

## Article

# Synthesis of ZnO/g-C<sub>3</sub>N<sub>4</sub> Composites Obtained by Pyrolysis of a Ternary Deep Eutectic Solvent and Their Application as Catalysts in Different AOPs

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**Abstract:** This study investigates the synthesis and evaluation of ZnO/g-C<sub>3</sub>N<sub>4</sub> composites as efficient green catalysts for advanced oxidation processes (AOPs) targeting the treatment of contaminated water. The composites were synthesized using a ternary deep eutectic solvent and physically–chemically characterized in detail, confirming their structural integrity and successful synthesis. Photocatalytic, photo-Fenton- and electro-Fenton-like experiments were conducted using Rhodamine B as a model contaminant to evaluate the catalytic performance, reuse and stability of the synthesized material. The synthesized ZnO/g-C<sub>3</sub>N<sub>4</sub> composites demonstrated excellent photocatalytic activity under LED light (395 nm), achieving a pollutant removal of around 59% in 90 min. The combined effect of the designed catalyst and Fenton-like process, a photo-Fenton-like process, significantly improved this performance, achieving removal of close to 95% in 60 min due to the synergistic effects of the irradiation and H<sub>2</sub>O<sub>2</sub> activation. Finally, the catalytic action of synthesized ZnO/g-C<sub>3</sub>N<sub>4</sub> composites in the electro-Fenton-like process exhibited superior efficiency, achieving 90% removal within 45 min and kinetic constants four times higher than those of anodic oxidation alone. In addition, reuse studies confirmed the stability and catalytic activity of the composites for several cycles with high removal efficiencies, demonstrating their viability for long-term and scalable water treatment applications. These findings highlight the potential of ZnO/g-C<sub>3</sub>N<sub>4</sub> composites synthesized through DES as a sustainable and cost-effective alternative for water remediation technologies.

**Keywords:** ZnO/g-C<sub>3</sub>N<sub>4</sub> composites; deep eutectic solvent; photocatalytic; photo-Fenton like; electro-Fenton like



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## 1. Introduction

As is well known, following the pace of world population growth, industry has developed and grown rapidly in recent years. The wastewater generated in these industrial processes may contain hazardous, toxic, and difficult-to-degrade pollutants. This is the case in several industries, such as the textile, paper, food, and hair dye industries, among others, which discharge wastewater containing dyes into bodies of water [1–3]. If these waters are not adequately treated before discharge, they can reduce oxygen transfer, endanger aquatic life, and alter the chemical composition of the water [1]. In addition, they also present significant risks to human health due to the carcinogenic, mutagenic, and bactericidal properties of certain dyes [2,4,5]. Conventional water treatment methods often fail to effectively degrade these persistent pollutants, necessitating the development of more

effective, innovative, and environmentally friendly techniques to mitigate the negative impact of these pollutants on the environment [2,6–8]

Advanced oxidation processes (AOPs) have emerged as a fundamental strategy for wastewater treatment and environmental remediation, especially in the case of recalcitrant and difficult-to-degrade pollutants. These processes are characterized by the generation of reactive oxygen species, such as hydroxyl radicals (OH), which can break down complex organic compounds into simpler and less-toxic products [9,10]. Among the different AOPs, photocatalysis and the electro-Fenton-like process have demonstrated significant potential, each offering unique advantages and limitations concerning efficiency, selectivity, and operating conditions [11].

Photocatalysis harnesses light energy to activate a semiconductor catalyst, generating free radicals that begin the degradation of pollutants. This technique is especially promising for large-scale industrial wastewater treatment because it can operate under relatively mild conditions and use readily available light sources [12]. In contrast, the electro-Fenton-like process, which combines electrochemical methods with the in situ generation of hydrogen peroxide and its decomposition in the presence of a catalyst, stands out for its ability to generate high concentrations of hydroxyl radicals, making it very effective for the oxidation of difficult organic pollutants [13]. In the search for greater process efficiency, catalysts play a fundamental role, since their nature, structure, and activity directly influence the generation of reactive species and pollutant degradation kinetics [14]. Research into advanced catalysts, particularly those based on materials such as carbon nanotubes [15], graphene, and metal oxides [16], has opened new perspectives for optimizing AOPs.

Graphitic carbon nitride ( $g\text{-C}_3\text{N}_4$ ) has recently attracted attention given its non-toxic properties, chemical stability, and efficient visible-light absorption (2.7 eV band gap). However, this material presents several limitations that hinder its photocatalytic activity, such as the fast electron/hole recombination photogenerated, its small specific surface area, and its weak redox capacity [17,18]. Similarly, zinc oxide (ZnO), a semiconductor with a wide band gap of 3.3 eV, is known for its good stability, non-toxicity, high electron mobility, and strong oxidation potential, but it is restricted to activation under ultraviolet (UV) light [18,19]. Studies suggest that combining these materials can regulate the band gap structure, modulating the light utilization efficiency and the redox capacity [20–22]. Consequently, this study explores the combined behavior of  $g\text{-C}_3\text{N}_4$  and ZnO as a composite material.

Therefore, the development of environmentally friendly, cost-effective, and efficient solid-phase catalysts has become a major issue in the fields of chemistry, engineering, and materials science. Researchers around the world are actively working to develop more environmentally friendly methods for catalyst synthesis. Their efforts focus on minimizing the use of hazardous solvents during synthesis and purification, avoiding toxic substances, reducing energy consumption, and promoting synthesis under ambient conditions. In this context, deep eutectic solvents (DESs) have gained prominence. DESs are liquid systems formed by the interaction of two or more components, usually a hydrogen bond donor and a hydrogen bond acceptor, in specific molar ratios, resulting in a eutectic mixture with unique solvent properties [23,24]. DESs represent a new class of low-cost, environmentally friendly solvents with great potential to replace traditional solvents. They emerge as promising substitutes for volatile organic solvents and ionic liquids, mainly due to their simple preparation procedure and the variety of low-cost starting components from natural, biodegradable, and sustainable sources [25]. Due to their high thermal stability, good dispersibility, remarkable ionic conductivity, wide electrochemical window, and self-assembly capability, DESs have recently been selected as suitable media for the chemical synthesis of metal catalysts for electrochemical and photocatalytic use [25,26]. Moreover, a key advantage of DESs is their compatibility with numerous metal salts, which

favors their incorporation into the final product [16,27–29]. For these reasons, DESs have recently gained attention for the synthesis of catalytic materials, especially in combination with AOPs for water treatment, offering a sustainable alternative to conventional methods. Therefore, given their non-toxicity, easy accessibility, low price, and the fact that they are considered green solvents, in this article, it was decided to choose a DES as a starting point for the elaboration of a novel catalyst.

This research investigates the novel synthesis of a catalyst of a ZnO/g-C<sub>3</sub>N<sub>4</sub> composite using a ternary DES and evaluates its application in different AOPs for the treatment of dye-contaminated water. Through the pyrolysis of the DES, it is intended to obtain composites formed by ZnO and g-C<sub>3</sub>N<sub>4</sub> (ZnO/g-C<sub>3</sub>N<sub>4</sub> composites). The characterization allows us to confirm the correct synthesis of these composites. Photocatalytic, photo-Fenton-like, and electro-Fenton-like tests are performed to evaluate its catalytic capacity and reusability by the degradation of Rhodamine B. This dye is widely used as a model pollutant to evaluate the usefulness of different types of catalysts in various AOPs in recent years [30–34]. The final objective is to study the feasibility of the synthesized catalyst by evaluating its effectiveness in water treatment applications. Given the limited exploitation of this field, this research aims to provide a more sustainable and cost-effective alternative to existing methods.

