

Synthesis of Bio-Photocatalysts and their Application for the Degradation of Organic Pollutants

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Abstract— Photocatalysis is a cost-effective and efficient approach to remove the toxic organic pollutants from wastewater. Eco-friendly approaches, such as the development of photocatalysts using renewable materials, have been discussed in an attempt to follow green technologies. These renewable innovations are of concern because they are low cost and easy to assemble. A great deal of attention has recently been paid to moving towards environmentally friendly and keeping the environment away from pollutants, which is why several reports have been issued. The use of plants (leaves, stems, flowers and fruits) on their process of development and the use of these green synthetic materials in photo-catalysis has been researched and documented on the treatment of wastewater. This paper will focus on the review of the different types of photo-biocatalysts; their synthesis and application for the photo-degradation of organic pollutants.

Keywords- Photo-Biocatalysis; Organics Pollutants; Degradation.

I. INTRODUCTION

Low cost and non-toxic photo-catalysts such as ZnO and TiO₂ have been identified as outstanding candidates for light-duty water depollution [1]. Nevertheless, their use is constrained by the wide bandgap that imposes a UV constraint on the generation of electron-hole pairs [2-5]. For example, to achieve a successful and sufficient energy supply in the system, the following will need to adhere: the semiconductor will need to extend its ability in the lifespan of charge carriers [6]. Environmental remediation has been a challenge for researchers, which is why new treatment approaches, such as photo-catalysis, are being investigated to ensure safe and reliable clean water. Industries such as cosmetics, paper and leather manufacture wastewater containing a variety of organic pollutants such as methylene blue (MB), methyl orange (MO),

dyes, rhodamine blue (RhB) and many others [7].

These industrial effluents pollute natural reservoirs such as rivers, lakes, and dams. There has been substantial growth in the need to develop effective economic approaches for handling water. Several processes, including microbial oxidation, reverse osmosis, adsorption and photo-catalysis, have been used to clear organic pollutants from wastewater. These approaches have one type of downside or another, for example, microbial degradation is time-consuming, unsuccessful for some of the organic pollutants, and may generate carcinogenic materials [8]. Other processes, such as adsorption, although widely studied, appear to be expensive and the regeneration process is difficult [9].

However, the general downside to all these approaches is that they sometimes convert organic pollutants from one step to another and do not fully remove these contaminants, thus producing secondary pollutants. The key advantage of photo-catalysis over other approaches is that it distinguishes organic pollutants from less toxic intermediates. This is an innovative oxidation process that is mainly used because it is cheap and environmentally safe [10].

For the reasons pointed out above, environmentally sustainable methods are required to prevent the degradation of the ecosystem. Eco-friendly approaches, such as the synthesis of nanostructures using green technology, have been investigated to reduce these. These green nanostructures are of concern because they are cost-effective and simple to manufacture. The simplest and safe way to manufacture these nanostructured semiconductor materials is by using plant agents [11]. In the recent past, many materials such as activated charcoal, biochar and low-cost adsorbents produced from a range of resources have been studied for the decontamination of water. Recently, the use of nanostructured materials for scavenging and oxidation of harmful water pollutants has acquired enormous significance due to their peculiar size-dependent properties such as wide surface area, short intra-particle diffusion time, compressibility with marginal surface area reduction, excellent resilience, exceptional reusability and recyclability [12].

Bio-based nanoparticles (NPs) were also used for photocatalytic degradation of toxins in aqueous solutions. Various plant sections, such as leaves, buds, seeds, pods, fruit peels, stems, roots, etc., have been used for NP synthesis [13]. Many types of plant biomass may be used for the synthesis of NPs. Some research groups used fresh biomass for extraction,

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while others used dry/powdered biomass for the same purpose [12]. In recent years, biogenic processing of nano-sized materials has offered an enticing alternative to traditional routes due to their low cost and environmental benignity. However, the optimisation and conservation of key characteristics such as size regulation, monodispersity and durability of biologically derived NPs are of concern [12].

