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The role of rare earths in the structure of Zinc Oxide (ZnO): A review

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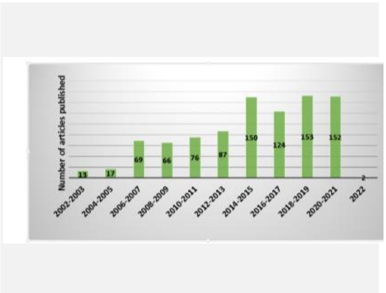

In this review, we present a search for articles using rare earth metals in ZnO doping for environmental remediation. Furthermore, the type of synthesis, the rare earth metals used, and the challenges in developing these materials were analyzed. This review highlights recent advances in the preparation of photocatalysts with high efficiency in the degradation of contaminants. The results obtained through the study showed that doping ZnO with rare earths, an important doping agent in the structure of this semiconductor, can suppress the rapid recombination of charge carriers, which is one of the main disadvantages reported for ZnO in photocatalytic systems.

Introduction

Heterogeneous photocatalysis is a simple and effective method for degrading organic compounds. As it is a type of Advanced Oxidative Process (AOP), the formation of different oxygenated species promotes the degradation of the pollutant (Miranda et al. 2021). In photocatalysis, the degradation reaction is mediated by a semiconductor activated by radiation (UV or visible). In this case, the different redox reactions of the photogenerated charge carriers (electron and hole) promote the oxidation of the target pollutant, with hydroxyl radicals OH being the main species involved in this process (Hirakawa et al., 2007).

Zinc oxide (ZnO) is a prominent semiconductor in photocatalytic systems. However, rapid recombination of charge carriers is one of the main disadvantages reported for this material (Senthilraja et al., 2014). Doping the ZnO structure with rare earths has been explored as an alternative to delay the recombination of charge carriers. It is known that doping promotes the formation of additional energy levels in the band gap region, which will serve as traps to capture photogenerated charges and increase the time that these species remain available on the surface of the semiconductor (Qi et al., 2017).This work aims to carry out a prospective study on the use of rare earth metals as dopants in the ZnO network for photocatalytic application in the degradation of dyes.

Material and Methods

The research used scientific databases, such as Web of Science and Scopus. The articles examined were surveyed in January 2022, with a publication interval from 2002 to 2022. For the word "ZnO doped with rare earth for photocatalytic degradation" (central theme), the following refinement keywords were defined: ZnO doped rare Earth, ZnO doped rare Earth and dye, ZnO doped rare earth and photocatalytic, ZnO and rare Earth, in the advanced search the review articles were excluded. The prospective study regarding published, issued, or filed patents was carried out in the patent databases: World Intellectual Property Organization (WIPO) and United States Patent and Trademark Office (USPTO). The patent data collection was carried out in January 2022, and there was no time restriction for searching the patents.

, 1645 articles were found, 736 of which were in Scopus and 909 in Web of Science To cross the keywords related to ZnO doped with rare earths. The number of articles found for the terms "ZnO doped rare earth and dye" and ZnO doped rare Earth and photocatalytic" was lower than the others, indicating the possibility of future studies on the proposed topic.

Results and Discussion

Figure 1 shows the number of articles published yearly in the Web of Science database referring to the keyword ZnO-doped rare Earth in the last 20 years (2002-2022). The number of articles published with this keyword has increased over the years. The most significant number of publications was in the last four years (2018 to 2022), with 305 articles. Concern about environmental issues has been one of the reasons for the increase in publications on the topic, where doping with rare For this work, the selection criteria were articles that presented ZnO doped with rare earths and applied in the photodegradation process. The keywords used were "ZnO doped rare earth and dye" and "ZnO doped rare earth and photocatalytic," totaling 178 articles, of which 47 articles were excluded as they were repeated in both databases (Scopus and Web Of Science). Therefore, 131 articles were found using the above keywords.

The analysis of articles using ZnO doped with different rare earths and synthesized by different synthesis methods in the degradation of dyes showed very satisfactory results in the degradation of contaminants, demonstrating that they are efficient catalysts with high degradation rates that provide better photocatalytic activity of ZnO in degradation of dyes as contaminants. For example, Irtiqa et al. (2021) prepared ZnO nanoparticles co-doped with Cerium (Ce) and Dysprosium (Dy) synthesized by the low-temperature co-precipitation method. They evaluated the photocatalytic activity of the nanoparticles through the degradation of the dye Rhodamine B (RhB) under UV irradiation. The results showed that the ZnO photocatalyst co-doped with Ce and Dy presented a satisfactory photocatalytic performance of 98% dye degradation. Ahmad et al. (2021) produced ZnO nanoparticle photocatalysts co-doped with Aluminum (Al) and Cerium (Ce) synthesized by the combustion route method and analyzed the photocatalytic activity through the degradation of the Methyl Orange (MO) dye. The results showed that the material is an efficient catalyst, degrading 95% of the dye (MO) in just 45 minutes under visible light irradiation. Table 1 summarizes some of the scientific articles that used ZnO doped with rare earths and studies the photocatalytic activity of the material, presenting the dopant, synthesis method used, percentage of degradation, and the dyes used as photodegraded substrates.

