



# Article Green Synthesized Cu<sub>2</sub>O-Cu(OH)<sub>2</sub>@Cu Nanocomposites with Fenton-like Catalytic Properties for the Degradation of Cationic and Anionic Dyes

Hala A. Al-Jawhari \* and Nuha A. Alhebshi 🝺

Department of Physics, King Abdulaziz University, Jeddah 21589, Saudi Arabia \* Correspondence: haljawhari@kau.edu.sa

Abstract: In this work, we introduce an environmental and sustainable approach to grow free standing heterogeneous  $Cu_2O-Cu(OH)_2$  nanocomposites on a Cu mesh using spinach leaf extract and glycerol. Structural characterizations for samples annealed at 200 °C revealed that there is more  $Cu(OH)_2$  than  $Cu_2O$  on the mesh surface. The photocatalytic activity of the green synthesized catalyst was studied for degradation of a cationic dye methylene blue (MB), an anionic dye methyl orange (MO) and a mixture of both dyes. The effect of changing the dye's initial pH value on the photodegradation process was explored. After 40 min of irradiation under sunlight, with a maximum intensity of 5 mW/cm<sup>2</sup>, a basic MB dye (pH-11) showed about 80% color removal with an average kinetic rate of 94.5 m·min<sup>-1</sup>. In contrast, 93% of the acidified MO dye (pH-2) was degraded with an average kinetic rate of 126.5 m·min<sup>-1</sup>. Moreover, the versatility of the  $Cu_2O-Cu(OH)_2$ @Cu mesh was evaluated using a remarkable selective separability for a mixture of MB and MO at pH = 2, in the dark and under normal sunlight. Such promising outcomes indicate the potential of our green composites to degrade dyes as both photocatalysts under daylight and as Fenton-like catalysts in darkness.

Keywords: Cu<sub>2</sub>O-Cu(OH)<sub>2</sub> nanocomposites; spinach leaf extract; Fenton-like catalyst

# 1. Introduction

With the growth in textile consumption and production, industrial colored wastewater containing persistent pollutants, which can lead to health problems and threaten aquatic environments, has increased to a concerning level [1]. Textile dyes, which are artificially synthesized to resist fading upon exposure to water, light and oxidizing agents, are made of aromatic highly complex organic compounds [2,3]. Azo dyes, which include one or more (N=N) groups, constitute over 60% of the various groups of dyes used in the textile industry [4]. Nonetheless, other dyes with chromophoric groups, such as C = O, C-NH, CH =N and C-S, are still toxic and potentially carcinogenic [5]. Thus, the development of a selective efficient color removal process is a crucial necessity. Essentially, as explained in the literature [1-3], colored wastewater can be treated biologically, physically or chemically or by employing a combination of these methods. Recently, advanced oxidation processes (AOPs), based principally on the generation of hydroxyl radicals (•OH), have emerged as promising chemical techniques that degrade almost all types of organic contaminants to harmless products such as  $H_2O$  and  $CO_2$  [6]. Photocatalysis [7,8] and both dark and photo-assisted Fenton-like [3,9] reactions are considered among the most efficient and cost-effective AOPs for wastewater remediation.

Photocatalysis involves employing a semiconductor catalyst that can absorb photons from sunlight and create electron-hole pairs which aid in decomposing organic dyes in a nontoxic and environmentally friendly method [10]. It is of great importance to utilize catalysts that can absorb visible light on one hand, and meet several practical demands on



Citation: Al-Jawhari, H.A.; Alhebshi, N.A. Green Synthesized Cu<sub>2</sub>O-Cu(OH)<sub>2</sub>@Cu Nanocomposites with Fenton-like Catalytic Properties for the Degradation of Cationic and Anionic Dyes. *Crystals* **2022**, *12*, 1328. https://doi.org/10.3390/ cryst12101328

Academic Editor: Yanyan Cui

Received: 22 August 2022 Accepted: 17 September 2022 Published: 20 September 2022