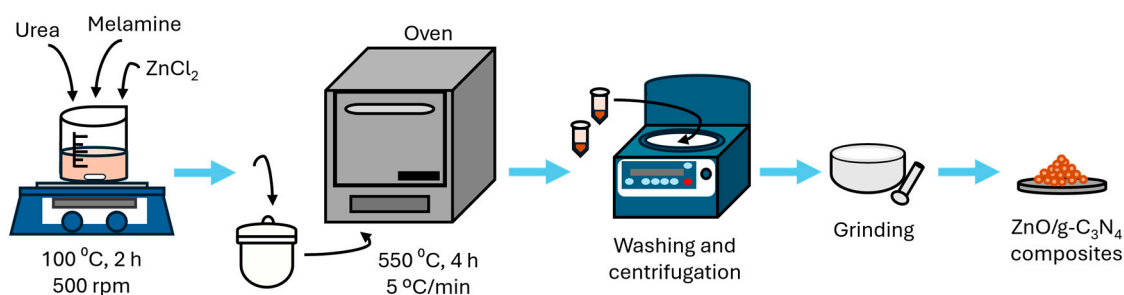
## 2. Materials and Methods

### 2.1. Chemicals

The reagents used for the synthesis of ZnO/g-C<sub>3</sub>N<sub>4</sub> composites included urea, melamine (99%), zinc chloride (ZnCl<sub>2</sub>), and ethanol supplied by VWR (Barcelona, Spain), Thermo Fisher Scientific (Madrid, Spain), Sigma Aldrich (Madrid, Spain), and Merck (Madrid, Spain), respectively. Rhodamine B, provided by Panreac (Barcelona, Spain), was used as a model contaminant. Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>, 30% *w/v*) for the photo-Fenton-like experiments was supplied by Foret (Barcelona, Spain).

### 2.2. Synthesis of ZnO/g-C<sub>3</sub>N<sub>4</sub> Composites

The ZnO/g-C<sub>3</sub>N<sub>4</sub> composites were obtained by the pyrolysis of a ternary DES, based on the method reported by Mou et al. [35]. In this case, a mixture of 7.10 g of urea, 0.62 g of melamine, and 1.34 g of ZnCl<sub>2</sub> was heated at 100 °C and stirred at 500 rpm for 2 h to obtain a homogeneous liquid. The resulting mixture was poured into a ceramic well and placed in the oven at 550 °C (heating 5 °C/min) and maintained for 4 h under atmospheric conditions. After this, it was naturally cooled to room temperature, washed several times with distilled water and ethanol, and dried under vacuum overnight at 60 °C. For a better understanding of the process, Figure 1 shows an outline of the stages carried out.



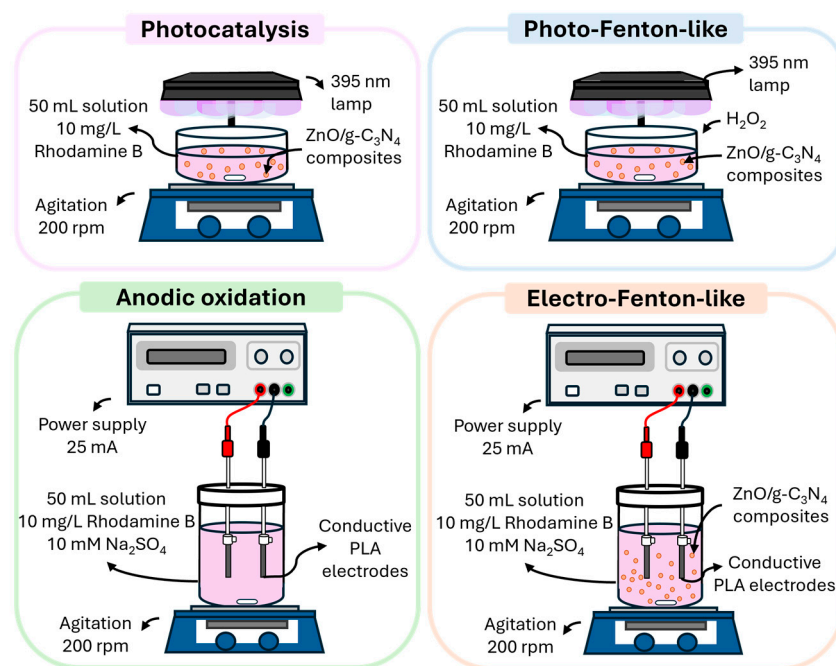
**Figure 1.** Scheme of the steps carried out in the synthesis of the ZnO/g-C<sub>3</sub>N<sub>4</sub> composites.

### 2.3. Characterizations

X-ray diffraction (XRD) analysis was performed using a Siemens D5000 diffractometer (Ks Analytical Systems, Aubrey, TX, USA) with a Cu K $\alpha$  radiation source to better study the structure of the synthesized ZnO/g-C<sub>3</sub>N<sub>4</sub> composites. To identify all functional groups, Fourier transform infrared spectroscopy (FTIR) was carried out on a Nicolet 6700 spectrometer (Thermo Fisher Scientific, Madrid, Spain). To understand the structural details, X-ray photoelectron spectroscopy (XPS) was performed using a Thermo Scientific NEXSA instrument equipped with aluminum K $\alpha$  monochromatized radiation at 1486.6 eV X-ray source. The surface characterization of the catalyst was performed by scanning electron microscopy and energy-dispersive spectrometry (SEM/EDS) using a JEOL JSM6010LA (JEOL, Tokyo, Japan) with EDS Oxford AZtecOne SEM (Oxford Instruments, Abingdon, UK). The metal content was quantified by inductively coupled plasma–optical emission spectrometry (ICP-OES) using a Thermo Scientific™ iCAP™ PRO XP DUO. All the equipment mentioned above was used at the Centro de Apoyo Científico-Tecnológico á Investigación (CACTI) of the Universidade de Vigo, Spain.

### 2.4. Degradation Experimental Methods

All the tests were performed using an initial solution of 10 mg/L of Rhodamine B. This solution was kept under constant agitation (200 rpm) for the duration of each test, using a stirring plate (IKA® RCT Basic, Wilmington, NC, USA). The configuration and elements used varied according to the AOP carried out. Each of them is explained in detail below, providing a scheme for better understanding (Figure 2).



**Figure 2.** Diagram of the configuration of the different tests performed.

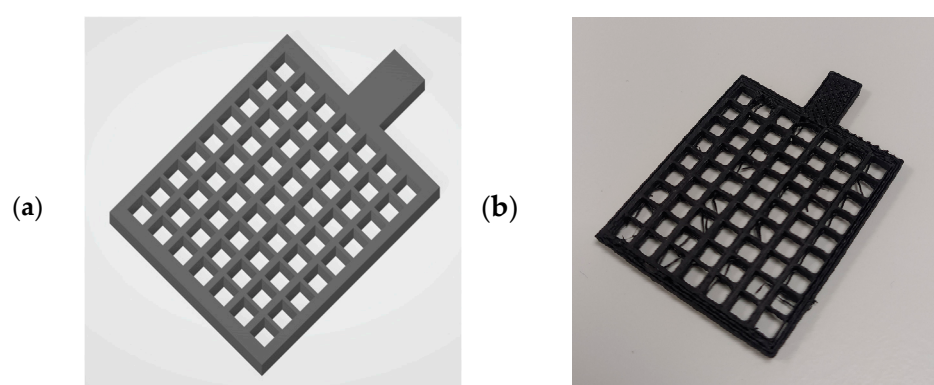
#### 2.4.1. Photocatalysis and Photo-Fenton-like Tests

In this case, the degradation tests were performed in a reaction cell with a diameter of 8 cm and a height of 4.5 cm. A working volume of 50 mL was maintained for all experiments. An LED lamp (model CHX-FL-A-30W, 395 nm, Shenzhen Chuanghuaxing Technology, Shenzhen, China) was placed 3.5 cm above the liquid surface. The amount of ZnO/g-C<sub>3</sub>N<sub>4</sub> composites used to evaluate the catalytic performance ranged from 25 to

100 mg. For the photo-Fenton-like experiment, the required amount of hydrogen peroxide was added immediately prior to the start of each experiment.

