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The Role of Bismuth in Developing Bio-Based Materials for Efficient Polyphenol Adsorption and Solar Photodegradation

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Abstract (maximum 250 words): Olive oil production is one of Europe's best-performing agricultural sectors. It produces olive oil and undesirable by-products (wastes), such as olive mill wastewater (OMWW) and organic waste. OMWW contains large amounts of organic compounds (primarily polyphenols, phenols, and tannins). Polyphenols have dual effects: beneficial for nature and humans but harmful in high concentrations in wastewater. If not adequately treated in wastewater, polyphenols can threaten biodiversity, ecological balance, and water quality and pose a risk to human health. Effective management of these compounds in industrial waste is an urgent task for scientists. However, in a circular economy vision, the possibility of recovering polyphenols in large quantities represents an important challenge. Based on these premises, the purpose of the present work is developing and optimizing different bismuth-modified, easily recoverable materials composed of alginate spheres modified with a magnetic core and bismuth oxyhalides or Bi^{3+} ions as an active phase to recover and/or photodegrade polyphenols under solar light irradiation.
Here, we present our first results obtained using synthetic wastewater containing gallic acid (GA), 3,4,5-Trimethoxybenzoic acid (345TMBA), and 4-Hydroxybenzoic acid (4HBA) as model polyphenols. After adequately optimizing the conditions, 98% of polyphenols were collected, and the remaining part was effectively and quickly photodegraded.

Keywords: Photocatalysis; adsorption; polyphenols

1. INTRODUCTION

Global olive cultivation spans over 10.8 million hectares, with the majority, 97%, concentrated in the Mediterranean region. Spain leads in olive oil production, contributing more than 52% of global output, whereas Italy accounts for 33% of the EU's production [1]. During the olive oil extraction process, both olive oil and undesirable by-products (wastes), namely olive husks or crude olive cake and olive mill wastewaters (OMWW), are produced. These latter have a complicated composition and contain about 15-18% organic compounds, mainly phenols and polyphenols, ranging from 1 to 8 g/L [2]. If, on the one hand, these latter have antioxidant properties and may have potential health benefits, on the other hand, an excess in wastewater can cause environmental problems, such as changes in the chemical conditions of aquatic ecosystems and negative effects on aquatic organisms [3]. The recovery of polyphenols from OMWW as well as other waste is a hot topic for food and cosmetics industry. However, at the same time, it is imperative to develop effective methods for the purification of OMWW that comply with clear legal restrictions.

Treatment of wastewater from olive oil production is an integral part of modern industrial processes to minimize negative environmental impacts. There are several methods of wastewater treatment, each of which is used depending on the scale of production and the chemical characteristics of the wastewater.

It is worth noting that modern technology is constantly improving, and researchers are currently working to develop more efficient and environmentally sustainable methods for wastewater treatment, which is essential for maintaining a balance in the environment.

In this regard, advanced oxidation processes, especially heterogeneous photocatalysis, can play an important role. BiOX (X = Cl, Br, I) has recently attracted considerable attention as photocatalysts for environmental remediation. The unique physicochemical properties of these materials (band structures and layered nanostructures) are considered a pivotal point in improving their photocatalytic performance using visible light. Although the use of photocatalysts in the form of dispersed powders into the reaction medium (slurry configuration) allows taking advantage of the whole active surface area of the catalyst, if used in large amounts, the active materials might possibly contaminate the environment since they are challenging to manage and prone to dispersion. Therefore, this approach poses severe problems in large-scale industrial applications. Their immobilisation strikes a compromise between the benefits of the photocatalysts and the necessity to ensure their appropriate application by improving stability and facilitating simpler handling. Floating photocatalysts give the advantage of maximizing both light utilization and surface aeration since they can float on the air-water interface. Their use also decreases the post-treatment cost. Based on these premises, this work aims to develop materials that are able to recover polyphenols when present in large amounts and degrade them when their concentration in solution is low by sunlight irradiation. Different easily recoverable materials based on BiOBr and Bi^{3+} ions were developed and tested for the recovery and photodegradation of model molecules: gallic acid, 3,4,5-trimethoxybenzoic acid, and 4-hydroxybenzoic acid. The key role of bismuth in both the processes (adsorption and photodegradation) is investigated.

2. MATERIALS AND METHODS

2.1 Materials preparation and characterization

BiOBr powders: BiOBr was prepared by co-precipitation method [4], using $CaBr_2$ and $Bi(NO_3)_3$ as Br and Bi precursors, respectively.

Fe_3O_4 nanoparticles (NPs): Fe_3O_4 NPs were prepared according to the procedure reported by Della Pina *et al*. [5] with some modifications.

BiOBr- and Bi-modified magnetic alginate spheres (FAB and BiAS): alginate spheres were synthesized according to a protocol detailed by Falletta *et al.* in a recent publication [6].

A proper amount of Fe_3O_4 NPs was added to an aqueous sodium alginate solution. This suspension was then introduced dropwise into a 3 wt.% Ca^{2+} aqueous solution over 2 hours, resulting in the formation of magnetic alginate spheres. A two-step approach prepared BiOBr-modified magnetic spheres (FAB): at first, the magnetic spheres were immersed into a Bi^{3+} solution (step 1) and then into a $CaBr_2$ solution (step 2). This procedure was repeated several times to enhance the percentage of BiOBr on the surface of the spheres (38%).

Bi-modified alginate spheres (BiAS) were prepared by adding an aqueous solution of sodium alginate dropwise into a 3 wt.% Bi^{3+} aqueous solution over 2 hours.

All the synthesized materials were properly characterized by several analytical techniques to investigate their physico-chemical properties.

