

# Use of PET Structures for TiO<sub>2</sub> Immobilization in the Decontamination of Textile Effluents: An analysis of kinetic models.

Clarice M. Beserra<sup>a</sup>, Evelle D. C. Oliveira<sup>a</sup>, Ivana C. F. Araujo<sup>a</sup>, Luciano C. Almeida<sup>a\*</sup>

<sup>a</sup>Department of Chemical Engineering, Federal University of Pernambuco, 50.740-521 Recife, Pernambuco, Brazil

## Abstract

The textile industry, which is the most important part of the global economy, is a major source of environmental pollution due to the intensive use of synthetic dyes. This study investigated the adsorption of the textile dye reactive black 5 (RB5) using titanium dioxide (TiO<sub>2</sub>) immobilized in PET (polyethylene terephthalate reuse bottle) structures and TiO<sub>2</sub> powder. Sample preparation involved creating PET monoliths and applying a TiO<sub>2</sub> suspension via the washcoating technique. The adsorption kinetics were analyzed using pseudo-first order (PPO), pseudo-second order (PSO), and Elovich models. The results showed that the Elovich model provided the best fit for the experimental data, with R<sup>2</sup> values of 0.991 for TiO<sub>2</sub>/PET and 0.988 for TiO<sub>2</sub> powder. The maximum adsorption capacities of the TiO<sub>2</sub>/PET and TiO<sub>2</sub> powders were 13.92 and 18.96 mg.g<sup>-1</sup>, respectively, for the TiO<sub>2</sub> powder, indicating the greater adsorption efficiency of the TiO<sub>2</sub> powder. However, the use of TiO<sub>2</sub> powder presents challenges related to the constant loss of material and the need for recovery, which makes the reuse process difficult. On the other hand, PET monoliths containing TiO<sub>2</sub> showed promise because of their ease of recovery and reuse despite their low initial adsorptive capacity. This study demonstrates that although TiO<sub>2</sub> powder offers greater adsorption efficiency, immobilization on PET substrates is a practical solution to recovering and reuse problems, making it a viable alternative to decontaminating textile effluents.

*Keywords: Monolith; PET; adsorption; dyes anionic; kinetic models.*

## 1. Introduction

The Textile industry is a major contributor to the global economy. However, it is a major source of environmental pollution due to the intensive use of synthetic dyes. These dyes are complex and potentially toxic organic compounds that are often released into water bodies through industrial effluents, causing serious environmental and public health problems [1, 2].

Effectively removing these dyes from textile effluents is therefore a significant challenge for both industry and researchers. Among the available treatment techniques, adsorption is one of the most efficient and versatile, offering advantages such as operational simplicity, low cost, and high efficiency in removing a wide variety of contaminants, including dyes [3]. The efficiency of this method is intrinsically linked to the characteristics of the adsorbents used.

Titanium dioxide (TiO<sub>2</sub>) can be considered a good adsorbent due to its advantageous properties and affordable cost for environmental applications and can be used in the form of fine powders, pellets or immobilized on substrates. Several studies have used

TiO<sub>2</sub> in the form of a fine powder because it has a larger available surface area and, consequently, greater efficiency. On the other hand, its main disadvantages are the constant waste of the adsorbent and the need to recover it for later reuse. Therefore, one way to address these problems is to immobilize them on structured substrates with high surface areas [4, 5].

Various materials can be used as structures for adsorbent impregnation. In this sense, PET (Polyethylene Terephthalate) from reused bottles is an attractive material because it has high mechanical and chemical resistance, resists aggressive agents, is unbreakable and lightweight, and is 100% recyclable and inert [6].

In this perspective, the aim of this research is to analyze batch adsorption for the removal of the textile dye reactive black 5 (RB5) using two applications: a structured monolith made of PET and a powder adsorbent.

## 2. Methodology

### 2.1 Preparation of monoliths

For the structured monolith adsorbents, the PET sheets were cut, washed to remove residues, and dried

in compressed air. To increase roughness and improve the adhesion of the suspension, a sponge was applied ten times to each side of the sheets. After creating grooves, the sheets were washed again and then modulated to create ripples and channels. To build the monolith, a smooth, wavy sheet was rolled together and tied with kanthal thread. Finally, the monoliths were immersed in ethyl alcohol, subjected to an ultrasonic bath for 10 min, and dried in compressed air.

### 2.2 Preparation of Titanium Dioxide suspension

The PET monoliths were coated using a suspension containing 10% solids by mass of the TiO<sub>2</sub>-G5 adsorbent. TiO<sub>2</sub>-G5, polyvinyl alcohol (PVA), and distilled water were used, the pH of which was adjusted to 4 using nitric acid. The water was heated to 80°C, and PVA was gradually added until it dissolved. After cooling, TiO<sub>2</sub>-G5 was slowly added to the mixture of PVA and acidified water under magnetic stirring to homogenize it. The adsorbent was slowly divided into two parts to disperse the particles. After the additions, the suspension was kept for 24 h on a magnetic stirrer at 400 RPM.