The results of the searches carried out in the patent databases are presented in Table 2. The numbers were found for the keywords "ZnO doped rare Earth," "ZnOdoped rare Earth and dye," "ZnO doped rare earth and photocatalytic," and "ZnO and rare Earth." Among the total number of patents using the keywords "ZnOdoped rare Earth and dye" and "ZnO doped rare earth and photocatalytic," and excluding repeated patents between the databases, 25 were found. Carrying out an analysis of the 25 patents, we found that five are directly related to using ZnO doped with rare earths as a material for degradation or removal of contaminants. It shows that research on this topic is innovative, corroborating the low amount of research highlighted in the articles. Furthermore, table 3 shows that the Brazilian patent databases do not contain data on deposits for the terms mentioned; therefore, the work developed in this area can provide significant support for national technological development.

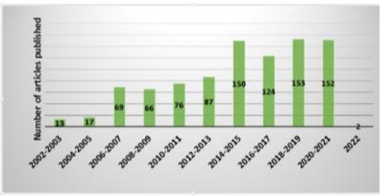

Figure 1. Number of articles published per year referring to the Web of Science database

Table 2. Patents found in the WIPO and USPTO databases.

Keywords	USPTO	WIPO
ZnO doped rare Earth	85	116
ZnO doped rare Earth and dye	10	2
ZnO doped rare Earth and photocatalytic	6	7
ZnO and rare Earth	297	618

Table 1. Scientific articles that used ZnO doped with rare earths.

Material	Synthesis Method	Photogenerated Dye	% Degradation	Source
ZnO co-doped Ce e Dy	Co-precipitation	Rhodamine B (RhB)	98%	Irtiqa *et al.* 2021.
ZnO co-doped Al e Ce	Combustion Route	Methyl Orange (MO)	95%	Ahmad *et al.* 2021.
ZnO doped Sm	Sol-gel	Acid Red (AR)	95%	Kiran *et al.* 2020.
ZnO co-doped Eu e Tb	Combustion	Methylene Blue (MB)	100%	Ahmad *et al.* 2020.
ZnO doped Sm	Chemical Precipitation	Methyl Orange (MO)	94,94%	Sukriti *et al.* 2020.
ZnO co-doped La, Er e Sm	Electrospinning	Congo Red	95,8%	Pascariu *et al.* 2019.
ZnO doped Gd	Microwave Hydrothermal	Methylene Blue (MB)	73%	Marinho *et al.* 2019.
ZnO co-doped Er e Sm	Chemical Solution	Rhodamine B (RhB)	96,5%	Zang *et al.* 2019
ZnO co-doped Lan e Dy	Co-precipitation	Methylene Blue (MB)	96%	Rahman *et al.* 2017.
ZnO doped Eu	Microwave	Methyl Orange (MO)	91%	Korake *et al.*2017.

Table 3. Data related to the patents found**.**

Patent Number	Title	C.I*	Country
CN108855040	Preparation method of Dy-doped ZnO photocatalytic material doped with modified graphene quantum dots	B01J; B01D	China
CN107597093	ZnO-doping, preparation method, and applications thereof	B01J; C02F	China
CN110170318	Nano-zinc oxide doped with rare earth elements and its application	B01J; C02F	China
CN111298783	Method for preparing nano-microsphere photocatalyst by doping rare earth Ce with ZnO and catalytic degradation method of nano-microsphere photocatalyst	B01J; C02F	China
CN113198450	Binary or ternary compound ZnO-based Ti rare earth doped photocatalyst and preparation method.	B01J; C02F	China

Conclusions

The prospective study showed that the use of doping ZnO with rare earths provides better photocatalytic activity of ZnO in degrading dyes as contaminants. Several synthesis routes are addressed, with the sol-gel method being the most used. The synthesized materials showed efficient results in degrading dyes in photocatalytic tests. The few patents filed for ZnO doped with rare earths for photocatalysis in the degradation of dyes show that it is a field yet to be explored. Therefore, this is an area of research that still needs to be extensively studied. There are no patents from Brazilian researchers relating to the material studied in the research.

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