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ECOTECHNOLOGICAL STRATEGIES FOR THE REUSE OF PORONGO WASTE USING HETEROGENEOUS PHOTOCATALYSIS[1]

ESTRATÉGIAS ECOTECNOLÓGICAS PARA REUTILIZAÇÃO DO PORONGO RESÍDUOS USANDO FOTOCATÁLISE HETEROGÊNEA

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ABSTRACT

Waste management is an essential issue in environmental management, as the majority of this waste is not reused or has an incorrect destination. In this way, the porongo (*Langenatia siceraria*) is a curcubitaceae known in the southern region of Brazil and used culturally to prepare the drink in the state of Rio Grande do Sul. However, during its processing, significant amounts of waste are generated becoming a socio-environmental problem. An alternative for the treatment and adequate disposal of this waste is the production of catalysts using Advanced Oxidative Processes (AOPs), highlighting the heterogeneous photocatalysis. The present work denoted ecotechnological strategies for reusing of residual porongo biomass, highlighting its application in heterogeneous photocatalysis to photodegrade organic pollutants.

Keywords: Advanced Oxidative Processes; catalysts; ecotechnology; *Langenatia siceraria*; sustainability.

RESUMO

O gerenciamento dos resíduos é uma questão essencial na gestão ambiental, em virtude que a maioria destes resíduos não são reaproveitados ou têm um destino incorreto. Deste modo, o porongo (Langenatia siceraria) é uma curcubitácea conhecida na região sul do Brasil, utilizada culturalmente para preparar a bebida do estado do Rio Grande do Sul. No entanto, durante o seu processamento, quantidades significativas de resíduos são geradas, tornando-se um problema socioambiental. Uma alternativa para o tratamento e descarte adequado desses resíduos é a produção de catalisadores para aplicação em Processos Oxidativos Avançados (POAs), destacando a fotocatálise heterogênea. O presente trabalho apresenta estratégias ecotecnológica para o reaproveitamento de biomassa residual de porongo, destacando sua aplicação em fotocatálise heterogênea para degradar poluentes orgânicos.

Palavras-chave: *Processos Oxidativos Avançados; catalisadores; ecotecnológica; Langenatia siceraria; sustentabilidade.*

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1. INTRODUCTION

The manufacture of products using *Langenatia siceraria* is little explored and can play an important role in several sectors. Additionally, materials with similar characteristics are used such as fibers of vegetable origin in the textile and civil industry denoting cotton, linen, hemp, sisal, and wood making them a potential renewable alternative source (Murmu, 2022; Satankar *et al.*, 2023)

The specie *Langenatia siceraria* is generally cultivated in the southern region of Brazil, being used mainly in the production of gourds for *chimarrão* due to its versatility in adapting to the region's climate and its ease of cultivation standing out as an important agricultural crop. (Pertille; Hartmann; Philipp, 2015). However, during the processing of porongo significant amounts of waste are generated (e.g., during the gourd manufacturing process, only the upper part is used, while around of 50% of the material in each fruit is incinerated or crushed for produce fertilizer) (Lago, 2013).

Parallelly, incorrect disposal of porongo is harmful to the environment due to its composition containing toxic components as petroleum products, pharmaceutical compounds, chlorine, nitrophenols, polycyclic aromatic hydrocarbons, organic dyes, pesticides, and heavy metals (Athalathil *et al.,* 2015). Additionally, biomass residues have aroused interest for application in advanced oxidative processes with an emphasis on heterogeneous photocatalysis, can be used as possible precursors of photocatalysts in the degradation of organic pollutants (Subramaniam *et al.,* 2023). Thus, scientific research has sought alternatives in achieving ecological processes to find appropriate means for porongo waste demonstrated in Table 1.

Table 1 - Ecotechnological applications of porongo waste.

Application	Comments	Reference
Energy reserve	Characterization of porongo as biomass for energy source	Paust; Lourenço, 2017
Biosynthesized nanoparticles	ZnO nanoparticles biosynthesized with porongo cellulose extract for anti-dandruff, antimicrobial, and anti-arthritic applications	Kalpana *et al.,* 2017
Biosorbents	Biosorbents synthesized from porongo with ZrO_2 for application in the removal of textile dye RB19	Petrović *et al.,* 2015
	Preparation, characterization, and comparison of different biosorbents from porongo for removing methylene blue textile dye	Stanković *et al.,* 2012
Activated charcoal	Study of adsorption using activated carbon prepared from porongo peels for the removal of fluoride	Hanumantharao *et al.,* 2012

In this context, the study aims to conduct a Boolean exploratory search using the *ScienceDirect* platform to use porongo in applications involving the degradation of organic pollutants such as pesticides, pharmaceuticals, and dyes. It is worth mentioning that the abundance of porongo waste when discarded incorrectly is a problem mainly in Rio Grande do Sul resulting in toxic and harmful effects on the environment. Additionally, it relates to the achievement of the sustainable development goals (SDGs), specifically goal six (Clean Water and Sanitation), and goal fourteen (Life Below Water) (SDG, 2022).