#### 2.4.2. Anodic Oxidation and Electro-Fenton-like Tests

All tests were performed in a cylindrical reaction cell, measuring 5 cm in diameter and 7.5 cm in height, with an operating volume maintained at 50 mL. The selected anode and cathode were conductive PLA electrodes made by 3D printing using our own design (Figure 3). Each electrode measured  $3.5 \times 3$  cm, with an immersed surface area of  $2.5 \times 3$  cm, and the spacing between them was 2.5 cm. The electric field was applied through a power supply (E3612A 30W, Agilent, Santa Clara, CA, USA). A working current of 25 mA was set for all tests. All the solutions used in the experiments had a concentration of 10 mM  $\text{Na}_2\text{SO}_4$  to improve their conductivity.  $\text{ZnO/g-C}_3\text{N}_4$  composites were only added in the electro-Fenton-like assays.



**Figure 3.** Conductive PLA electrodes made by 3D printing: (a) 3D software design; (b) real electrode printed.

#### 2.5. Analytical Procedures

The monitoring of the dye concentration over time was conducted using a UV–Vis spectrophotometer (Thermo Fisher Genesys M-150, Waltham, MA, USA) at 554 nm. The concentration was determined by using a calibration curve. All the results are the average of the duplicated assays, and the standard deviations were below 5%.

#### 2.6. Reaction Rate Kinetics

The kinetic behavior of the different trials was evaluated, and the kinetic coefficients for reactions of the zero, pseudo-first, and pseudo-second orders were calculated following Equations (1), (2), and (3), respectively.

$$\frac{dC}{dt} = -k \quad (1)$$

$$\frac{dC}{dt} = -k \cdot C \quad (2)$$

$$\frac{dC}{dt} = -k \cdot C^2 \quad (3)$$

where  $C$  is the concentration of Rhodamine B (mg/L),  $t$  is the reaction time (min), and  $k$  is the kinetic constant for zero order ( $\text{g} \cdot \text{L}^{-1} \cdot \text{min}^{-1}$ , Equation (1)), pseudo-first order ( $\text{min}^{-1}$ , Equation (2)) and pseudo-second order ( $\text{L} \cdot \text{g}^{-1} \cdot \text{min}^{-1}$ , Equation (3)).

### 2.7. Determination of Rhodamine B Degradation

The degradation of Rhodamine B for each of the tests performed was calculated according to Equation (4).

$$\text{Degradation (\%)} = \left(1 - \frac{C}{C_0}\right) \cdot 100 \quad (4)$$

where  $C$  (mg/L) is the final concentration of Rhodamine B and  $C_0$  (mg/L) is the initial concentration of Rhodamine B.

### 2.8. Determination of Energy Consumption

The specific energy consumption per unit of dye removed ( $EC$ ) was calculated for each anodic oxidation and electro-Fenton-like experiment following Equation (5).

$$EC \left( \frac{kWh}{g_{\text{Rhodamine B}}} \right) = \frac{U \cdot I \cdot t}{V \cdot \Delta C_{\text{Rhodamine B}}} \quad (5)$$

where  $U$  is the average cell voltage (V),  $I$  is the applied current intensity (A),  $t$  is the reaction time (h),  $V$  is the volume (L), and  $\Delta C_{\text{Rhodamine B}}$  is the difference in the pollutant concentration (mg/L) before and after the reaction.

## 3. Results and Discussion

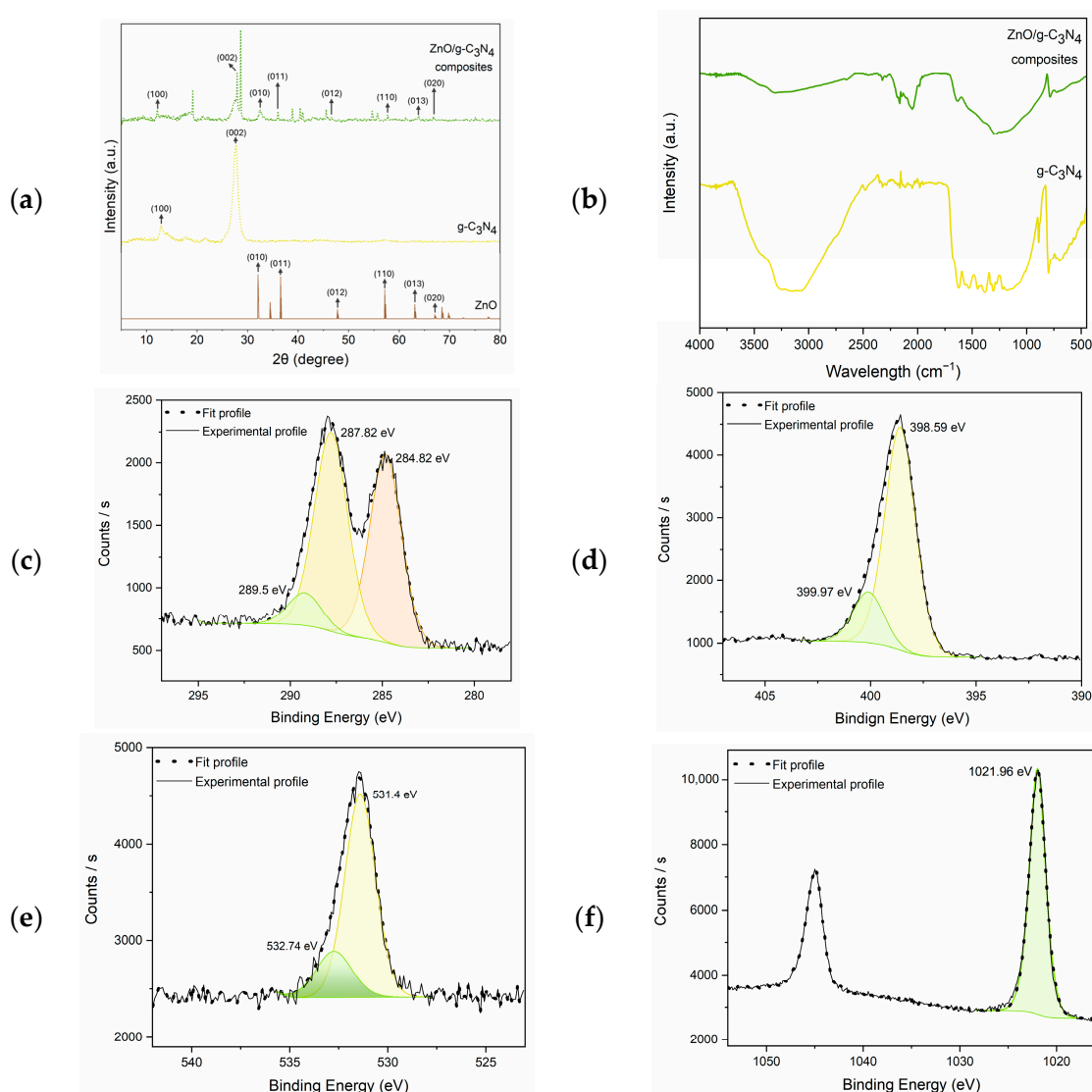
### 3.1. ZnO/g-C<sub>3</sub>N<sub>4</sub> Composites Characterization

The ZnO/g-C<sub>3</sub>N<sub>4</sub> composites synthesized using DES as a precursor were initially characterized to analyze their structural properties and confirm a successful synthesis. Therefore, the morphological and chemical characterization was performed using XRD, FTIR, XPS, SEM, and EDS mapping techniques.

The crystalline structure of the catalyst was analyzed by XRD. Figure 4a shows the XRD pattern obtained for the synthesized composites. The sharp diffraction peaks indicate a high degree of crystallinity in the prepared material. The existence of diffraction peaks at  $2\theta = 13.1^\circ$  and  $27.5^\circ$ , which can be assigned to the (100) and (002) planes, respectively, are characteristic of g-C<sub>3</sub>N<sub>4</sub> [36,37]. This confirmed the formation of g-C<sub>3</sub>N<sub>4</sub> during the pyrolysis process. However, when compared with the standard pattern, the intensity of the peak corresponding to the (002) plane was significantly weakened. This may indicate that the introduction of ZnO could restrict the growth of pure g-C<sub>3</sub>N<sub>4</sub> crystals [38]. Additionally, the spectrum also showed characteristic patterns that can be attributed to the theoretical crystal structure of ZnO at  $2\theta = 31.9^\circ$ ,  $36.4^\circ$ ,  $47.8^\circ$ ,  $56.8^\circ$ ,  $63.2^\circ$ , and  $66.7^\circ$ , corresponding to the (010), (011), (012), (110), (013), and (020) planes. These results are consistent with others reported in the literature, where catalytic materials containing ZnO were synthesized [39–41].

