MACEIÓ - ALAGOAS
EBA15
15° ENCONTRO BRASILEIRO SOBRE ADSORÇÃO
15th Brazilian Meeting about Adsorption

# Study on the synthesis of a nanomaterial to act as adsorbent for the treatment of pharmaceutical compounds

Maryne Patrícia da Silva[a,],Tiago José Marques Fraga[a], Pedro Lucas Araújo do Nascimento[a], Marcos Gomes Ghislandi[a,b], Maurício Alves da Motta Sobrinho[a*]

*[a] Department of Chemical Engineering, Federal University of Pernambuco (UFPE), 1235 Prof. Moraes Rego Av, Cidade Universitária, zip code: 50670-901, Recife/PE, Brazil*
*[b]Engineering Campus – UACSA, Federal Rural University of Pernambuco (UFRPE), 300 Cento e sessenta e Três Av., Cabo de Santo Agostinho/PE, Brazil*

## Abstract

The rising presence of active pharmaceutical compounds in water bodies underscores the inadequacy of conventional processes in eliminating these contaminants and emphasizes the necessity for alternative treatment approaches. In this work, a comparative study was conducted between titanium oxide functionalized with graphene oxide, reduced titanium oxide, and titanium oxide synthesized by liquid phase deposition, in the multicomponent adsorption of diclofenac and venlafaxine. Surface characterization of these materials was performed using SEM, where it was observed that the titanium oxide was not uniformly distributed on the surface of the GO. Additionally, $TiO_{2-x}$ exhibited a spherical morphology. Regarding adsorption, none of the materials were able to adsorb venlafaxine in a multicomponent study. $TiO_{2-x}$ completely adsorbed diclofenac, while GO-$TiO_2$ adsorbed only 60% of diclofenac. The standard material was not able to adsorb any of the pharmaceuticals.

*Keywords:* Pharmaceutical active compounds; adsorption; graphene oxide; reduced titanium dioxide.

## 1. Introduction

Active pharmaceutical compounds (APCs) belong to the class of emerging contaminants (ECs), which constitute a growing matrix of anthropogenic agents commonly found in water bodies and have recently been identified as potential pollutants. When carried into water bodies, APCs can cause environmental imbalances depending on the type, concentration, and organism that comes into contact with the contaminant. In humans, they can disrupt the endocrine system, leading to adverse reproductive, neurological, developmental, and immunological effects. Studies have found that continuous exposure to diclofenac and aspirin can cause brain and liver damage in children, and in the long term, induce cirrhosis due to their bioaccumulation in tissues [1, 2].

Therefore, due to this pollutant potential, more efficient and complementary techniques to existing treatment processes for this class of contaminants have been studied by environmental sciences and engineering [3].

Due to its optical and electrical properties, chemical stability, corrosion resistance, and low cost, titanium dioxide ($TiO_2$) is one of the most studied and widely used materials. Doping with non-metallic elements such as C, S, and N in $TiO_2$ is a method used to shift the material's absorption region to the visible region, thereby achieving better utilization of the radiation incident and adsorption applicaitons [4, 5].

Reduced titanium oxide ($TiO_{2-x}$) is the result of processes that cause defects in the crystalline structure of $TiO_2$, leading to the narrowing of the band gap and increased light absorption [6, 7].

Thus, this work aims to synthesize and characterize titanium oxide functionalized with graphene oxide and reduced titanium oxide to understand their properties and improvements in the application of these nanomaterials as adsorbent for the treatment of diclofenac and venlafaxine. In addition, the adsorption of that pharmaceutical was tested using $TiO_2$ produced by liquid phase deposition to serve as a standard material in a comparative study.

## 2. Methodology

### *2.1 Graphene oxide synthesis and functionalization*

Graphene oxide was synthesized by Hummers and Offeman method and modified according Pedrosa et al. (2018) [8, 9].

### *2.2 Synthesis of reduced dioxide titanium*

Reduced titanium oxide was synthesized using the chemical reduction method similar to that proposed by Xing et al. (2013) [10].

### *2.3 Characterization*

SEM analysis was performed using a Tescan Vega3 microscope with tungsten filament electron sources.