**Publisher's Note:** MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



**Copyright:** © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). the other, such as multi-functionality, low cost, recyclability and facile methods of fabrication. For these reasons, cuprous oxide (Cu<sub>2</sub>O), cupric oxide (CuO) and copper hydroxide (Cu(OH)<sub>2</sub>), with their narrow energy gaps, seem to be promising candidates [11]. Moreover, heterogeneous structures based on two or more copper compounds, such as Cu<sub>x</sub>O@Cu [12–14] or Cu<sub>x</sub>O-Cu(OH)<sub>2</sub> [15,16], have proved to be more efficient photocatalysts than pure copper oxides. Such an enhancement was attributed to the formation of heterojunctions which boost the separation of the photogenerated electron-hole pairs and, hence, improve the photocatalytic activity [17].

On the other hand, the main idea of Fenton degradation is to use a metal with multiple oxidation states, known as a catalyst, to transform the oxidizing agent hydrogen peroxide  $(H_2O_2)$  into •OH radicals [9]. The Fenton process originated using materials containing  $(Fe^{+2})$ , but as iron forms stable complexes with the degradation products, the newly formed sludge, e.g., iron hydroxide precipitates, gives rise to another environmental hazard [3]. In a Fenton-like method, copper compounds have been considered due to a redox cycle similar to that of iron, with the benefit of forming temporary complexes with the degradation products and, hence, leaving the active sites available for a continuous catalytic cycle [3]. It has been reported that employing copper-based compounds as heterogeneous catalysts exhibited interesting Fenton-like catalytic properties [18].

However, since photocatalytic oxidation primarily occurs on the catalyst surface, the substrate adsorption on the catalyst surface plays a crucial role in any degradation process. The pH of solutions along with the ionic state of the organic dye are two important factors that control the electrostatic interactions between the adsorbent and the adsorbate [19]. As a result, the rate of adsorption and, hence, the photocatalysis or Fenton-like degradation, will vary with the pH of an aqueous medium [20].

In this work, we aim to enhance the performance of our earlier reported 3D  $Cu_xO@Cu$  heterogeneous [14] made with spinach leaf extract, by fabricating  $Cu_xO-Cu(OH)_2@Cu$  via adding glycerol and reducing the process temperature. Our fabricated 3D nanocomposites will be examined to degrade methylene blue (MB), as a cationic non-azo dye; methyl orange (MO), as an anionic azo dye; and a mixture of both dyes. The impact of changing the initial pH value and irradiation conditions on the dye degradation will be explored. The differences between the supposed degradation pathways will be clarified and the mechanism of kinetics will be investigated.

#### 2. Materials and Methods

#### 2.1. Catalysts Synthesis

In this work, the oxidation process of a copper substrate is a modified version of the green synthesis method published elsewhere by our team [14]. The role of spinach extract in the synthesis of  $Cu_2O-Cu(OH)_2$  is clarified in the supplementary information [21,22].

Figure 1 illustrates the steps of extracting the spinach solution and treating the copper mesh with it. Briefly, 100 g of washed spinach leaves were boiled in 100 mL of distilled water followed by double-filtration through Whatman filter paper (no.4). A commercial copper mesh (99.99% Cu, the Mesh Company, Warrington, UK) was cut into 6 cm diameter circles which were ultrasonically and sequentially cleaned in 1 M HCl, ethanol and distilled water. The clean copper mesh circles were then immersed for 1 h at 90 °C in a mixture of filtered spinach extract and glycerol at a ratio of (3:1). After picking up the wetted substrates, they were annealed for 1 h in a box furnace at 200 °C in air. The copper mesh that was treated with spinach extract and glycerol are denoted in this paper by (SG-CuM@200). For the sake of comparison, control samples of raw Cu mesh (CuM) and clean Cu mesh annealed at 200 °C without green treatment (CuM@200) were used.



**Figure 1.** An illustration of the green synthesis steps, materials and equipment for preparing the catalyst Cu<sub>2</sub>O-Cu(OH)<sub>2</sub>@Cu mesh (Created with BioRender.com).