The functional groups of the composites were explored by FTIR (Figure 4b). The spectra corresponding to g-C<sub>3</sub>N<sub>4</sub> and the ZnO/g-C<sub>3</sub>N<sub>4</sub> composites presented several adsorption peaks in common. Thus, this allowed for ensuring the presence of g-C<sub>3</sub>N<sub>4</sub> in the composites. The intensity of the adsorption peak at  $785 \text{ cm}^{-1}$  was attributed to the out-of-plane bending of the tris-s-triazine ring [42,43]. The peak at  $1632 \text{ cm}^{-1}$  corresponded to stress in the C=O group and in the amide group (CONH) and the peak at  $1567 \text{ cm}^{-1}$  to stress in the C=N bonds [42,44,45]. The peaks appearing in the range  $3100\text{--}3300 \text{ cm}^{-1}$  indicated N-H bond stresses of non-condensed amine groups [42,46], while those present between  $3300\text{--}3600 \text{ cm}^{-1}$  would correspond to the O-H bond stresses of the hydroxyl group of adsorbed water molecules. On the other hand, the characteristic bands of ZnO appeared in the range of  $400\text{--}800 \text{ cm}^{-1}$ , corresponding to the vibration of the Zn-O bond [19]. Thus,

the spectrum of the composites revealed vibrational bands characteristic of pure g-C<sub>3</sub>N<sub>4</sub> and ZnO, confirming the generation and stability of the ZnO/g-C<sub>3</sub>N<sub>4</sub> composites.

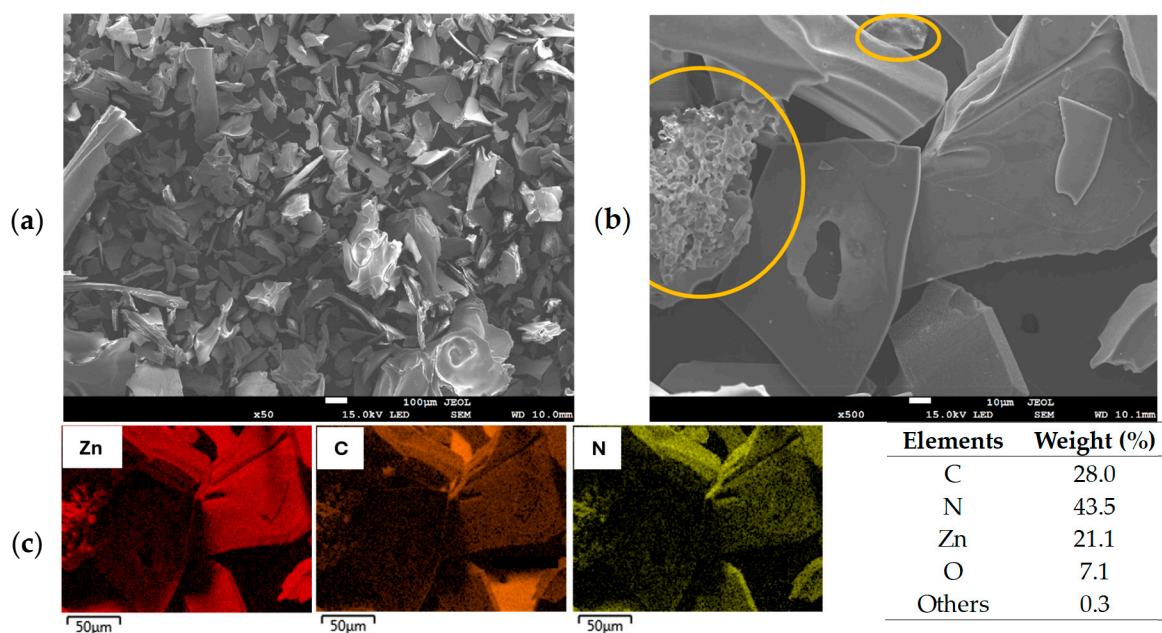


**Figure 4.** Characterization results of obtained ZnO/g-C<sub>3</sub>N<sub>4</sub> composites: (a) XRD of ZnO model (brown line), g-C<sub>3</sub>N<sub>4</sub> (yellow line), and ZnO/g-C<sub>3</sub>N<sub>4</sub> composites (green line); (b) FTIR spectra of g-C<sub>3</sub>N<sub>4</sub> (yellow line) and ZnO/g-C<sub>3</sub>N<sub>4</sub> composites (green line); (c–f) XPS spectra of C 1s, N 1s, O 1s, and Zn 2p, respectively.

To confirm the results obtained by FTIR and to better understand the structural details of the ZnO/g-C<sub>3</sub>N<sub>4</sub> composites, XPS analyses of the C, N, O, and Zn elements were performed. As shown in Figure 4c, the C 1s peaks could be fitted to three peaks located at 284.8, 287.8, and 289.5 eV, which were attributed to C-C or C-H bonds, sp<sup>2</sup> carbon–nitrogen (N=C=N) bonds of aromatic ring systems and ester (O-C=O) and carbamate (O-C(N)=O)-type bonds, respectively [47,48]. The N 1s spectrum (Figure 4d) was fitted into two peaks. A major one was located around 398.59 eV, which can be assigned to the sp<sup>2</sup> bonded nitrogen of the triazine rings (-C=NH), and another one at 399.97 eV is associated with the pyridine-type nitrogen atoms [47,48]. Meanwhile, the O 1s spectrum in Figure 4e could be divided into two peaks at 531.4 and 532.74 eV, corresponding to N-C-O bonding, OH groups, and even to O<sub>2</sub> in the lattice and carbon–oxygen functionalities [35]. Figure 4f shows the characteristic peak at approximately 1021.96 eV, which was assigned to the Zn 2p<sub>3/2</sub> species, confirming that Zn existed in the Zn<sup>2+</sup> oxidation state in the form of ZnO [49].

The results obtained from XRD, FTIR, and XPS analyses confirmed the correct synthesis and, therefore, the formation of the ZnO/g-C<sub>3</sub>N<sub>4</sub> composites using this method.

SEM imaging was employed to analyze the morphology of the prepared ZnO/g-C<sub>3</sub>N<sub>4</sub> composites. The images obtained are presented in Figure 5a,b, where it was observed that the synthesized composites exhibited a porous structure characterized by thin nanosheets. This morphology closely resembles that reported by Juan et al. [35], who synthesized composites of metal oxide nanoparticles and g-C<sub>3</sub>N<sub>4</sub> nanosheets (g-C<sub>3</sub>N<sub>4</sub>/Fe<sub>2</sub>O<sub>3</sub> composites) using a DES composed of FeCl<sub>3</sub>, urea, and melamine. Moreover, this morphology agrees with the structure usually presented by g-C<sub>3</sub>N<sub>4</sub> obtained by the thermal decomposition of urea and melamine, as reported in several studies [50–52]. Figure 5b shows in detail some zones of more porous aggregate growth on the nanosheets. This could have formed during polymerization due to the gas bubbles produced [52].



**Figure 5.** Morphological characterization of ZnO/g-C<sub>3</sub>N<sub>4</sub> composites: (a,b) SEM images with magnifications of  $\times 50$  and  $\times 500$ , respectively; (c) Elemental mapping corresponding to the elements Zn, C and N.