II. ORGANIC POLLUTANTS IN WASTEWATER

More than 0.7 million tons of organic dye are manufactured globally per year. It is known that over 10,000 commercially available dyes are listed as acidic, reactive, dispersive, vat, metal complex, mordant and sulfur dyes. For a variety of factors, reactive dyes have been described as the most environmentally harmful compounds in clothing dye effluents. Second, because of their desired output and their growing market share, reactive dyes are used intensively. Third, they are very soluble and about 10–15% of the weight of the reactive dye added is discharged from various industries and households. Fourth, traditional wastewater treatment systems, which depend on sorption and aerobic biodegradation, have a poor recovery capacity for reactive and other anionic soluble dyes. As a result, they cause tainted water sources and environmental concerns, and contaminants are moved to another process and are not discarded [14].

III. VARIOUS PHOTO-BIOCATALYST

Though many photo-catalyst have been studied and applied in the degradation of organics pollutants, we have come to realize that they are still room for improvement and application of an environmentally friendly technology. Degradation performance of various organic compounds is strongly dependent on experimental conditions such as light irradiation source, reaction time, pollutants form and photo-biocatalyst weight [15]. Any of the contaminants are biologically recalcitrant and inhibitory to tissues, which dramatically decrease the capacity of the microorganism to biodegrade substances before or in practice after treatment [17].

In recent years, a recurring mix of heterogeneous photocatalytic and biological processes for the treatment of various toxic effluents has been proposed. Progress is focused on the achievement of appropriate biodegradability for the shortest photocatalytic degradation (optimal treatment) and the subsequent application of biological degradation, which makes the overall procedure quicker and more desirable. The green synthesis of metal oxides has been studied and concluded in various applications of photo-biocatalyst on the mineralization of recalcitrant organic pollutants in various aqueous solution [14].

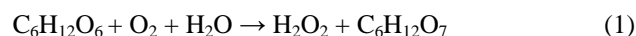
The following sections discuss the different types of photo-biocatalysts used in many applications, their effectiveness and optimisation on the removal of pollutants.

A. $GOx/TiO_2/Fe^{2+}/Metal\ Foam\ Photo-biocatalyst$

The formation of the $GOx/TiO_2/Fe^{2+}/Metal\ Foam\ Photo-biocatalyst$ stated by [17-19] was reported in comparison of the enzymes and the microorganisms. The enzymes were preferred rather than microorganisms based on

their ability to be handled and stored. They are also believed to be highly productive and are produced by microorganisms. The most popular enzyme of interest is glucose oxidase (GOx), which creates hydrogen peroxide in situ in the presence of glucose [15]. FOX1 method can be used to measure the produced H_2O_2 after the production of the photo-biocatalyst, which can later be utilized in wastewater as it holds a strong oxidization affinity. It has several advantages such: a) destroying toxic organics pollutants without pollution transfer to another phase, b) does not produce harmful residues, c) can be combined with other catalysts and other oxidizers, d) efficient in treating almost all organics pollutants and removing some toxic metals, e) works for water disinfection and destruction of microorganisms [20].

One of the most widely used enzymes known as oxidoreductase GOx, catalyzes the reaction by which all electrons (β glucose) are taken from the substrate and transferred to O_2 to produce in situ H_2O_2 [11].



Then, with hydrogen peroxide, ferrous ions respond by producing ferric ions and hydroxyl radicals [21]. A UV-A lamp < 390 nm with an energy band of 3.2 eV was glazed with the TiO_2 semiconductor photo-catalyst to generate a positive charge hole and free electrons [22]. Doing so revealed the photo-catalyst effectiveness under UV-A lamp radiation.

i. Immobilization of TiO_2 nanoparticles on AgO metal-foam

The preparation and the immobilisation of TiO_2 NPs on AgO using Sonoplus Ultrasonic Homogenizer HD 2200 (Germany) was considered. This method was successfully approached where the immobilization of TiO_2 on AgO metal foam was undertaken to generate the photo-catalyst under particular parameters such as temperature, pH and chemical additives. At a selected temperature, a measured concentration of HCl addition to preserve a pH of 5.5 was carefully determined in the production of photo-catalyst [23].

ii. Immobilization of GOx on TiO_2/AgO metal-foam

There are various methods for the immobilization of enzymes, such as physical adsorption, covalent bonding and trapping [24, 25]. The advantages of using the enzymes are, low cost and minimal denaturation which are the most important criteria for selecting the right treatment [26]. Among the various methods mentioned on the immobilisation of enzymes, the physical adsorption of enzyme (GOx) was preferred [27] to be suitable on the immobilisation on the TiO_2/AgO metal-foam to produce a photo-biocatalyst.