### *2.4 Analytical method*

The contaminates concentration was measured using a high-performance liquid chromatography (HPLC) HP VWR-Hitachi LaChrom Elite model equipped with a UV–visible DAD L-2455 detector. Separation was performed on a Merck Purospher STAR RP-18 (5 µm) LiChroCART 125-4 column using methanol and oxalic acid (v/v = 60/40) as the mobile phase. The HPLC flow rate was 0.6 mL.min$^{-1}$, and the wavelength used was 226 nm.

### *2.4 Adsorption experiments*

Adsorption tests were conducted with the synthesized materials, using venlafaxine and diclofenac as contaminants. A solution containing 20 mg/L of each pharmaceutical was prepared. Subsequently, 300 mL of the contaminant solution was placed in contact with 80 mg of each material under study. The system was isolated from any radiation source and subjected to agitation at 300 rpm. Aliquots were taken at predetermined time intervals.

## 3. Results

Analyzing the surface of the GO-$TiO_2$ (Fig. 1.a), the presence of $TiO_2$ agglomerates on the GO sheets can be observed. Additionally, the distribution of titanium oxide on the GO surface is not uniform. This can be explained by the mechanism proposed by Suttiponarnit et al. (2011), which states that when nanoparticles are dispersed in an aqueous solution at a constant pH, they undergo surface ionization, resulting in the generation of surface charges that cause agglomeration due to electrostatic attraction [9, 11, 12]. In Fig. 1.b, the spherical morphology of $TiO_{2-x}$ nanoparticles can be observed. The literature reports the formation of reduced titanium oxide in various morphologies, such as nanotubes, plates, films, core-shell nanostructures, fibers, spherical and tubular structures, with these differences attributed to the synthesis conditions [6, 13].

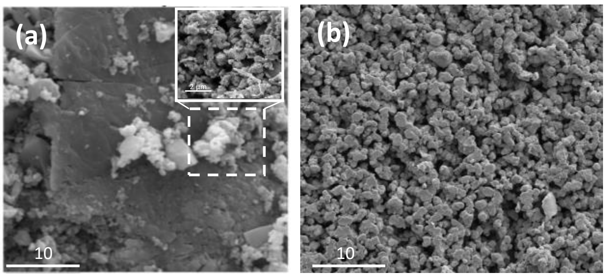

Fig. 1. SEM images of GO-$TiO_2$ (a); $TiO_{2-x}$ (b)

Figure 2 reports the kinetic results for the adsorption of venlafaxine and diclofenac by GO-$TiO_2$, $TiO_{2-x}$ and $TiO_2$ produced by liquid phase deposition.

Analyzing the graphs in Fig. 2, it is possible to observe that none of the materials were able to adsorb venlafaxine in a multicomponent test. However, for diclofenac, GO-$TiO_2$ managed to adsorb 60% of the diclofenac, with an adsorption coefficient of 31.13 mg.g$^{-1}$ after 60 minutes. For $TiO_{2-x}$, diclofenac was 100% adsorbed, and the adsorption coefficient was 56.17 mg·g$^{-1}$, achieved within 40 minutes of reaction. The standard material was not able to adsorb any of the pharmaceuticals.

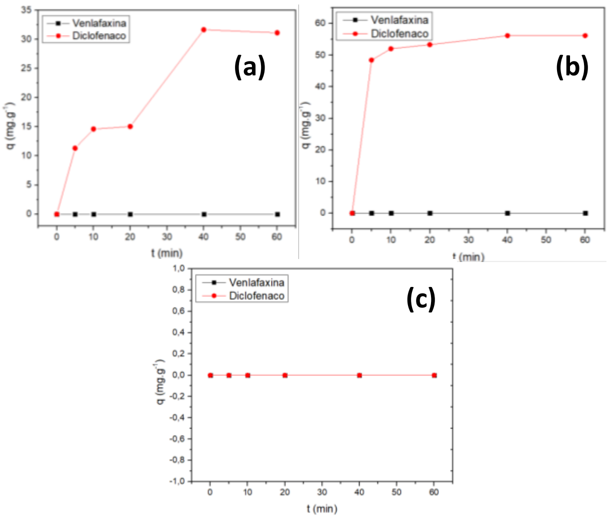

Fig. 2. Kinetic results for adsorption of venlafaxine and diclofenac by GO-$TiO_2$ **(a)**, $TiO_{2-x}$ **(b)** and $TiO_2$ LPD **(c)**

## Conclusion

The results indicate that the presence of graphene oxide and the reduction of $TiO_2$ improved the adsorptive properties of the material. However, to perform mathematical modeling of the results and better understand the adsorption process, it is necessary to conduct monocomponent tests.