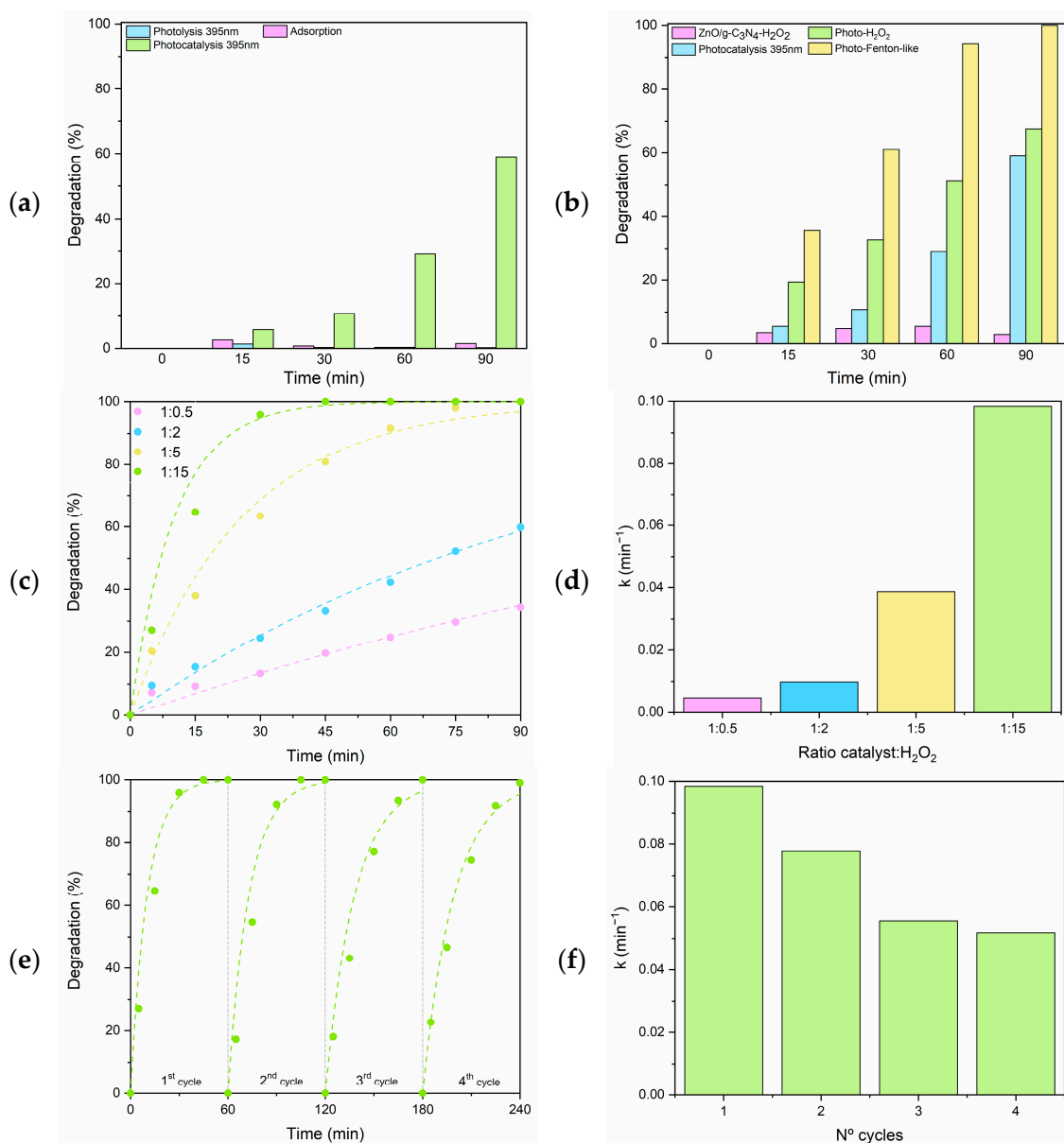
Finally, to prove the distribution of the different elements and the presence of Zn in the composites, EDS mapping was performed. The results for Zn, C, and N are presented in Figure 5c and confirm their uniform distribution in the structures. Regarding the quantification obtained for these elements (Table in Figure 5c), the amounts of N and C obtained correspond to a C/N ratio close to the theoretical 0.75, suggesting the presence of g-C<sub>3</sub>N<sub>4</sub> structures [53]. In addition, the amount of Zn in the samples was found to be 21.1%. This value is similar to 23.41%, obtained by ICP-MS analysis, which confirmed the presence of Zn in the structure. These results confirmed the successful synthesis of the composites, finding metallic zinc particles on the g-C<sub>3</sub>N<sub>4</sub> structures.

### 3.2. Photocatalytic Tests

After confirming the successful synthesis of the ZnO and g-C<sub>3</sub>N<sub>4</sub> in the composites by characterization, their combined photocatalytic potential was ascertained. For this purpose, experiments were conducted using UV radiation at 395 nm using a constant amount of catalyst (25 mg).

First of all, the adsorption capacity of the composites for the removal of Rhodamine B was assessed. As shown in Figure 6a, the composite alone exhibited a negligible removal

capacity, rapidly reaching an adsorption–desorption equilibrium with removal values below 3%. The photolysis control assay demonstrated that light exposure alone, without the presence of a catalyst, had no significant effect on Rhodamine B degradation, with removal rates below 1%. This confirmed that the dye was stable under irradiation in the absence of a catalyst, which is consistent with the findings reported by Osman et al. [17].

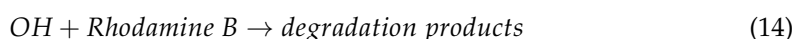
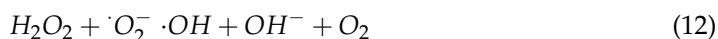


**Figure 6.** Results of Rhodamine B degradation experiments using various treatments and conditions: (a) profiles of Rhodamine B removal in adsorption, photolysis, and photocatalyst; (b) profiles with/without H<sub>2</sub>O<sub>2</sub>; (c) profiles of dye degradation obtained from different catalysts–H<sub>2</sub>O<sub>2</sub> molar ratio; (e) profiles of dye degradation during 4 successive cycles using photo-Fenton like with a catalyst–H<sub>2</sub>O<sub>2</sub> molar ratio of 1:15. Dashed lines depict the pseudo-first-order kinetic fitting for all experiments with a  $R^2 > 0.98$ . (d,f) Apparent pseudo-first-order constant ( $k$ ) values for each cycle.

When the photocatalytic activity was evaluated under the LED light source, it was observed that, operating at 395 nm, significant catalytic performance was obtained. After 90 min of treatment, 59% of the dye was degraded. This good catalytic activity presented by the composites was due to the fact that ZnO is a good photocatalyst between the wavelengths of UV (280 to 400 nm) and g-C<sub>3</sub>N<sub>4</sub> in visible (between 400–460 nm) light. As already

pointed out in the introduction, several studies confirmed that the combination of both materials reduces the band gap energy in the ZnO/g-C<sub>3</sub>N<sub>4</sub> composites [18,38]. The results of this study confirmed that, although the band gap was reduced, the catalytic activity of the composites was effectively maintained at 395 nm, highlighting their suitability for photocatalytic-driven applications.

Several previous studies have demonstrated that H<sub>2</sub>O<sub>2</sub> is generated during photocatalytic treatment and plays a significant role in degradation processes [54–57]. To confirm this phenomenon, the concentration of H<sub>2</sub>O<sub>2</sub> in the treated solution was measured at the end of the experiment, yielding a value of 2 mg/L. This result confirmed the in situ production of H<sub>2</sub>O<sub>2</sub> during the treatment. To better understand the mechanisms and species involved in the photocatalytic degradation process, a literature review was carried out. Based on several works, Equations (7)–(15) present the main reactions involved [17,18,38,40,54,58,59]. When the ZnO/g-C<sub>3</sub>N<sub>4</sub> composites were irradiated, both ZnO and g-C<sub>3</sub>N<sub>4</sub> simultaneously generated electron–hole pairs following Equation (7). The electrons jumped to their respective conduction bands, leaving holes in the valence band. These photogenerated holes reacted with water, producing the ·OH radical (Equations (8) and (9)). In the conduction band, the photogenerated electrons reacted with the O<sub>2</sub> adsorbed on the surface to give rise to the O<sub>2</sub><sup>·−</sup> radical (Equation (10)) and, on the other hand, to the generation of H<sub>2</sub>O<sub>2</sub> (Equation (11)). The H<sub>2</sub>O<sub>2</sub> generated could give rise to ·OH radicals through a reaction with O<sub>2</sub><sup>·−</sup> or under the incidence of light (Equations (12) and (13)). Finally, all the generated radicals degraded the dye, giving rise to the degradation products (Equations (14) and (15)).