2.2 Adsorption and photocatalytic performances of the synthesized materials

The prepared materials' adsorption capacity and photocatalytic activity were evaluated using three model polyphenols (gallic acid, 3,4,5-trimethoxybenzoic acid, and 4-hydroxybenzoic acid). The photodegradation studies were investigated under solar light and LED irradiation. HPLC analyses monitored the pollutant degradation, and when possible, TOC analyses investigated the mineralization percentage.

3. RESULTS AND DISCUSSION

3.1 Materials characterization

FESEM investigated the morphology and composition of FAB coupled with EDS, as demonstrated in Figure 1, revealing a minimal presence of iron on the sample's surface, suggesting that most of the Fe_3O_4 NPs are encapsulated within the alginate spheres rather than being dispersed on the exterior. The percentage of Fe inside was evaluated to be 1%. The presence of BiOBr on the surface is confirmed.

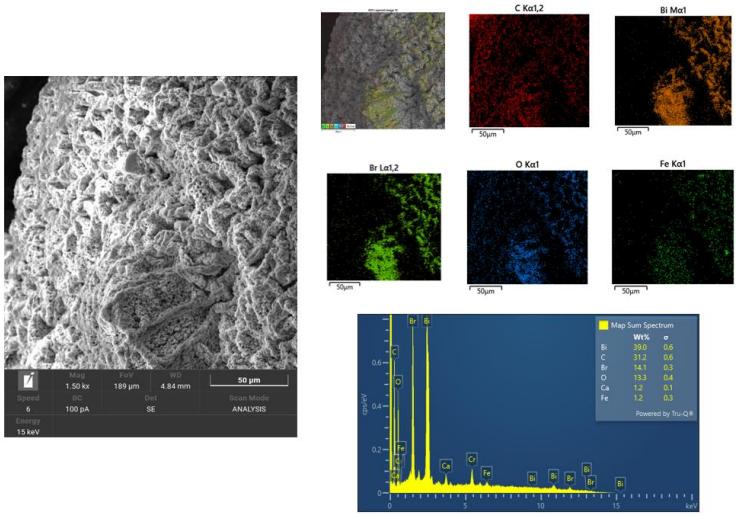

Figure 1. FESEM images and EDS analysis of FAB.

The adsorption capacity and photocatalytic activity of FAB were evaluated using gallic acid (GA), 3,4,5-trimethoxybenzoic acid (345TMBA), and 4-hydroxybenzoic acid (4HBA) as model molecules. Generally, it was observed that for low polyphenols concentration (10 ppm), the material exhibits a high ability of both adsorption and photodegradation (under both solar and visible light irradiation), reaching 80% of GA and 4HBA) removal in the dark and the complete molecules degradation under light irradiation. In the case of a medium level of polyphenols concentration (50 ppm), the activity decreased for both processes. The photodegradation remained significant under sunlight, while no activity was detected under visible light. Finally, for high levels of polyphenol concentration (100 ppm), only minor photocatalytic activity was detected under sunlight, with none under visible light. In the case of 345TMBA, the catalyst exhibited higher activity, achieving 100% conversion after 120 minutes, even at a polyphenol concentration of 100 ppm under sunlight. In each scenario, visible light did not induce photocatalytic activity. The different results can be related to the diverse chemical structures of the investigated polyphenols. In fact, hydroxy groups on the benzene ring of GA and 4HBA promote Bi-chelation.

In contrast, the methoxy groups of 345TMBA do not play the same role. However, it is evident that the presence of Bi centres on the surface of the spheres allows for the adsorption of polyphenols. In order to exploit and maximize the Bi-chelation effect for the recovery of large amounts of polyphenols (GA and 4HBA), BiAS were employed with exciting results. Therefore, to optimize the recovery of polyphenols and then degrade the remaining traces in solution, 0.5 g/L and 1 g/L of GA were first put in contact with BiAS to adsorb the polyphenol as much as possible, and then the remaining percentage of the pollutant was photocatalyzed using FAB (Figure 2).

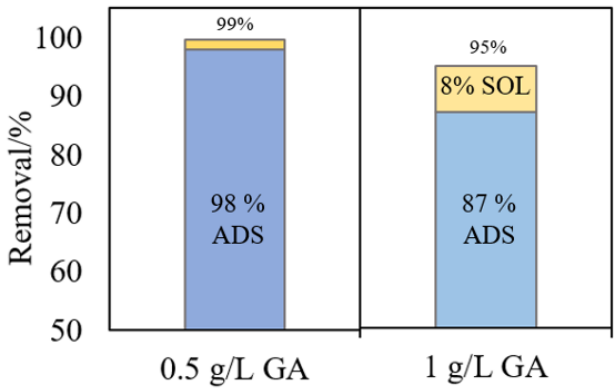

Figure 2. Adsorption and photodegradation tests of 0.5 g/L and 1 g/L GA in the dark adsorption (10g ABi) and under solar light irradiation (10g FAB).

The results of the experiments indicate that after 210 minutes, BiAS spheres were able to adsorb 98% of GA when the polyphenol concentration was 0.5 g/l and 87% when the concentration was 1 g/L. With the subsequent addition of FAB spheres and the sunlight exposure for 210 min, the GA removal was completed, reaching 100% of GA abatement when the GA initial concentration was 0.5 g/l and 95% for 1 g/l of initial GA.

CONCLUSIONS

In summary, this study focused on developing innovative Bi-based materials with easily recoverable properties to reduce the concentration of polyphenols in solution by both adsorption and photodegradation. Bi-modified alginate spheres with the feasibility of achieving high rates of polyphenols adsorption were synthesized. These materials are designed to be cost-effective and environmentally efficient, providing an alternative to traditional solutions. These materials permit not only the adsorption but also the photodegradation of polyphenols. This work paves the way for an innovative approach to the easy recovery of polyphenols to water and the subsequent degradation of these molecules as traces in solution.

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