## Acknowledgements

The authors acknowledge the technical support provided by the Laboratory of Characterization of Materials at UACSA, Federal Rural University of Pernambuco.

## References

[1] T. Rasheed, M. Bilal, F. Nabeel, M. Adeel, H. M. N. Iqbal. Environmentally-related contaminants of high concern: Potential sources and analytical modalities for detection, quantification, and treatment. Envir Inter, 2019; 122: 55-16

[2] P. Izadi, P. Izadi, R. Salem, S. A. Papry, S. Magdouli, R. Pulicharla, S. K. Brar. Non-steroidal anti-inflammatory drugs in the environmet : Where were we and how far we have come? Envir Polut, 2020; 267:115370-19.

[3] V. K. Parida, D. Saidulu, A. Majumder, A. Srivastava, B. Gupta, A. K. Gupta. Emerging contaminants in wastewater: A critical review on occurence, existing legislations, risk assessment, and sustainable treatment alternatives. J. of Envir Chem Eng, 2021, 9:105966-20.

[4] A. Kulistakova. Removal of pharmaceutical micropollutants from real wastewater matrices by means of photochemical advanced oxidation processes – A review. J. of Wat Proces Eng, 2023; 53:103727-17.

[5] J. Rengifo-Herrera, C. Pulgarin. Why five decades of massive research on heterogeneous photocatalysis especially on $TiO_2$ has not yet driven to water disinfection and detoxification applications? Critical review of drawbacks and challenges. Chem Eng J, 2023; 477: 146875-16.

[6] Z. Li, S. Wang, J. Wu, W. Zhou. Recent progress in defective $TiO_2$ photocatalysts for energy and environmental applications. Renew and Sus Ener Revi, 2022; 156:111980-24.

[7] J. Wang, R. Guo, Z. Bi, X. Chen, X. Hu, W. Pan. A review on $TiO_{2-x-}$ based materials for photcatalytic $CO_2$ reduction. Nanoscale, 2022;14: 11512-17.

[8] W. S. Hummers, R. Offeman. Preparation of Graphitic Oxide, 1957, 1339.

[9] M. Pedrosa, L. M. Pastrana-Martínez, M. F. R. Pereira, J. L. Faria, J. L. Figueiredo, A. M. T. Silva. N/S- doped graphene derivatives and $TiO_2$ for catalytic ozonation and photocatalysis of water pollutants. Chem Eng J, 2018; 348:888-10.

[10] M. Xing, W. Fang, M. Nasir, Y. Ma, J. Zhang, M. Anpo. Self-doped $Ti^{3+}$ - enhanced $TiO_2$ nanoparticles with a high-performance photocatalysis. J Catalysis; 2013; 297: 236-8.

[11] P. M. Martins, C. G. Ferreira, A. R. Silva, B. Magalhães, M. M. Alves, L. Pereira, P. A. A. P. Marques, M. Melle-Franco, S. Lanceros-Méndez. $TiO_2$/ graphene and $TiO_2$ / graphene oxide nanocomposites for photocatalytic applications: A computer modeling and experimental study. Comp Part B, 2018;145:39-8.

[12] K. Suttiponparnit, J. Jiang, M. Sahu, S. Suvachittanont, T. Charinpanitkul, P. Biswas. Role of surface area, primary particle size, and crystal phase on Titanium Dioxide Nanoparticles dispersion properties. Nanosc Resear Lett, 2011; 6: 27-8.

[13] S. G. Ullattil, S. B. Narendranath, S. C. Pillai, P. Periyat. Black $TiO_2$ Nanomaterials: A review of recent advances, 2018;343:708-29.