The addition of GOx to the preparation mentioned in Section A(i) above the TiO_2 / AgO metal foam immobilization was carried out. Where a new chemical additive phosphate buffer (PBS) was applied, a photo-biocatalyst was obtained at a new temperature and pH value [28, 29].

Table I below displays the data obtained at various periods and the ratio combination with and without the inclusion of UV and GOx, and it has been found that the mixture of the

TiO₂+Fe+GOx+UV has a higher efficiency in the removal of malachite green (MG) from the aqueous solution.

TABLE I: DESCRIPTION OF EXPERIMENTAL EFFECTS OF MG REMOVAL UNDER UV LIGHT WITH [MG]₀ = 20 MG / L; INLET FLOW RATE = 5 ML / MIN [23].

MG Decolourization process	Decolourization (%)		Decolourization rate constant (k, min ⁻¹)
	20 min	60 min	
TiO ₂ +UV	42.17	59.15	2.8 × 10 ⁻²
TiO ₂ +Fe	49.27	55.15	3.3 × 10 ⁻²
TiO ₂ +Fe+UV	55.07	64.67	3.9 × 10 ⁻²
TiO ₂ +GOx	50.03	54.64	3.4 × 10 ⁻²
TiO ₂ +GOx+Fe	58.55	63.54	4.5 × 10 ⁻²
TiO ₂ +GOx+UV	66.09	71.73	5.3 × 10 ⁻²
TiO ₂ +Fe+GOx+UV	84.36	89.85	8.9 × 10 ⁻²

The photo-biocatalyst mixture of Glucose oxidase, titanium dioxide, ferrous iron and metal foam (GOx / TiO₂ / Fe²⁺/MF) had a high tendency to extract 84.37% malachite green (MG) from the aqueous solution under UVA-LED for 20 minutes. It has also been shown that increasing the glucose dose still has a beneficial effect on the elimination of MG as stated by Abdi et al. [23].

B. NiFe₂O₄/T/GOx Photo-biocatalyst

To examine the degree of mineralization of indigo carmine (IC) attained during photo-degradation, a complete organic carbon (TOC) experiment was conducted for NiFe₂O₄ / T / GOx photo-biocatalyst. The use of tannin and GOx was both applied in the synthesis of the NiFe₂O₄/T/GOx photo-biocatalyst. NiFe₂O₄ was prepared using the solvothermal process [26] and was functionalized with tannin. GOx was then immobilized when NiFe₂O₄ and tannin were modified. This biological approach results in low costs and low environmental risks [31].

i. Synthesis of NiFe₂O₄ magnetic nanoparticles and modification of NiFe₂O₄ MNPs by tannin

Nickel Iron Oxide (NiFe₂O₄) MNPs were synthesized by the solvothermal method [30]. NiFe₂O₄ has a narrow band gap and semiconductors material in a broad application. NiFe₂O₄ exhibits lower photocatalytic activity because of a fast recombination of photoelectron-hole pairs. The morphological and the particle size were determined using a field-emission scanning electron microscope (FE-SEM, SUAPR55, Germany Zeiss) with energy-disperse X-ray spectroscopy (EDS) [32].

ii. Glucose oxidase immobilization and protein assay

During the glucose immobilization, a similar approach was carried out as in Section (A) above and different chemical additive sodium phosphate buffer solutions were used during the glucose oxidase immobilization and protein assay production. Under certain conditions, the desired photo-biocatalyst NiFe₂O₄ / T / GOx was obtained, as stated by Bradford et al. [33].

Table II below indicates various samples and their efficacy, but it was observed that the photo-biocatalyst NiFe₂O₄ / T / Gox-UV had a higher removal ratio after 90 min.

Based on the two Fenton processes and UV light conditions, it was also shown that UV had a good affinity in the higher removal ratio after 90 min relative to Fenton.

