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PHOTODEGRADATION OF ORGANIC COMPOUNDS FROM TITANATES: A REVIEW

FOTODEGRADAÇÃO DE COMPSOTOS ORGÂNICOS A PARTIR DE TITANATOS: UMA REVISÃO

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ABSTRACT

Contamination of wastewater for dyes; such as Rhodamine B (RhB), Methylene Blue (MB), and Methyl Orange (MO), has caused environmental problems, such as an imbalance in the aquatic ecosystem and a decrease in photosynthetic activity. Thus, for the treatment of waste in water, advanced oxidative process (AOPs) is used, such as the heterogeneous photocatalysis, in which they have been used in the photodegradation of organic pollutants, enabling the use of alternative materials (nanocatalysts). Titanates (TiO_2X) have optical-electronic properties, such as the absorption of a wide range of light and semiconductor behavior, presenting catalytic activity. The analysis of this review in the *ScienceDirect* and *Scopus* databases (2017 - Nov 2022) allowed us to demonstrate the different types of titanates with Al^{+2}, Bi^{+4}, Na^{+2}, and W^{+4} ions for photodegradation of dyes resulting in high percentages of degradation (>80%) mainly due to the formation of free radicals ((•OH) and (•O)) causing oxidation processes in organic compounds. Moreover, properties directly affected the degradation results, such as surface area (allowing an increase in interactions with organic compounds) and band gap energy (allowing the application under visible light). The tendency is that different types of titanates (with metallic ions) are more researched and investigated mainly for photocatalytic applications, allowing the understanding of the synergism mechanism between Ti and metallic ions, to meet sustainable development and the generation of clean energy.

Keywords: Dyes, organic pollutants, sustainability, titanates, visible-light photocatalysis.

RESUMO

A contaminação de águas residuais por corantes; como Rodamina B (RhB), Azul de Metileno (MB) e Alaranjado de Metila (MO), tem causado problemas ambientais, como um desequilíbrio no ecossistema aquático e uma diminuição na atividade fotossintética. Deste modo, para o tratamento de resíduos em água são utilizados os processos oxidativos avançados (POAs), como o processo de fotocatálise heterogênea, no qual, têm sido utilizados na fotodegradação de poluentes orgânicos, possibilitando o uso de materiais alternativos (nanocatalisadores). Assim, titanatos (TiO_2X) possuem propriedades óptico-eletrônicas, como a absorção de uma ampla gama de luz e comportamento semicondutor, apresentando atividade catalítica. A análise desta revisão consistiu em procurar nas bases de dados ScienceDirect e Scopus (2017 - Nov 2022) permitindo demonstrar os diferentes tipos de titanatos com íons de Al^{+2}, Bi^{+4}, Na^{+2} e W^{+4} para fotodegradação de corantes resultando em elevadas porcentagens de degradação (>80%) principalmente devido à formação de radicais

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livres ((•OH) e (•O)) ocasionando processos de oxidação em compostos orgânicos. Além disso, propriedades afetaram diretamente os resultados de degradação como área superficial (permitindo um aumento nas interações com os compostos orgânicos) e energia de band gap (possibilitando a aplicação na visível). A tendência é que diferentes tipos de titanatos (com íons metálicos) sejam mais pesquisados e investigados principalmente para aplicações fotocatalíticas, possibilitando o entendimento do mecanismo do sinergismo entre o Ti e os íons metálicos indo ao encontro do desenvolvimento sustentável e a geração de energia limpa.

Palavras-chave: *Corantes, poluentes orgânicos, sustentabilidade, titanatos, fotocatálise de luz visível.*

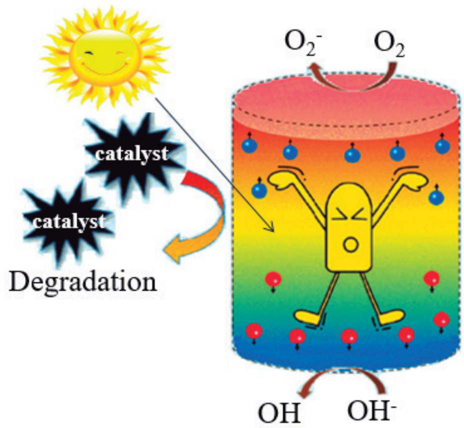
INTRODUCTION

The deterioration of wastewater quality has increased considerably, mainly due to the expansion of human industrial activities caused by the release of untreated or partially treated effluents occasioning adverse effects on the environment and human health. (YENNAWAR; BHOSLE; SHAIKH, 2014). Thus, the textile industry is characterized as one of the potentially polluting industrial sectors since it consumes a large volume of water in the coloring and finishing processes of products (generally precious stones), generating about 700.000 tons of wastewater contaminated for synthetic organic dyes (SAMSAMI *et al*., 2020).