2. LITERATURE REVIEW

2.1. ADVANCED OXIDATIVE PROCESSES (AOPS)

Advanced oxidative processes (AOPs) are denominated as physicochemical processes based on the formation of species with high oxidizing power around 2.8 eV, where the hydroxyl radicals ($^{\bullet}OH$) are generated and effective in the degradation mineralizing the organic pollutants (López *et al.,* 2023; Sivaranjani *et al.,* 2023). Furthermore, the great advantage of AOPs is the treatment of mineralized organic compounds that are not transferred from one phase to another (including photochemical and photocatalytic processes) generally occurring in conventional water treatment processes (Javanbakht; Mohammadian, 2021).

2.1.1. Heterogeneous Photocatalysis

Heterogeneous photocatalysis is a process that involves redox reactions induced for radiation on the surface of semiconductors denominated photocatalysts (Teran, 2014). The semiconductors are characterized for having two energy bands, where a low-energy band without the electron movement (valence band), and a high-energy band with free electron movement (conduction band) (Mansur *et al.,* 2014). In this way, the band gap (between the valence, and conduction bands) corresponds to the minimum energy required to activate the photocatalyst for the excitation of electrons jumping from the smaller band to higher energy-generating oxidative radicals (Li *et al.*, 2016).

The photocatalysis process is based on the irradiation of a photocatalyst for the absorption of energy of the photon with greater or equal band gap energy to promote the electronic transition. Moreover, the electrons are promoted from the valence band to the conduction band forming oxidizing and reducing sites reacting with the electrons acceptor and donor species adsorbed on the semiconductor enabling the chemical reactions of photocatalysis (Zhou *et al.,* 2024). It is worth highlighting that oxygen is of great importance for the reaction since hydroxyl and superoxide radicals are primary oxidants in the photocatalytic oxidation process, where the degradation of the reaction must depend on the concentration of dissolved oxygen in water (Khataee; Mansoori, 2012).

In the photocatalytic process, some interferences occur, as; (a) the presence of large quantities of oils, greases, and solids affecting the useful life of its energy sources; (b) the presence of solids on the surface of the blade preventing the passage of radiation and its contact with the oxidizing agent; (c) concentration of the organic pollutants; (d) photocatalyst concentration; and (e) the luminous intensity of the radiation source. However, the catalyst easily comes into contact with the irradiation depending on how it is homogenized (Balarama *et al.,* 2022; Manojkumar *et al.,* 2023).

The second-order Langmuir Hilshewood model (Equation 1 and 2) is generally used to study the kinetics of heterogeneous photocatalysis, where the formation of electrons (e_{bc}^{-}) and holes (h_{bv}^{+}) occurs due to the photoexcitation of the catalyst decaying the molecules undergoing chemical reactions generating products simpler and regenerating the catalyst surface (Gogate; Pandit, 2004; Gaya; Abdullah, 2008). Additionally, the study of the thermodynamics of photocatalysis uses the Arrhenius equation (Equation 3) to evaluate the activation energy of the catalyst, where temperatures greater than 70 °C make the adsorption process difficult reducing the photodegradation of pollutants (Ghasemi; Younesi; Zinatizadeh, 2016). Thus, treating organic pollutants is appropriate in temperatures close to environmental conditions.

$$(-r_i) = -\frac{dC_i}{dt} = \frac{k_s * K * C_i}{1 + K * C_i} \qquad (1)$$

$$C_i = C_{i0} * e^{-k*t} \qquad (2)$$

$$\ln{(k)} = A^{-\frac{Ea}{R*T}} \qquad (3)$$

Where: is the reaction rate; is the adsorption constant; is the apparent constant of reaction; is the initial organic pollutants concentration; is the organic pollutants concentration; k is the apparent rate of the pseudo first-order reaction, t is the reaction time; A is the Arrhenius factor; Ea is the activation energy (J); R is the ideal gas constant which is equal to 8.314 J K^{-1} mol^{-1} and T is the temperature (K).

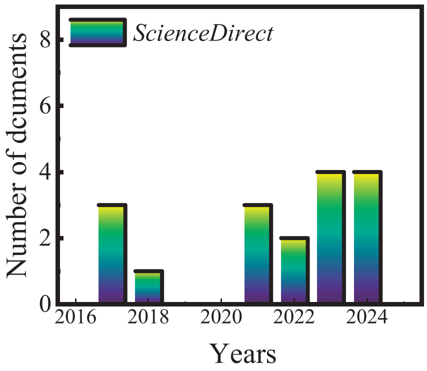
3. METHODOLOGY

To prepare this work, the Boolean tertiary research was carried out based on studies for authors relevant to the subject in the *ScienceDirect* research platform (www.sciencedirect.com) using the descriptors “heterogeneous photocatalysis”, “biomass waste” and “organic pollutants” from 2013 to 2024.