TABLE II: KINETICS DATA OF IC REMOVAL IN THE PRESENCE OF A CATALYST [31].

Samples	Rate constants, k (min ⁻¹)	decolourization ratios after 90 min (%)
NiFe ₂ O ₄ -Fe	0.0034	25.3
NiFe ₂ O ₄ -UV	0.0037	29.7
NiFe ₂ O ₄ /T-Fe	0.0040	32.9
NiFe ₂ O ₄ /TUV	0.0047	41.6
NiFe ₂ O ₄ /T/GOx-Fe	0.0044	37.6
NiFe ₂ O ₄ /T/GOx-UV	0.0545	98.6

C. ZnAILDH-HRP biohybrid Photo-biocatalyst

The essential organic compounds with poisonous, mutagenic and carcinogenic effects are phenols and their degradation derivatives [34]. Several methods have also been used for the depollution of organic compounds (phenols and their derivatives) in aqueous solution, such as filtration, flotation, dilution,

adsorption, physicochemical, biological and photochemical approaches [35].

TABLE III: CATALYTIC PERFORMANCES OF PHENOL DEGRADATION FOR PHOTO-BIOCATALYTIC AND ENZYMATIC PROCESSES [35].

ZnAILDH + hv	HRP	ZnAILDH -HRP	ZnAILDH -HRP + hv	
% Phenol degradation	20	41	25	35
Degradation type	Photo-degradation	Enzymatic polymerization	Enzymatic polymerization	Mainly photo-degradation

Layered hydroxide layers (LDHs), Horseradish peroxidase (HRP) and Zinc Aluminum Alloy (ZnAl) were used for the synthesis of the photo-biocatalyst. Under solar irradiation, the ZnAILDH - HRP biohybrid demonstrates an improvement in efficiency relative to ZnAILDH.

Even if the HRP is an effective biocatalyst in limited amounts, it is toxic, vulnerable to denaturation and inactivation [36]. ZnCrLDH and its derivative formulations have been identified as good materials for photo-degradation of rhodamine B by Liu et al. [37], methylene blue Chen et al. [38], orange II, 4-chlorophenol Paušová et al. [39], 2-nitrophenol, rhodamine 6G Mohapatra et al [36] and naphthalene Xia et al. [41], photocatalytic reduction of CO₂ Katsumata Wang et al. [38], water splitting Wang et al. [43] and H₂ production Luo et al. [44] under visible light.

i. Synthesis of photo-biocatalysts

The preparation of ZnCr LDH powder was reported by Gunjekar et al [45] with an addition of NaOH at a certain condition in order to obtain ZnCr LDH nanosheets. Since the O₂ generation caused by visible light occurs primarily on the surface of Zn-Cr-LDH. Exciting progress has been made in the development of new synthesis methods; According to Luo, Song [44] composites with a different mass ratio of ZnCr LDH nanosheets modified g-C₃N₄ were obtained [45].

It is revealed on Table III below that ZnALDH- HRP + hv photo-biocatalyst had mainly influence on the photo-degradation of organic pollutants (phenols). The inclusiveness of +hv has greater effectiveness in the depollution and the removal of organics pollutants. Though the HRP also played a vital role as an anti-recalcitrant pollutant, the UV or UV-vis enhanced the process.

D. GOx/TiO₂/PU Photo-biocatalyst

Efforts have been made in recent years to develop heterogeneous catalytic processes by integrating photo-catalysis with biological systems [46, 47]. Later, a photo-biocatalyst containing glucose oxidase immobilized with TiO₂ / polyurethane was successfully used under UV for the removal of orange acid 7 [15]. Biological processes are inexpensive and environmentally sustainable alternatives for the treatment or the disinfection of wastewater [48].

Hybrid techniques, combined with photochemical and biochemical processes, have recently been widely attractive and shown to be more effective for reducing contaminants as well as reported by Shoabargh et al. [15].

Glucose oxidase (GOx) was immobilized with TiO₂ / polyurethane (PU). This process has been tested for the elimination of Acid Orange 7 (AO7). Fast removal efficiency (> 99%) was achieved after 22 min using a GOx / TiO₂ / PU photo-biocatalyst [15].

i. The Immobilization of TiO₂ nanoparticles on PU

According to Shoabargh and Karimi [11] the immobilization of TiO₂ nanoparticles on PU was conducted using the similar approach as section B and C.