Dyes consist of organic pollutants of considerable chemical stability, highly soluble in water, low biodegradability and carcinogenic for nature directly affecting our lives, being difficult to remove in wastewater by conventional treatment processes, such as physicochemical processes (e.g. coagulation and chemical precipitation) and biological (e.g. aerobic and anaerobic systems) (ATUL *et al*., 2013; DONKADOKULA *et al*., 2020; LEDAKOWICZ; PAŹDZIOR, 2021). Thus, advanced treatment processes (such as adsorption and heterogeneous photocatalysis) are popularly adopted due to its versatility, selectivity and high ability to remove persistent organic pollutants (NETO *et al*., 2018; BABU *et al*., 2019; HUA; LINA; HU, 2019).

Heterogeneous photocatalysis stands out as an alternative since it has great potential for a series of complex organic compounds, such as dyes and drugs (UDDIN *et al*., 2012; BAGAL; GOGATE, 2014; SKIKER *et al*., 2018; MURARO *et al*., 2020). Thus, the heterogeneous photocatalysis process (Figure 1) consists of the photoactivation of a catalyst (semiconductor), under solar or ultraviolet radiation, promoting the generation of oxidization reactions induced onto the surface catalyst (FOTEINIS *et al*., 2018). During this process, free radicals are formed, generally hydroxyl (•OH), capable of reacting non-selectively with several resistant organic compounds, mineralizing them in non-toxic forms, such as CO_2 and H_2O (ABBASI *et al*., 2018).

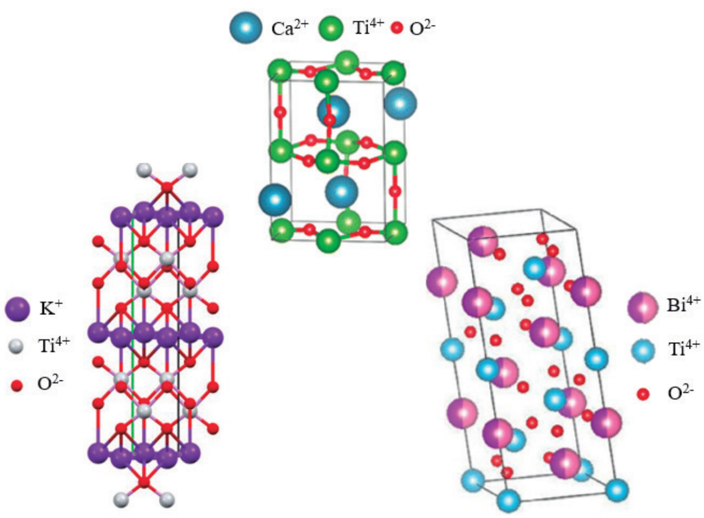
Figure 1 - Scheme of the heterogeneous photocatalysis process.



Source: Author's construction.

Parallelly, titanium dioxide (TiO_2) is a semiconductor material with band gap of the 3.2 eV, with photocatalytic properties, generally, in the application of heterogeneous photocatalysis, it causes the conduction of the electronic transition from the lowest stable valence band to the empty conduction band, mineralizing high energy organic molecules through visible radiation and oxygen in the suspension (GERHARDT; JELL; BOCCACCINI, 2007; RODRÍGUEZ-GONZÁLEZ; TERASHIMA; FUJISHIMA, 2019). Thus, titanates are inorganic compounds whose composition dominates the titanium oxides, usually, the Ti^{4+} cation, have mechanical, bioactive, and photocatalytic properties and can be synthesized utilizing the citrate/EDTA, sol-gel, metal-organic decomposition, solid-state reaction, assisted by hydrogen peroxide, hydrothermal and solvothermal (HECTOR; WIGGIN, 2004; PARK *et al*., 2005; KIDCHOB *et al*., 2009, 2010). Thus, titanates have been used in the photodegradation of dyes, which can adsorb and degrade with high efficiency (WANG *et al*., 2013). Figure 2 shows the types of titanate structures with different ions.

