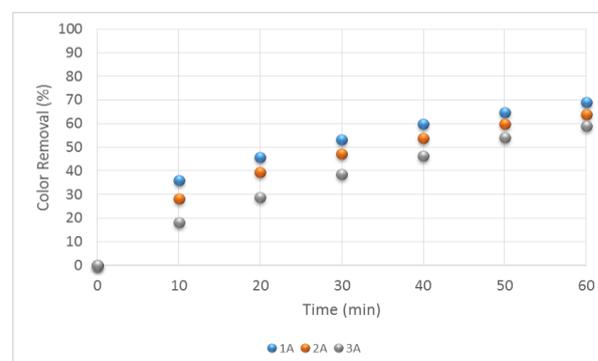
Figure 4. Photocatalytic degradation of methylene blue for samples 1A, 2A, and 3A without prior use.

In order to evaluate the kinetics of the photocatalytic degradation reaction of methylene blue, it was hypothesized that this reaction follows pseudo-first order kinetics, since the dye is sufficiently diluted. Figure 5 shows the results obtained for photocatalytic degradation of the dye in the presence of the synthesized catalyst 3A and UVC radiation. This is verified with a line that passes through the origin, with a coefficient of adjustment equal to 0.9923, proving that the

hypothesis is true. Thus, the specific rate of reaction, k, for these conditions is 0.0155 min^{-1}.
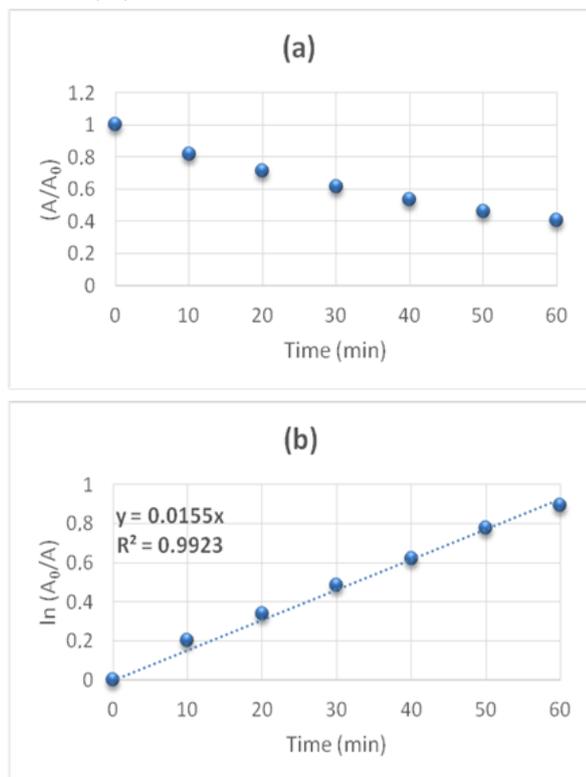
Figure 5. Pseudo-first order kinetics for photocatalytic degradation of the dye: (a) Variation of the absorbance of the dye with the reaction time (b) Linear adjustment of a pseudo-first order reaction.

The catalysts lose their activity during the reaction time. Catalytic deactivation can be caused by aging or sintering, clogging or coke formation, or by poisoning[15]. In order to evaluate the deactivation of the synthesized catalysts, three subsequent tests were carried out with each sample of ceramic material supported with TiO$_2$ (Figure 6).
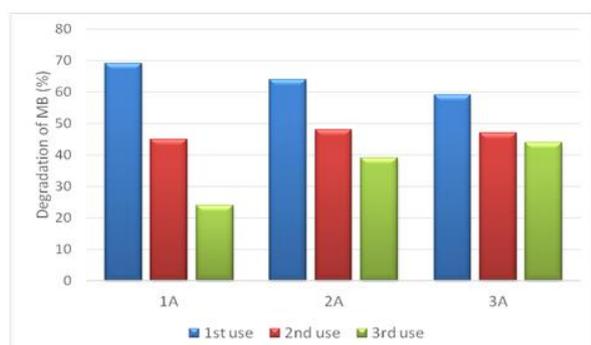
Figure 6. Influence of reuse cycles for ceramics material supported with TiO$_2$ for degradation of new solutions of methylene blue.

Figure 6 presents the results of photocatalysis for TiO$_2$ supported in ceramic materials previously used and now in a second and third reuse cycle to verify their potential and behavior for photocatalysis. It is possible to observe that the samples 1A, 2A and 3A presented a very similar behavior concerning their reuse cycles for methylene blue degradation. The sample 1A presented higher percentage for degradation of methylene blue in the first use and presented greater deactivation, losing about 24 % of its photocatalytic activity in the second use and 45 % in the third use. However, sample 3A, which presented lower degradation of the dye in the first use, maintained higher photocatalytic activity during reuse, obtaining in the third use a dye degradation of 44 %, comparable to the degradation obtained by sample 1A in the second use (45 %). The difference of the percentage of degradation of methylene blue for the three samples is due the heterogeneity of the ceramic samples produced. The porosity is an important factor for supporting photocatalytic material as well as the parameters related to operational control and sample reconditioning. Also, it is possible that saturation of adsorbed species that are usually ions do not desorb and are associated as by products in photocatalysis.

According to Rodrigues[16], the higher the mass of catalyst deposited on the support, the longer the lifespan of the sample, since a larger mass takes more time to deactivate, justifying the smaller deactivation of the synthesized catalyst in sample 3A, which presented a higher impregnated TiO$_2$ mass than catalysts 1A and 2A.

4. Conclusions

The present work studied the application of a porous ceramic material produced from the use of industrial waste and supported with a TiO$_2$ photocatalyst in the photocatalytic degradation of methylene blue. Furthermore, the deactivation of the synthesized catalysts was evaluated. The experiments were carried out in a batch reactor irradiated by a UVC lamp. The results show that the reaction of photocatalytic degradation of the dye followed pseudo-first order kinetics, with degradation values between 60 and 70 % of the dye in 60 minutes of reaction. The evaluation of the deactivation of the catalysts synthesized showed that catalyst 1A, which obtained the greatest

degradation, presented the greatest loss of photocatalytic activity, about 45 % in the third use. While catalyst 3A, with a higher impregnated TiO_2 mass, maintained greater photocatalytic activity during the second and third uses, losing only 15 % of the activity in the third use. Ceramic material was an important factor for supporting TiO_2 and was easy to handle avoiding its use in liquid media and porosity of ceramic material plays an important role to operational control and sample reconditioning for reuse cycles for methylene blue degradation.

5. Acknowledgments

6. References

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