#### 2.2. Characterization Techniques

An X-ray photoelectron spectroscope (XPS, Kratos Axis Supra DLD spectrometer, Manchester, UK) was used to identify the surface compositions of the fabricated copper oxide/hydroxide thin film. The XPS peak fitting analysis was optimized using the Gaussian function. The morphology of all samples was imaged at nanometer and micrometer scales via scanning electron microscope (SEM, JSM-7600F, JEOL, Peabody, MA, USA). In addition, the elemental spectra of the copper oxide/hydroxide were qualitatively detected and analyzed using energy dispersive spectroscopy (EDS, X-Max, Oxford Instrument, Abingdon, UK) to verify the absence of any undesirable heavy impurities that could be left on the mesh from the green extract.

## 2.3. Catalytic Activity Measurements

As water pollutants, 10 mg/L of MB ( $C_{37}H_{27}N_3Na_2O_9S_3$ ) and MO ( $C_{14}H_{14}N_3NaO_3S$ ) solutions were individually prepared by mixing 5 mg of each dye powder in 500 mL of distilled water. To study the effect of changing the pH values on dye degradation, several drops of 1M HCl or 1M NaOH were added to the colored water to obtain an acidic or basic medium, respectively. The pH numbers were measured using a pH meter (HI9811-5, HANNA, Woonsocket, RI, USA).

The catalytic activity was performed by immersing one circle of the treated mesh into a petri dish containing 20 mL of the dye under consideration. For the photodegradation case, samples were exposed to natural sunlight in a shaded area with a low irradiation range between 4 and 5 mW/cm<sup>2</sup> as recorded using a photodetector (1918-R, Newport). However, for examining Fenton-like degradation, sample were placed inside a dark black box at room temperature. It is worth mentioning that both degradation experiments were performed without adding any amount of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>).

Absorbance spectra for each batch were then recorded every 10 min for a total duration of 90 min using a UV–Vis spectrophotometer (Genesys 10S, Thermo Scientific, Waltham, MA, USA). The degradation rate of the dye was calculated according to the relation:

(

$$\frac{(A_0 - A_t)}{A_0} \times 100\tag{1}$$

where  $(A_0)$  and  $(A_t)$  are, respectively, the absorbance peak of each dye initially and after the catalytic treatment for time intervals (*t*). Finally, the pH of all samples was measured again after completing the degradation process to detect any effect of the catalyst mesh on the neutralization of the solution.

To predict the rate and the order of organic pollutants degradation, three standard kinetic models were applied, explicitly; the first and second order of linear regression in addition to the Behnajady–Modirshahla–Ghanbery (BMG) model developed by Behnajady et al. [23]. Mathematically, those models can be expressed as; Equations (2)–(4), respectively [24];

$$\ln\left(\frac{A_{\rm t}}{A_0}\right) = -k_1 t \tag{2}$$

$$\frac{1}{A_t} - \frac{1}{A_0} = k_2 t \tag{3}$$

$$\frac{t}{1 - \left(\frac{A_{\rm t}}{A_0}\right)} = m + bt \tag{4}$$

where  $k_1 \pmod{1}$  and  $k_2 \pmod{1} \operatorname{L} \min^{-1}$  are the rate constants for the first and second order models, respectively; *m* (min) and *b* (dimensionless) are two distinctive constants for the BMG model that are related to reaction rates and oxidation capacity, respectively.

The order of the reaction was determined by fitting the experimental data to those equations and verifying how close the coefficient of determination ( $R^2$ ) values were to 1.

#### 3. Results and Discussion

#### 3.1. Structural and Morphological Properties

The XRD measurements for all three samples, illustrated in Figure S1a, revealed three main diffraction peaks located at 43.3°,  $50.4^{\circ}$  and  $74.2^{\circ}$  that refer to the (111), (200) and (220) planes, respectively, of the metallic Cu phase. However, for the two annealed meshes, a small peak located at  $36.45^{\circ}$  could be noticed indicating the existence of Cu<sub>2</sub>O phase on the surface of our samples.