### 2.3 Washcoating coating

The PET monoliths (TiO<sub>2</sub>/PET) were coated using the washcoating technique of successive coatings, starting with the immersion and emersion of the monolith at a constant speed of 3 cm.min<sup>-1</sup>. This was followed by the removal of excess mass using a centrifuge at 4000 RPM for 20 s and then placed to dry in an oven for 1 h at a temperature of 60°C, after which the monoliths were weighed and subjected to the same procedure until they reached the desired mass of 472 mg, which corresponds to 2 mg of suspension per cm<sup>2</sup>, the monoliths were left in the oven for 24 h at a temperature of 60°C, and then weighed and the final mass gain was calculated.

### 2.4 Adsorption kinetics

Adsorption studies in a batch system were carried out in a mixing tank under mechanical agitation (Fig. 1). The volume of the dye solution to be treated was 1 L, and the initial concentration was approximately 25 mg.L<sup>-1</sup>. In this process, the adsorbent and the adsorbate came into contact, and the process was carried out in two ways: in the first way, two monoliths were attached to the paddle of the mechanical agitator so that they were submerged in the dye solution. In the second step, to study the powdered adsorbent, a suspension of TiO<sub>2</sub>-G5 and PVA was dried at 60°C and macerated. The mass of

this powder was equivalent to the mass adhered to the monoliths (around 0.9913 g).



Fig. 1. Schematic illustrating the batch system used in the RB5 dye adsorption tests.

The adsorption behavior of RB5 on TiO<sub>2</sub>-G5 in the two processes were evaluated using pseudo-first order (PPO), pseudo-second order (PSO), and Elovich kinetic models. The PPO kinetic model assumes that the adsorption rate is proportional to the number of active sites available on the adsorbent and is expressed by Equation 1 [7].

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (1)$$

where,  $k_1$  is the pseudo-first order adsorption rate constant (min<sup>-1</sup>),  $q_e$  is the adsorption capacity at equilibrium (mg.g<sup>-1</sup>) and  $q_t$  is the adsorption capacity at time  $t$  (mg.g<sup>-1</sup>).

The PPS model is generally associated with processes in which multiple steps control the total adsorption kinetics [8]. This model mainly depends on the amount of adsorbate present on the surface of the adsorbent and its equilibrium state. The adsorption rate was proportional to the square of the difference between the amount adsorbed and the amount at equilibrium, suggesting the presence of significant chemical interactions. The pseudo-second-order equation can be expressed by Equation 2.

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (2)$$

where,  $k_2$  is the pseudo-second-order adsorption rate constant (g.mg<sup>-1</sup>.min<sup>-1</sup>),  $q_e$  is the adsorption capacity

at equilibrium ( $\text{mg.g}^{-1}$ ) and  $q_t$  is the adsorption capacity at time  $t$  ( $\text{mg.g}^{-1}$ ).

The Elovich model describes the kinetics of adsorption on heterogeneous surfaces, assuming that the adsorption rate decreases exponentially with increasing surface coverage because of the variation in the energy of the different adsorption positions. This model is used to describe the chemisorption of gases on solids and has been used efficiently for the adsorption of various chemical species in liquid media. Equation 3 also gives better results at slower adsorption rates.

$$q_t = \frac{1}{\beta} \ln(1 + \alpha\beta t) \quad (3)$$

where  $\alpha$  is the initial adsorption rate ( $\text{mg.g}^{-1}.\text{min}^{-1}$ ) and  $\beta$  ( $\text{g.mg}^{-1}$ ) is the desorption constant.

### 3. Results and Discussions

#### 3.1 Adsorption kinetics

The adsorption processes were evaluated using PPO, PSO, and Elovich kinetic models, and the adsorption capacity of the RB5 dye by  $\text{TiO}_2$ -G5 over time was analyzed (Fig. 2).

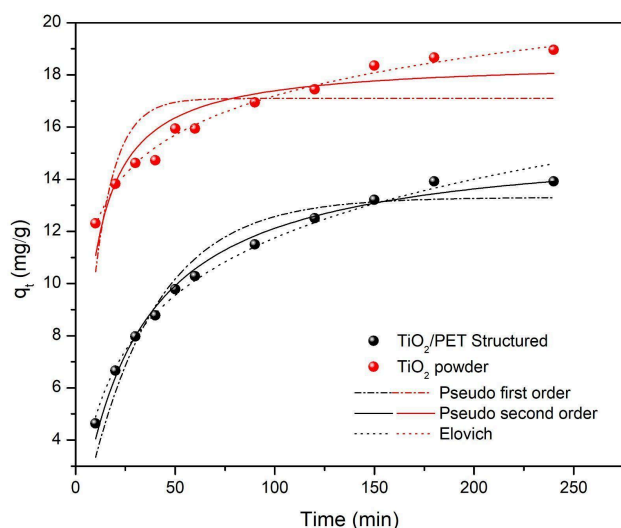


Fig. 2. Kinetic study and fitting of RB5 adsorption kinetic models for  $\text{TiO}_2$ /PET structured and  $\text{TiO}_2$  powder.