Figure 2 - Types of titanate structures.



Source: Author's construction.

In this context, the present work aims to present a bibliographic review qualitative and exploratory of the titanates, highlighting the application of heterogeneous photocatalysis for the photodegradation of dyes. Thus, the research was realized using the *ScienceDirect* (https://www.sciencedirect.com/) and *Scopus (*https://www.scopus.com/) platforms. (https://www.scopus.com) from 2017 to Nov 2022. The novelty of the work showed the different types of titanates for application for the photodegradation of dyes.

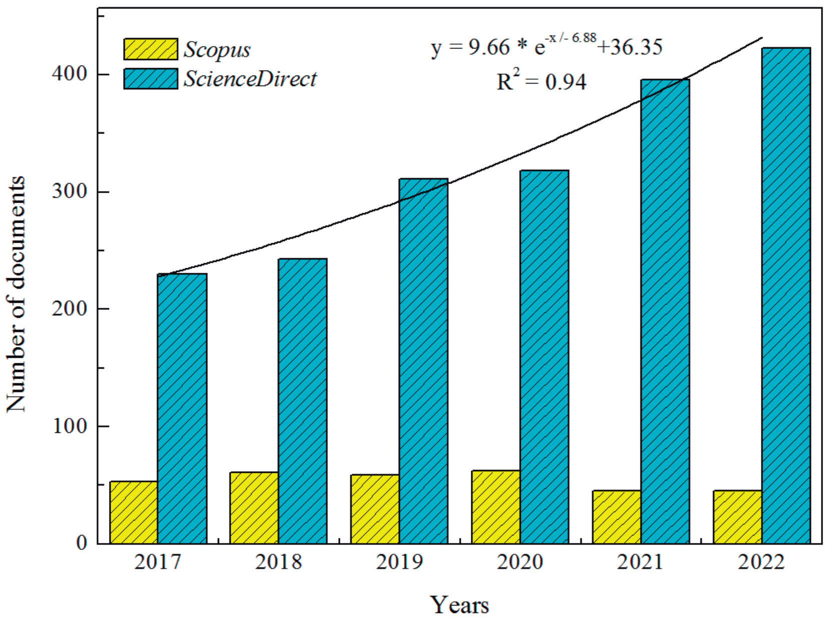
METHODOLOGY

The realization consisted of the analysis of articles on the *ScienceDirect* (https://www.sciencedirect.com) and *Scopus* (https://www.scopus.com) platforms, following the Boolean logic, from 2017 to November 2022, demonstrating the different types of titanates for photodegradation of dyes utilizing heterogeneous photocatalysis. Moreover, the following words were used for the search: 'photodegradation' and 'titanates' and their respective descriptors in English: All the studies analyzed were those that presented the theme described, aiming to analyze the main mechanisms and parameters (properties) that directly affect the photodegradation of dyes.

RESULTS AND DISCUSSIONS

Figure 3 presents the articles found on the platforms *Science Direct* and *Scopus* from 2017 to November 2022 (period selected to draw an overview in the last 5 years).

Figure 3 - Published papers for years in the *Science Direct* and *Scopus* databases (2017- nov. 2022).



Source: Author's construction.

According to Figure 3, 1923 and 329 scientific articles were found in the *ScienceDirect* and *Scopus* databases, respectively, where 6 papers were chosen due to their greater compatibility with the theme of the review study. Briefly, the topic of titanates with application in photodegradation (dyes and organic pollutants) showed a growing trend of published articles correlating the different properties of titanates (surface area, particle size and band gap energy) with the percentage of degradation of the organic pollutant. The increase in the number of articles was possibly due to the new research involving photocatalytic properties with applications for photodegradation and energy generation. Furthermore, the increase in the number of articles occurs on both platforms (database) from 2017 to October 2022, showing a percentage increase of articles in *ScienceDirect* of 183.9%, denoting a current, important and relevant topic. Moreover, the differences found in the databases may be due to the number of journals associated with the *Scopus* platforms and *ScienceDirect*.