The photocatalytic process was quite slow, reaching the total degradation of the dye after 3 h of treatment. Therefore, once it was confirmed that the wavelength of 395 nm effectively activates the ZnO/g-C<sub>3</sub>N<sub>4</sub> composites and that the generation of H<sub>2</sub>O<sub>2</sub> enhances the reaction, the performance of the photo-Fenton-like process was evaluated. To this end, an experiment was carried out under the same conditions as the previous tests. Before starting, H<sub>2</sub>O<sub>2</sub> was added to achieve a final concentration of 73.57 mM in the solution, aiming to accelerate the Rhodamine B removal process.

As can be seen in Figure 6b, clear differences in photocatalytic efficiency are evident. In the case of photo-Fenton like, the degradation of Rhodamine B was considerably higher compared to that obtained for photocatalysis at 395 nm. Total degradation was achieved in 90 min. The results obtained with the photo-Fenton-like treatment were compared with the performed controls, ZnO/g-C<sub>3</sub>N<sub>4</sub>-H<sub>2</sub>O<sub>2</sub>, and photo-H<sub>2</sub>O<sub>2</sub>. In Figure 6b, it can be seen how H<sub>2</sub>O<sub>2</sub> over the catalyst without light had practically no effect on the degradation

of Rhodamine B (<6%). As for photo-H<sub>2</sub>O<sub>2</sub>, as explained above (Equation (13)), H<sub>2</sub>O<sub>2</sub> is activated by the incidence of light generating  $\cdot OH$  radicals, so the degradation of the dye in this case was relevant. If the values obtained after 1 h of treatment are compared, the degradations were around 51% and 94% for photo-H<sub>2</sub>O<sub>2</sub> and photo-Fenton like, respectively. At the end of the treatment, the improvement was 32.36%. The concentration of Rhodamine B decreased exponentially in both cases, according to a pseudo-first-order kinetic model (Equation (2)). The values of the kinetic constants calculated for each of the treatments were 0.0115 and 0.0514 min<sup>-1</sup>, respectively. This fact evidences the synergistic effect obtained in the photo-Fenton-like treatment, where the H<sub>2</sub>O<sub>2</sub> activation under the selected light is added to the photocatalytic effect of the composites, obtaining a higher and faster degradation.

### 3.2.1. Effect of Catalyst–H<sub>2</sub>O<sub>2</sub> Ratio

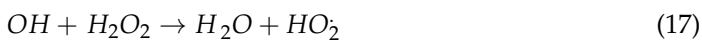
A detailed study varying the amount of catalyst and H<sub>2</sub>O<sub>2</sub> added during the photo-Fenton-like process was carried out. Amounts of catalyst between 25 and 100 mg and H<sub>2</sub>O<sub>2</sub> between 1.96 and 235.50 mM were tested. Figure 6c illustrates the results obtained under different catalyst–H<sub>2</sub>O<sub>2</sub> molar ratios, revealing the influence of H<sub>2</sub>O<sub>2</sub> concentration on the reaction kinetics. As the catalyst–H<sub>2</sub>O<sub>2</sub> ratio increases, the degradation rate improves significantly, as evidenced by the steeper curves and lower dye concentrations observed for higher ratios. Specifically, at a ratio of 1:15, nearly complete dye removal was achieved within 45 min, with no detectable concentration remaining beyond this point. Similarly, at a ratio of 1:5, degradation progresses rapidly but at a slightly slower rate, achieving complete removal by 75 min.

In contrast, the lower ratios, 1:0.5 and 1:2, exhibit slower degradation rates. For the 1:0.5 ratio, the process is remarkably inefficient, with approximately 35% of the dye remaining after 90 min, suggesting insufficient H<sub>2</sub>O<sub>2</sub> availability to generate enough reactive species. The 1:2 ratio shows improved performance compared to 1:0.5, but it was still much less efficient than the higher ratios, which emphasizes the importance of optimizing the H<sub>2</sub>O<sub>2</sub> concentration for effective degradation.

The dashed lines in the graph represent the pseudo-first-order kinetic fit for all experiments with R<sup>2</sup> values greater than 0.98, indicating that the degradation process follows pseudo-first-order kinetics. The kinetic constants, obtained from the pseudo-first-order kinetic fitting, are presented in Figure 6d. These kinetic constants provide a quantitative measure of the degradation rates observed in each experiment. As the catalyst–H<sub>2</sub>O<sub>2</sub> ratio increased, the value of the constant increased significantly. The highest value was observed for the ratio 1:15, confirming the rapid elimination of Rhodamine B under these conditions. On the contrary, the 1:0.5 and 1:2 ratios showed considerably lower k values, correlating with the gentler slopes of their respective degradation profiles.

These results are consistent with AOPs, where the  $\cdot OH$  generated from H<sub>2</sub>O<sub>2</sub> serves as the main oxidizing agent responsible for the degradation of pollutants. The faster kinetics observed at higher concentrations of H<sub>2</sub>O<sub>2</sub> can be attributed to a higher production of the  $\cdot OH$  radical, which accelerates the decomposition of Rhodamine B. However, excessively high concentrations of H<sub>2</sub>O<sub>2</sub> could potentially lead to radical-scavenging effects, as was highlighted in previous studies [60,61]. Specifically, the recombination of  $\cdot OH$  radicals (Equation (16)) becomes more frequent, reducing the availability of active radicals. In addition, H<sub>2</sub>O<sub>2</sub> can react with  $\cdot OH$  radicals to produce less-reactive species, such as HO<sub>2</sub> radicals (Equation (17)), which reduces the overall efficiency of the degradation process [62,63]. These findings highlight the critical role of H<sub>2</sub>O<sub>2</sub> in improving the reaction rate while emphasizing the importance of optimizing the catalyst-to-H<sub>2</sub>O<sub>2</sub> ratio to achieve maximum process efficiency and sustainability.





Finally, the optimized results obtained for the photocatalysis and photo-Fenton like were compared with those obtained in other recent studies to evaluate the effectiveness of the synthesized material. In analyzing the degradation values obtained by the present study, the total degradation was achieved after 3 h of treatment, which is slow compared to other studies already carried out (Table 1), but the power of the lamps used in those cases is between three and five times higher. This means an increase in energy consumption and, therefore, in treatment costs. In the case of photo-Fenton like, considering the power of the lamp used and the amount of catalyst in the solution to treat, the result obtained with the synthesized ZnO/g-C<sub>3</sub>N<sub>4</sub> composites is very competitive, being the one that achieves the total degradation of Rhodamine B most rapidly. Therefore, the synthesized ZnO/g-C<sub>3</sub>N<sub>4</sub> composites are presented as a viable and highly effective alternative in photo-Fenton-like treatment.