4. RESULTS AND DISCUSSION

Figure 1 denotes the articles in the *ScienceDirect* platform from 2013 to March 2024.

Figure 1 - Scientific articles published in the *ScienceDirect* database from 2013 to March 2024.



According to Figure 1, 17 scientific articles were denoted in the *ScienceDirect* database. Briefly, the first articles published showed a percentage increase of articles in the *ScienceDirect* of 400% denoting a current important and relevant topic. In this sense, the biomass residues have aroused interest in their use in photocatalysis, where numerous sources of these biomasses are not satisfactorily and/or adequately utilized transforming them into industrial waste. Table 2 presents some ecotechnological strategies for using wastes and their applications in heterogeneous photocatalysis.

Table 2 - Biomasses used for application in heterogeneous photocatalysis.

Biomass	Application	Reference
Rice husk, spent acacia, and tobacco dust	Biomasses used as supports in the preparation of catalysts impregnated with $TiCl_4$ in the degradation of the rhodamine B dye under UV, and visible radiation	Da Silva *et al.,* 2016
	Precursor for the synthesis of a mixed TiO_2/SiO_2 catalyst for degradation of terephthalic acid under UV-C radiation	Yener *et al.,* 2017
	Precursor for the synthesis of a mixed SnO_2/SiO_2 catalyst	Ferreira *et al.,* 2015
Rice husk	Catalyst supported for the incorporation of titania under rice husk and tested on the degradation of methylene blue under UV radiation	Adam *et al.,* 2013
	Catalyst supported on rice husk to verify its influence on the degradation of phenol, and (4-CP) under UV radiation	Naeem; Ouyang, 2013
	Supported catalyst prepared from rice husk and used to determine the degradation kinetics of 2-deoxyribose	Karthikeyan; Sekaran, 2014
	Catalyst supported from rice husk and impregnated with $TiCl_4$ for the evaluate the photodegradation of methylene blue, naphthalene, phenol, and abamectin under UV radiation	Lattuada *et al.,* 2013
Cellulosic fibers	Catalyst supported from zinc-based cellulosic fibers for brilliant green degradation	Gao *et al.,* 2014
Pine cone	Synthesis of Ni-doped TiO_2 activated carbon for the photocatalytic degradation of anthracene	Baruah *et al.,* 2022
Punnai shell	Cobalt and nickel oxides supported activated carbon for the degradation methylene blue	Murugesan *et al.,* 2021
Macroalgae, *Sargassum Horneri*	Photocatalytic activity of TiO_2 by immobilization on activated carbon for degradation of aquatic naphthalene	Gao *et al.,* 2014

$TiCl_4$: titanium tetrachloride; UV: ultraviolet radiation; TiO_2: titanium dioxide; SiO_2: silicon dioxide; UV-C: ultraviolet C ray; SnO_2: tin dioxide; and 4-CP: 4-chloro-phenol.

According to Table 2, it was possible to verify that biomasses are used as precursors or supports for application in heterogeneous photocatalysis. Moreover, highlights the lack of scientific studies using porongo biomass, where it would denote as a considerable sustainable source to support the synthesis of photocatalysts specifically supported by heterogeneous photocatalysis. It is worth mentioning that the biomass produced from rice husks was used as support containing titanium dioxide (photoactive phase), which is known for the high degree of generation of oxidative radicals increasing heterogeneous photocatalysis.

5. CONCLUSION

In the present work, it was possible to identify the ecotechnological potential of reusing residual porongo biomass as a precursor or support for application in heterogeneous photocatalysis. The structural, morphological, and textural characterization of this residue to evaluate its applicability in the synthesis of photocatalysts for the degradation of organic pollutants is of fundamental importance so that there can be a diversification of the use of this raw material. In this way, the biomass produced was used as a catalytic support, mainly rice husk increasing the surface area and demonstrating photodegradation of organic pollutants, especially the dyes. Moreover, titanium nanoparticles were utilized in the photoactive phase increasing the generation of oxidative radicals. Therefore, porongo has different chemical elements that can be used as catalytic support for cationic and anionic pollutants.

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CREDIT AUTHOR STATEMENT

Pedebos, M.E.: conceptualization, data curation, formal analysis, investigation, validation, writing-original draft, writing-review, and editing; **Santos, G.;** conceptualization, validation, data curation, writing-review, and editing; **Druzian, D.M.:** conceptualization, validation, data curation, writing-review, and editing; **Da Silva, W.L.:** conceptualization, data curation, formal analysis, investigation, validation, writing-original draft, writing-review, and editing.

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