Table 1 presents the main results found for the photodegradation of dyes used in titanates on the *ScienceDirect* and *Scopus* platforms (2017-2022). It is worth mentioning that the selected articles contemplated in detail the use of titanates in the photodegradation of organic compounds.

Table 1 - Studies for different titanates for the application in photodegradation of dyes on *ScienceDirect* and *Scopus* platforms (2017- nov. 2022).

Titanates	Methodological aspects	Properties	Conditions	Photodegradation (%)	Reference
Titanate nanotubes (TNTs)	Hydrothermal/ Photodegradation crystal violet (CV)	S_{BET} = 187 m² g⁻¹	TNTs = [3 g L⁻¹], CV = [20 mg L⁻¹] and pH = 6.8	75 after 360 min (under ultraviolet radiation)	MOHANTYA; MOULICKB; MAJIA, 2020
Ni-TNTs	Hydrothermal/ Photodegradation MB	S_{BET} = 72.7 m² g⁻¹	Ni-TNTs = [0.05 g L⁻¹], MB = [100 mg L⁻¹] and pH = 7	97 after 180 min (under visible radiation)	SALEH *et al.*, 2021
Al_2TiO_5	Sol-gel/ Photodegradation MB	S_{BET} = 21.1 m² g⁻¹; Eg = 2.88 eV	Al_2TiO_5 = [0.2 g L⁻¹], MB = [2.5 mg L⁻¹] and pH = 9	46.7 after 60 min (under visible radiation)	AZARNIYA *et al.*, 2020
$g\text{-}C_3N_4$/ $Bi_4Ti_3O_{12}$	Electrospinning/ Photodegradation MO and RhB	S_{BET} = 78.6 m² g⁻¹; Eg = 2.55 eV	$g\text{-}C_3N_4/Bi_4Ti_3O_{12}$ = [0.02 g L⁻¹], MB = [20 mg L⁻¹]	RhB = 96.99 and MO = 80.72 after 30 min (under visible radiation)	SHI *et al.*, 2021
TNTs-W	Hydrothermal/ Photodegradation MB and basic violet 3 (BV3)	S_{BET} = 237 m² g⁻¹; Eg = 2.55 eV	TNTs-W = [1 g L⁻¹], MB and BV3 = [30 mg L⁻¹]	MB = 98.3 and BV3 = 72.58 after 180 min (under visible radiation)	MDLOVU *et al.*, 2022
$Bi_{12}TiO_{20}$/ $BiFeO_3$	Coprecipitation/ Photodegradation MO	nanoparticles of ~17 nm in diameter	$Bi_{12}TiO_{20}/BiFO_3$ = [0.1 g L⁻¹], MO = [8 mg L⁻¹] and pH = 3	100 after 40 min (under ultraviolet radiation)	SKIKER *et al.*, 2018

Source: Author's construction.

Titanate nanotubes (TNTs) degrade around 95% of the CV over 6 h, this can be explained due to the adsorption efficiency, which increases until the number of available sites is active, the remaining minimum numbers of photocatalyst, being able to degrade the CV in the presence of light-UV and amount of oxygen by the transfer of electrons from the photocatalyst (GUPTA; PAL; SAHOO, 2006; TACHIKAWA *et al*., 2006). TNTs were used to decrease the band gap energy and to increase the surface area of TiO_2 (187 m^2 g^{-1}), resulting in increased mass transfer and external diffusion of dye molecules (MOHANTYA; MOULICKB; MAJIA, 2020).

The possibility of producing Ni-doped TNTs by the heavy metal's adsorption process showed increased properties (surface area and electronic properties) being promising and multifunctional for the photodegradation of organic pollutants (OVCHINNIKOV *et al*., 2016; WANG *et al*., 2018). Thus, doping with Ni provided functional groups on the surface of TNTs, increasing interactions electrostatic with MB, and resulting in high photodegradation (SALEH *et al*., 2021).

The photocatalytic activity of Al_2TiO_5 was higher in an alkaline medium mainly due to the generation of hydroxyl radicals causing improved adsorption of the MB dye onto the catalyst surface and effectively separating the charge carriers involved (BOUANIMBA *et al*., 2015; JASEELA; GARVASIS; JOSEPH, 2019). Al was used to decrease the band gap energy from 3.2 eV to 2.88 eV, increasing the photodegradation of the methylene blue dye due to the increase in reactive oxygen species generation (AZARNIYA *et al*., 2020).