A similar approach was adopted by Bulmuş et al. [28] as Section A(i). However, parameters such as temperature, pH and chemical additives used for the immobilization of TiO₂ NPs on PU using the Sonoplus Ultrasonic Homogenizer HD 2200 (Germany) were different.

ii. Preparing GOx/TiO₂/PU photo-biocatalyst

The batch tests were conducted by Gumy et al. [27]. To obtain a successfully synthesized GOx / TiO₂ / PU photo-biocatalyst, as stated by Shoabargh et al. [15] during the immobilization of GOx to TiO₂ and PU.

Table IV below shows the decolourization process and the first-order rate constants which indicate a higher performance of GOx / TiO₂ / PU / UV.

TABLE IV: COMPARISON OF THE FIRST-ORDER RATE CONSTANT (K) AND COEFFICIENT OF DETERMINATION (R²) OF VARIOUS DECOLOURIZATION METHODS; [AO7] = 20 MG/L, 25 8C; TiO₂/PU = 0.42 G/G, AND RECYCLING RATE = 5 ML/MIN [15].

Decolourization process	k (min ⁻¹)	R ²
GOx/PU	0.009	0.997
TiO ₂ /PU/UV	0.0203	0.999
GOx/TiO ₂ /PU	0.0360	0.998
GOx/TiO ₂ /UV-without glucose	0.0521	0.998
GOx/TiO ₂ /PU/UV	0.207	0.998

E. Corn silk/TiO₂ photo-biocatalyst

The consideration of UV-Vis during the degradation of a pollutant (dye) using photo-biocatalyst was reported by Nadaroglu et al. [49]. The wavelength of a range of 300 to 900 nm was observed [49].

i. Synthesis of corn silk/TiO₂ photo-biocatalyst

The pioneering work of *corn silk/TiO₂* as a photo-biocatalyst, was reported by Nadaroglu et al. [49].

Photo-catalyst material of corn silk – TiO₂ was used and successfully applied to the degradation of Reactive Black 5 (RB5) as a typical azo dye under UV radiation. Quick discoloration capability (> 99 %) was achieved after 30 s using corn silk / TiO₂ photo-biocatalyst [49].

Various plant leaves or seeds can be used with a semiconductor to produce a photo-biocatalyst which may be useful during the removal of organic contaminants. The presence of UV contributes to the greater yield of the removal of organics pollutants.

The fact that the green synthesis biomolecules have a functional group that can be related to the ion metals. During this mixture of metal ions and biomolecules, the metal salt is reduced. This greener synthesis thus gives good sensitivity to its applications in diverse ways and further strengthens its assurance that fewer contaminants can be emitted during its biological applications.



Fig. 1: The photo-degradation from the combination of semiconductors and the biologicals products.

The improvement of the efficiency of the removal of pollutants can be achieved from a combination of metals oxide with an agro-waste.

IV. REUSABILITY OF THE PHOTO-BIOCATALYST

Reusability is one of the most significant considerations in catalytic science. It shows the skill and its usefulness in responding to the repetition of how many circles can be used all over again. This also included interactions between the materials used in the construction of the photo-biocatalyst using ion exchanges or chemical processes that could be responsible for holding the bonds among the compounds that are being used during the synthesis. The reusability of the photo-biocatalyst emphasizes its effectiveness during the enhancement on the removal of pollutants in various aqueous solutions, furthermore, it also covers the cost-effectiveness in the production. It is vital to construct a photo-biocatalyst that can have an affinity of being reusable as many times as possible.

V. CONCLUSION

The physico-chemical properties of photo-biocatalysts are determined by the enhancement of biogenic synthesis contributing to the success in the elimination of many organic contaminants. While the photo-biocatalyst can also be effective, several research studies have shown that its efficacy pertains to the agro-synthesis. During the synthesis of photo-biocatalyst

using metal oxides as agents, the organic compounds can potentially be activated by the aqueous solution. The incorporation of biological products has a larger effect with or without the influence of UV or UV-Vis. However, it showed greater yield with additional solar radiation or visible light.

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