The contact times between the adsorbent and adsorbate were 3 and 30 min for both processes. The maximum adsorption capacities were 13.92 and 18.96  $\text{mg.g}^{-1}$ , and the percentage of dye removal was 54.1% and 74.0% for  $\text{TiO}_2$ /PET and  $\text{TiO}_2$ , respectively. The greater adsorptive capacity of  $\text{TiO}_2$  can be attributed by the greater surface area

available to interact with the dye in the medium. Table 1 lists the adsorption kinetic parameters obtained from the nonlinear fitting of the data in Fig. 2. The quantitative evaluation of the model fits was performed by comparing the  $R^2$  values obtained for each model.

Table 1. Kinetic parameters of RB5 dye adsorption on  $\text{TiO}_2$ /PET structured and  $\text{TiO}_2$  powder.

Model	Parameters	$\text{TiO}_2$ /PET structured	$\text{TiO}_2$ Powder
PPO	$q_{\text{cal}}$ ( $\text{mg.g}^{-1}$ )	13.304	17.100
	$k_1$ ( $\text{min}^{-1}$ )	0.029	0.095
	$R_2$	0.943	0.520
PSO	$q_{\text{cal}}$ ( $\text{mg.g}^{-1}$ )	15.566	18.569
	$k_2$ ( $\text{g.mg}^{-1}.\text{min}^{-1}$ )	0.002	0.008
	$R_2$	0.989	0.862
ELOVICH	$\alpha$ ( $\text{mg.g}^{-1}.\text{min}^{-1}$ )	1.116	60.081
	$\beta$ ( $\text{g.mg}^{-1}$ )	0.302	0.461
	$R_2$	0.991	0.988

The kinetic parameters for the adsorption of the RB5 dye on  $\text{TiO}_2$ -G5 in the two processes (structured  $\text{TiO}_2$ /PET and  $\text{TiO}_2$  powder) were obtained from the non-linear fit of the data shown in Fig. 2 and are described in Table 1. The quantitative evaluation of the models was carried out by comparing the  $R^2$  values for each of them. In the pseudo-first order (PPO) model, structured  $\text{TiO}_2$ /PET showed a calculated adsorption capacity ( $q_{\text{cal}}$ ) of 13.304  $\text{mg.g}^{-1}$  and an adsorption rate constant ( $k_1$ ) of 0.029  $\text{min}^{-1}$ , with an  $R^2$  of 0.943, indicating a good fit for this model. In contrast,  $\text{TiO}_2$  powder had a  $q_{\text{cal}}$  of 17.100  $\text{mg.g}^{-1}$ , a  $k_1$  of 0.095  $\text{min}^{-1}$ , but an  $R^2$  of only 0.520, suggesting a less satisfactory fit.

For the pseudo-second-order (PSO) model, structured  $\text{TiO}_2$ /PET showed a  $q_{\text{cal}}$  of 15.566  $\text{mg.g}^{-1}$  and an adsorption rate constant ( $k_2$ ) of 0.002  $\text{g.mg}^{-1}.\text{min}^{-1}$ , with an  $R^2$  of 0.989. The  $\text{TiO}_2$  powder had a  $q_{\text{cal}}$  of 18.569  $\text{g.mg}^{-1}$ , a  $k_2$  of 0.008  $\text{g.mg}^{-1}.\text{min}^{-1}$ , and an  $R^2$  of 0.862, indicating a reasonable fit but inferior to structured  $\text{TiO}_2$ /PET. The Elovich model for structured  $\text{TiO}_2$ /PET showed an initial adsorption rate ( $\alpha$ ) of 1.116  $\text{g.mg}^{-1}.\text{min}^{-1}$  and a

desorption constant ( $\beta$ ) of 0.302 g.mg<sup>-1</sup>, with an R<sup>2</sup> of 0.991, indicating it as the best-fitting model. TiO<sub>2</sub> powder had an  $\alpha$  of 60.081 g.mg<sup>-1</sup>.min<sup>-1</sup>, a  $\beta$  of 0.461 g.mg<sup>-1</sup>, and an R<sup>2</sup> of 0.989, also indicating a good fit, but with different characteristics.