The nanocomposite g-C_3N_4/$Bi_4Ti_3O_{12}$ showed improved and persistent photocatalytic behavior for the organic pollutants MO and RhB, this can be attributed to the high specific surface increasing visible light absorption and the efficiency of photoinduced charge separation through the crystalline structure combination of compounds (TANG; ZOU; YE, 2003; SARAY *et al*., 2020). Moreover, the addition of g-C_3N_4 provided an increase in functional groups, causing an increase in the number of active sites improving adsorption (SHI *et al*., 2021).

The TNTs doped with 5% W showed high photodegradation of the MB and BV3 dyes, where the process was summarized in the diffusion of mass species (dyes) to the surface of the TNTs with the help of the driving force (concentration gradient and temperature of the phase homogeneous) (HABIBI; HASSANZADEH; MAHDAVI, 2005; YADAV *et al*., 2017). The doping of W in the TNTs provided an increase in the adsorption capacity of the dye molecules through the channels on the surface of the TNTs, possibly due to the lower energy and heat of adsorption (ABAD; BÖHME; ROMÁN, 2004; MDLOVU *et al*., 2022).

The $Bi_{12}TiO_{20}$/$BiFeO_3$ nanocomposite showed high photocatalytic activity, with the adsorption process playing a crucial role in photocatalytic efficiency due to electrostatic interactions between the nanocomposite and the dye molecules (KIM *et al*., 2014). Two main parameters can affect the photocatalytic activity such as; crystallinity (the crystal structure presented fewer defects causing an increase in electron-hole pairs) and particle size (the smaller the particle size, the more reactive the nanocatalyst surface will be, accelerating chemical reactions with the target molecule) (ZHANG *et al*., 2007; SOLTANI; ENTEZARI, 2013; SKIKER *et al*., 2018).

According to Table 1, different types of titanates were found, with bismuth titanate ($Bi_xTi_yO_z$) being the most used for the photodegradation of dyes increasing the surface area and providing high adsorption and photocatalytic activity (ZAMBRANO; NAVÍO; HIDALGO, 2019). Moreover, the choice of metal has consisted of the chemical composition of the titanate due to the modification in the crystalline structure causing different properties. Parallelly, the hydrothermal synthesis of titanates was the most used due to the ease of the method of doping the titanates with other elements such as; Ni, Fe, Al, Na, and W. Moreover, parameters such as surface area and band gap energy of titanates directly affect the heterogeneous photocatalysis process. Briefly, the photocatalysis process using the titanates consisted of producing hydroxyl radicals and super oxygen to degrade the dyes (MB, MO, RhB and CV, and BV3) transforming them into H_2O and CO_2, where the limiting step is the interaction of the organic pollutant (cationic or anionic) with the titanates. The nature of the dye is decisive as molecular mass and surface charge are factors influenced the steps of heterogeneous photocatalysis.

CONCLUSION

This review presented the different types of titanates (TNTs, Al_2TiO_5, and $Bi_4Ti_3O_{12}$) applied for the photodegradation heterogeneous of the dyes. Thus, the process of photodegradation of dyes utilizing titanates consisted of high percentages of degradation (>80%) due to the metallic ions in the structures of the titanates enabling the formation of free radicals (e.g. •OH and •O) causing the oxi-reduction process of the organic pollutants (dyes). Moreover, the properties such as surface area and bang gap energy affect the adsorption process and heterogeneous photocatalysis, providing an increase in the interactions of the catalyst and the target molecule. The tendency is that titanates with different types of metal ion doping are more researched and used mainly for photocatalytic applications, enabling sustainable development and clean energy generation.

FUTURE PERSPECTIVES

The tendency is that they produce/synthesize different types of titanates (with different metallic ions) always searching to improve the physical-chemical, biological, optical, mechanical, and especially electronic properties. Furthermore, the research and investigation of new titanates are important and relevant, as most articles do not provide detailed explanations of the synergism mechanism between titanium particles with others. However, the titanates approach correlating with experimental designs would facilitate the understanding of photocatalytic properties.

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