**Table 1.** Compilation of different recent works in which Rhodamine B was degraded by photocatalysis and photo-Fenton-like using different materials as catalysts.

| Catalyst                                                           | Initial Rhodamine B Concentration (mg/L) | Treatment                                 | Degradation (%) | Reference    |
|--------------------------------------------------------------------|------------------------------------------|-------------------------------------------|-----------------|--------------|
| ZnO/g-C <sub>3</sub> N <sub>4</sub> nanocomposites (1 g/L)         | 10                                       | Photocatalysis (200W Xe Lamp, 380 nm)     | 100 (80 min)    | [17]         |
| K-doped g-C <sub>3</sub> N <sub>4</sub> /ZnO (0.2 g/L)             | 20                                       | Photocatalysis (2 sun intensity, 420 nm)  | 92.00 (120 min) | [55]         |
| ZnO/g-C <sub>3</sub> N <sub>4</sub> composites (0.5 g/L)           | 10                                       | Photocatalysis (30 W UV Lamp, 395 nm)     | 100 (180 min)   | This article |
| Fe <sub>3</sub> O <sub>4</sub> -TiO <sub>2</sub> nanosheets (1g/L) | 30                                       | Photo-Fenton-like (6W UV Lamp, 365 nm)    | 98.12 (120 min) | [32]         |
| Cu-Cu <sub>2</sub> O/g-C <sub>3</sub> N <sub>4</sub> (0.4 g/L)     | 10                                       | Photo-Fenton-like (300 W Xe Lamp, 400 nm) | 90.00 (50 min)  | [30]         |
| Magnetite nanocubes (2 g/L)                                        | 10                                       | Photo-Fenton-like (48W UV Lamp, 365 nm)   | 94.04 (180 min) | [34]         |
| NH <sub>2</sub> -MIL-53(Fe) (0.08 g/L)                             | 40                                       | Photo-Fenton-like (500W Xe Lamp)          | 95.00 (120 min) | [64]         |
| ZnO/g-C <sub>3</sub> N <sub>4</sub> composites (0.5 g/L)           | 10                                       | Photo-Fenton-like (30 W UV Lamp, 395 nm)  | 100 (45 min)    | This study   |

### 3.2.2. Reusability Study of Photo-Fenton-like Treatment

In full-scale wastewater treatment, catalyst recovery and reuse are very important to reduce the cost and operability of the process. A stable catalyst should preserve its activity during several consecutive treatment cycles. The study of the stability and reusability of the composites was evaluated by performing four consecutive cycles of the photo-Fenton-like treatment, as shown in Figure 6e. These tests were conducted starting from a catalyst-H<sub>2</sub>O<sub>2</sub> molar ratio of 1:15, since it was the one that presented the best results in the previous section. Only one injection of H<sub>2</sub>O<sub>2</sub> was performed at the beginning of the first cycle. At the end of each cycle, a more concentrated dye injection was made to start from the same conditions, minimizing the catalyst losses and maintaining the amount of H<sub>2</sub>O<sub>2</sub> left over from the previous cycle because this was similar to what would occur in a larger scale process.

Figure 6e shows the behavior of the degradation capacity of the ZnO/g-C<sub>3</sub>N<sub>4</sub> composites throughout the four cycles. The first two cycles achieved approximately the same level of degradation within the same time, so the catalytic activity of the ZnO/g-C<sub>3</sub>N<sub>4</sub> composites remained stable. After 30 min of treatment, the degradation achieved in each of them was 95.91% and 92.23%, respectively, and in 45 min, the dye degradation was total in both cases. As for the third and fourth cycles, it can be observed that there was a decrease in activity. The degradation after 30 min was 77.12% in the third cycle and 74.44% in the

fourth cycle and reached total degradation after 60 min of treatment. This decrease was also reflected in the value of the kinetic constants, where it is observed that as the cycles progressed, their value decreased (Figure 6f). This could be due in part to the possible loss of composites in the sample collection and the possible erosion at their interfaces and solutions [60]. On the other hand, it could be attributed to the fact that  $\text{H}_2\text{O}_2$ , as seen above, plays an important role in degradation, so since only a single injection has been made, even though it is being generated, it may not be sufficient. This would affect the activity, and degradation would be lower and slower. Although the concentration of  $\text{H}_2\text{O}_2$  should be monitored during treatment, the viability of this material for multiple uses can be confirmed. This makes it viable for use in long-term treatments and, therefore, opens the possibility of using it in larger-scale trials.

### 3.3. Electro-Fenton-like Tests

After the study of the composites' photocatalytic activities, given the success of previous studies using Zn as a catalyst for heterogeneous electro-Fenton-like processes carried out in our research group [65], it was considered interesting to evaluate the electrocatalytic properties of the synthesized material. For this purpose, a series of tests were carried out following the procedure described in Section 2.4.2.

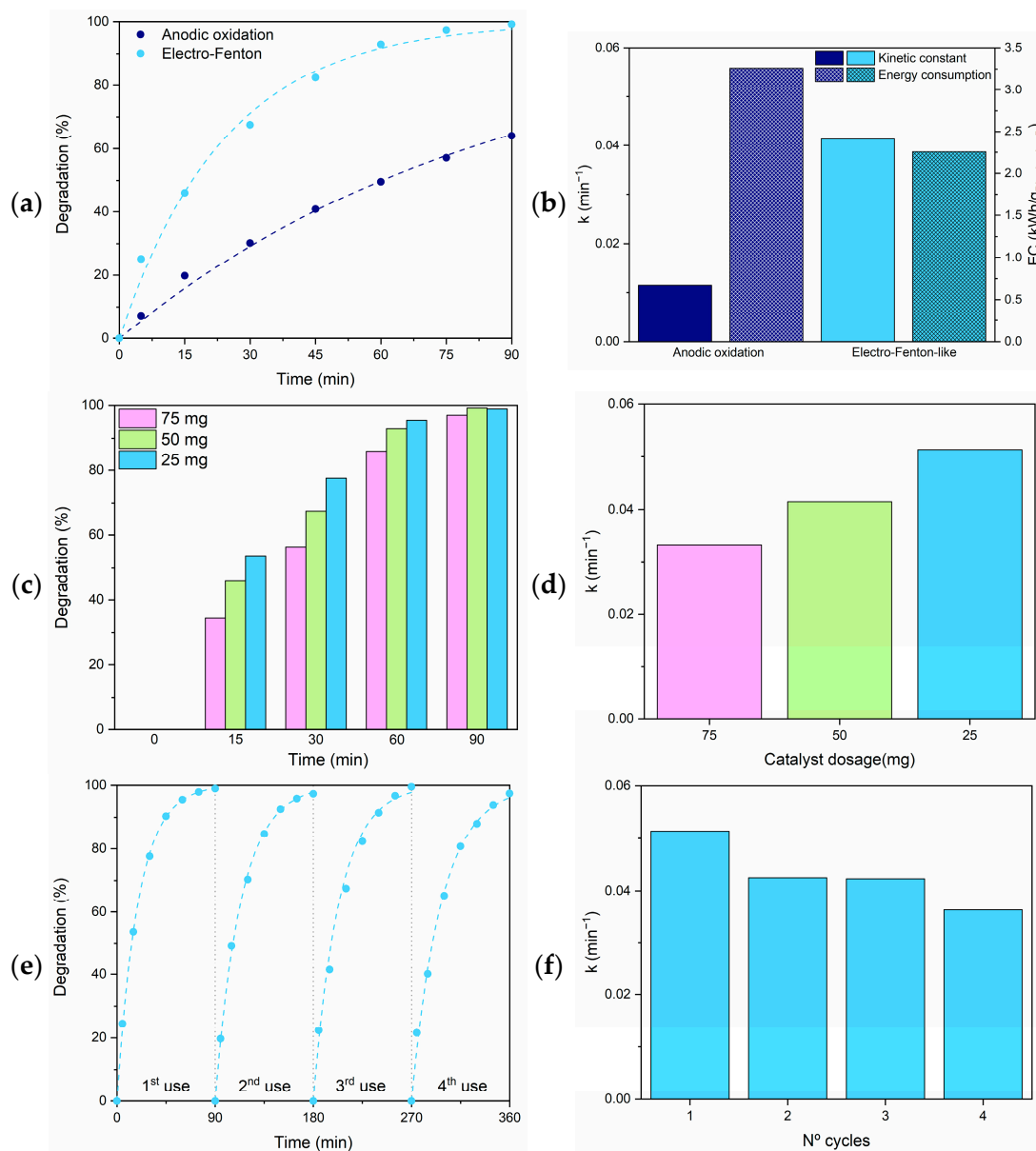
#### 3.3.1. Electro-Fenton-like vs. Anodic Oxidation

The first step was the evaluation of the removal of Rhodamine B by an electro-Fenton-like process. For this purpose, a test was performed using 50 mg of the  $\text{ZnO/g-C}_3\text{N}_4$  composites as a catalyst, and the obtained results were compared with the simplest AOP's anodic oxidation under the same conditions (25 mA). The degradation profiles, shown in Figure 7a, highlight the catalytic effect of the composites being clearly observed and reaching 82.39% degradation in 45 min. Comparing the total degradation achieved after 90 min, the electro-Fenton-like treatment demonstrated a 35% improvement over the anodic oxidation. Figure 7a also illustrates the exponential decrease in Rhodamine B concentration, following a pseudo-first-order kinetic model (Equation (2)). The kinetic constants calculated for each of the treatments are presented in Figure 7b, and their values were 0.0115 and  $0.0415 \text{ min}^{-1}$ , respectively. These results demonstrate the improved efficiency of the electro-Fenton-like process, with a kinetic coefficient four times higher than that of anodic oxidation.