The results obtained using the proposed PSO model were similar to those of the PPO model. Structured TiO<sub>2</sub>/PET showed a more accurate fit with a higher R<sup>2</sup>, despite having a lower adsorption capacity and rate. On the other hand, although powdered TiO<sub>2</sub> exhibited a higher adsorption capacity and rate, the PSO model exhibited a poorer fit. In view of these results, we found that the PSO model has higher R<sup>2</sup> values than the PPO model, has higher R<sup>2</sup> values, indicating a better fit to the experimental data. This suggests that adsorption is strongly influenced by the concentration of the adsorbate and that significant chemical interactions are involved on the surface of the adsorbent, which are better observed by the PSO model.

The Elovich model revealed that structured TiO<sub>2</sub>/PET exhibited a slower initial adsorption rate ( $\alpha$ ) and a lower desorption constant ( $\beta$ ) compared to powdered TiO<sub>2</sub>. This indicates a greater affinity and interaction between the adsorbate and the adsorbent and a slower release of the adsorbate from the surface of the adsorbent during desorption. In addition, structured TiO<sub>2</sub>/PET exhibited a higher coefficient of determination (R<sup>2</sup>), indicating that the Elovich model describes the adsorption kinetics in this system well. When analyzing each model separately for adsorption on the structured TiO<sub>2</sub>/PET system and on TiO<sub>2</sub> powder, we observed that the structured TiO<sub>2</sub>/PET system presented a more satisfactory fit to the models. In general, the Elovich model showed the best fit to the experimental data, followed by the pseudo-second-order model and finally the pseudo-first-order model. It is also the most suitable model for describing adsorption kinetics on heterogeneous surfaces, where the adsorption rate decreases exponentially as the surface becomes more covered.

## Conclusions

The results show that the use of structured TiO<sub>2</sub>/PET offers significant advantages in terms of the ease of recovery and reuse of the adsorbent despite its lower adsorption capacity compared to powdered TiO<sub>2</sub>. Evaluation of the kinetic models revealed that the Elovich model best describes the adsorption kinetics for both systems, with coefficients of determination (R<sup>2</sup>) of 0.991 for TiO<sub>2</sub>/PET and 0.988 for TiO<sub>2</sub> powder. These results also show that

the adsorption of RB5 on heterogeneous surfaces decreases exponentially as the surface becomes more covered. In addition, TiO<sub>2</sub> powder showed a higher adsorption capacity (qcal of 18.569 mg.g<sup>-1</sup> in the PSO model) but faces operational challenges due to the need to recover and recycle the powder, which is not a problem for structured TiO<sub>2</sub>/PET. Therefore, although structured TiO<sub>2</sub>/PET has a slightly lower efficiency, its practical application may be more advantageous due to its simplicity of handling and reuse, indicating a positive balance between efficiency and practicality in the removal of dyes in water treatments.

## Acknowledgements

The authors thank the National Council for Scientific and Technological Development (CNPq) and the Dean of Research and Innovation (Propesqi/UFPE) for the financial support provided.

## References

- [1] Berradi, M.; Hsissou, R.; Khudhair, M.; Assouag, M.; Cherkaoui, O.; El Bachiri, A.; El Harfi, A. Textile finishing dyes and their impact on aquatic environs. *Heliyon*, Vol. 5, N° 11, 2019.
- [2] Kant, R. Textile dyeing industry an environmental hazard. *Natural Science*, Vol. 4, N° 1, p. 22-26, 2012.
- [3] Crini, G.; Lichtfouse, E. Advantages and disadvantages of techniques used for wastewater treatment. *Environmental Chemistry Letters*, Vol. 17, N° 1, p. 145-155, 2019.
- [4] Dalponte, I.; Mathias, A. L.; Jorge, R. M. M.; Weinschutz, R. Degradação fotocatalítica de tartrazina com TiO<sub>2</sub> imobilizado em esferas de alginato. *Química Nova*, Vol. 39, N° 10, p. 1165-1169, 2016.
- [5] Borges, S. S.; Xavier, L. P. S.; Silva, A. C.; Aquino, S. F. Imobilização de dióxido de titânio em diferentes materiais suporte para o emprego em fotocatalise heterogênea. *Química Nova*, Vol. 39, N° 7, p. 836-844, 2016.
- [6] ABIPET. Associação Brasileira da Indústria de PET. Disponível em: <<https://abipet.org.br/o-que-e-pet/>>. Acesso em: junho de 2024.
- [7] Ezzeddine, Z.; Gener, I. B.; Pouilloux, Y.; Hamad, H. Removal of methylene blue by mesoporous CMK-3: kinetics, isotherms and thermodynamics. *Journal of Molecular Liquids*, 223, p. 763–770, 2016.
- [8] HO, Y.S.; MCKAY, G. Pseudo-second order model for sorption processes. *Process Biochemistry*, Vol. 34, N° 5, p. 451-465, 1999.