In addition, the energy consumption (EC) was evaluated by Equation (5). The values obtained (Figure 7b) show a significant reduction in EC for the electro-Fenton-like process compared to the anodic oxidation. These facts confirmed the good catalytic activity of the synthesized composites to decompose  $\text{H}_2\text{O}_2$  into reactive radicals. In this configuration, the selection of PLA conductive electrodes allowed for the generation of  $\text{H}_2\text{O}_2$ , reaching an excess concentration of 1.5 mg/L after 90 min in the degradation treatment. Given this maintained production,  $\text{O}_2$  was not added during the course of the treatment, which resulted in cost savings.

#### 3.3.2. Effect of Catalyst Dosage

After verifying the effective catalytic activity of the  $\text{ZnO/g-C}_3\text{N}_4$  composites in the electro-Fenton-like process, a series of experiments were carried out to investigate whether increasing or decreasing the catalyst dosage could improve the degradation efficiency. The behavior of the system was studied by testing three different amounts of catalyst, 25, 50, and 75 mg while maintaining a constant initial dye concentration constant (10 mg/L). The results obtained, shown in Figure 7c, indicated that, as the amount of catalyst increased, degradation showed a decreasing trend at the same reaction times, and when the amount of catalyst decreased, the opposite occurred.



**Figure 7.** Results of Rhodamine B degradation experiments by different treatments and conditions: (a) profiles of Rhodamine B degradation obtained from anodic oxidation and electro-Fenton like at 25 mA; (b) EC values and apparent pseudo-first-order constant constants obtained for anodic oxidation and electro-Fenton like after 90 min of treatment at 25 mA; (c) profiles of Rhodamine B using different dosages of ZnO/g-C<sub>3</sub>N<sub>4</sub> composites; (e) profiles of Rhodamine B degradation using successive cycles. Dashed lines depict the pseudo-first-order kinetic fitting for all experiments with an  $R^2 > 98\%$ . (b,d,f) Apparent pseudo-first-order constant ( $k$ ) values for each experiment.

Although after ending the treatment, the degradation achieved in the three cases was very similar, 98.93, 99.21, and 97.01%, respectively, when analyzing each of the other treatment times, it was observed that, with the amount of 25 mg, the degradation obtained was greater. For example, after 30 min of treatment, the degradations achieved were 77.61, 67.53, and 56.30% for 25, 50, and 75 mg, respectively. The degradation followed pseudo-first-order kinetics in all cases, and the kinetic constants obtained (Figure 7d) showed the same trend. In Figure 7d, it can be clearly seen how the value of the kinetic constant increased as the amount of composites used decreased. This is similar to the behavior observed in the photo-Fenton-like treatment, where an increase in the catalyst-H<sub>2</sub>O<sub>2</sub> molar ratio led to an improvement in the degradation process. Considering the H<sub>2</sub>O<sub>2</sub> generated,

the catalyst–H<sub>2</sub>O<sub>2</sub> molar ratios in the electro-Fenton-like treatment for 25, 50, and 75 mg of catalyst were 1:0.05, 1:0.027, and 1:0.013. So, the improvement as the ratio increases was also observed in the electro-Fenton-like process, although the mechanisms involved are different. In this case, the worsening of degradation could be due to the occurrence of side reactions that modify the mechanisms of the Fenton-like reaction. The secondary reactions would result in the production of other radicals such as hydroperoxyl radicals with lower oxidizing power than  $\cdot OH$  radicals [19,65–68].

The results obtained with the optimum amount of catalyst were compared with other studies already carried out in order to analyze the feasibility of using the synthesized material as a catalyst for the electro-Fenton process. In the case of Zhang et al. [69], a 97.20% degradation of Rhodamine B was achieved after 1 h of treatment using Fe/Cu kaolin particles (30 g/L) as a catalyst. Nidheesh et al. [70] reached a degradation of 97.30% of Rhodamine B after 3 h of treatment using Fe<sub>3</sub>O<sub>4</sub> (0.1 g/L) as a catalyst. The degradation achieved in this manuscript, in proportion to the amount of catalyst used in the treatment, was higher. Therefore, it can be concluded that the synthesized material is presented as a viable, competitive, and promising alternative for the degradation of dyes by electro-Fenton treatment.

### 3.3.3. Reusability Study of Electro-Fenton-like Treatment

Finally, as with the study of the photocatalytic activity of ZnO/g-C<sub>3</sub>N<sub>4</sub> composites, it is crucial to evaluate their stability, recyclability, and reusability. For this purpose, four electro-Fenton-like cycles were conducted at 25 mA and with 25 mg of catalyst. At the end of each cycle, a more concentrated dye solution was injected to ensure that the initial conditions were maintained while minimizing the catalyst losses throughout the process.

As illustrated in Figure 7e, the degradation capacity of the ZnO/g-C<sub>3</sub>N<sub>4</sub> composites remained practically stable during the four cycles performed, with a slight decrease more noticeable in the last cycle that could be attributed to the loss of catalyst in the sample collection. The degradation achieved in all cycles after 90 min of treatment was greater than 97%, making the material suitable for multiple reuses. Furthermore, not only did its degradation capacity remain unchanged, but there was also practically no change in the kinetic rate constant values throughout each cycle (Figure 7f). Although a minor reduction in degradation efficiency was noted during the final cycle, the overall results validate the reusability of the ZnO/g-C<sub>3</sub>N<sub>4</sub> composites. These findings underline the potential of this material for extended use in large-scale or continuous water treatment processes, offering a viable and sustainable solution for the degradation of pollutants.

## 4. Conclusions

The ZnO/g-C<sub>3</sub>N<sub>4</sub> composites synthesized in this study using a DES solvent demonstrated successful integration of ZnO and g-C<sub>3</sub>N<sub>4</sub> structures, as confirmed by thorough structural and chemical characterizations. The material exhibited a porous nanosheet morphology with uniformly distributed elements, highlighting its suitability for catalytic applications. These results validate DES as an efficient and sustainable synthesis method to create advanced composites for environmental remediation.

In terms of catalytic performance, the composites showed promising activity in various AOPs. Under irradiation at 395 nm, the photocatalytic degradation of Rhodamine B reached significant levels, demonstrating the ability of the material as a photocatalyst. This performance was further improved in the photo-Fenton-like process, where the synergistic activation of H<sub>2</sub>O<sub>2</sub> and irradiation substantially improved the degradation rates. Optimization of the catalyst-to-H<sub>2</sub>O<sub>2</sub> ratio was found to be a critical factor in maximizing the degradation efficiency. Nevertheless, the electro-Fenton-like process exhibited superior efficiency, achieving a rapid degradation of Rhodamine B with kinetic constants four times

higher than anodic oxidation, highlighting the exceptional catalytic activity of ZnO/g-C<sub>3</sub>N<sub>4</sub>. The reuse and stability studies revealed that the ZnO/g-C<sub>3</sub>N<sub>4</sub> composites maintained high degradation efficiencies during multiple cycles in both processes. The minimal decrease in catalytic activity and kinetic rate constants over successive cycles demonstrates the durability and long-term applicability of these composites in continuous or large-scale water treatment processes. This highlights the material's potential for operational flexibility in water treatment applications.

The DES-synthesized ZnO/g-C<sub>3</sub>N<sub>4</sub> composites provide a sustainable and cost-effective solution for treating water contaminated with dyes. Their excellent catalytic performance, stability, and scalability make them a promising candidate for industrial wastewater treatment. Future research should focus on applying these composites to real-world wastewater conditions to further validate their industrial potential and explore their broader environmental impact.

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