To validate the chemical compositions and verify the oxidation states for each sample, the XPS analyses were carried out as shown in Figure 2. The sharp characteristic peaks of  $Cu^0$  are detected in the pure copper mesh (CuM) spectrum (Figure 2a) with a binding energy separation of 20 eV between Cu  $2p_{3/2}$  and Cu  $2p_{1/2}$  as theoretically expected. The main peaks of Cu<sup>+</sup> and Cu<sup>++</sup> in Figure 2b for the sample prepared with spinach extract and glycerol (SG-CuM@200) are positioned at a binding energy of 932.5 eV and 934.5 eV, respectively, which are assigned to Cu<sub>2</sub>O and Cu(OH)<sub>2</sub> compounds [25–27]. Furthermore, the well-known shake-up satellite peaks that appeared in the spectrum of SG-CuM@200 confirm the presence of Cu(OH)<sub>2</sub>. In the CuM@200 sample, as shown in Figure 2c, similar peaks of Cu<sub>2</sub>O and Cu(OH)<sub>2</sub> are shown in addition to a new peak at 933.7 eV that is related to Cu<sup>++</sup> of CuO. The shake-up satellite peaks of Cu(OH)<sub>2</sub> seem to be overlapped with the dominant contribution by CuO. The area ratios of (Cu<sup>+</sup> in Cu<sub>2</sub>O:Cu<sup>++</sup> in CuO:Cu<sup>++</sup> in Cu(OH)<sub>2</sub>) are calculated from the curve fitting parameters to be (1:0:2) and (2:2:1) in samples SG-CuM@200 and CuM@200, respectively.

According to the area ratio (1:0:2), the amount of  $Cu^{++}$  is twice  $Cu^+$  which implies that the number of  $Cu(OH)_2$  molecules should be four times higher than that of  $Cu_2O$ molecules. This is estimated by taking into account that each  $Cu_2O$  molecule contains two  $Cu^+$  cations while only one  $Cu^{++}$  cation is involved in each  $Cu(OH)_2$  molecule.

Therefore, one can consider that adding glycerol to the synthesis mixture of the SG-CuM@200 sample leads to producing more Cu(OH)<sub>2</sub> than Cu<sub>2</sub>O on the mesh surface. In contrast, the peaks area ratio in the untreated copper mesh (2:2:1) indicate that Cu(OH)<sub>2</sub> molecules should be half the number of CuO molecules, and equal to the number of Cu<sub>2</sub>O molecules. These results highlight the effective role of incorporating glycerol with the spinach extract in increasing the formation of the copper hydroxide using our modified green method. Hydroxyl group is a preferred component on the catalyst surface as it could promote its wettability and endorse the diffusion of the reactant [18].

The oxygen state (O 1s) can contribute as an anion ( $O^{2-}$ ) in the lattice of CuO and Cu<sub>2</sub>O, or form the hydroxide group and the water molecule as adsorbed on the surface of the material, which is denoted here as (O-surf.) [25]. In Figure 2d representing the SG-CuM@200 sample, there is a clear peak of O-surf. in Cu(OH)<sub>2</sub> at 531.9 eV, with a peak area five times higher than that of  $O^{2-}$  in Cu<sub>2</sub>O centered at 530.8 eV. While in the CuM@200 sample, Figure 2e, the dominant oxygen contribution belongs to the composition of CuO as its peak center at 529.8 eV has the largest peak area compared to the oxygen in Cu<sub>2</sub>O and Cu(OH)<sub>2</sub>. These findings are well-matched with that resulting from the Cu 2p<sub>3/2</sub> of the two samples. Furthermore, it can be noticed that there are H<sub>2</sub>O molecules on the surface of both samples as indicated by the peak of 533.4 eV, which might be absorbed from

the air humidity before the XPS measurements. The values of all peak centers and peak areas of the Cu 2p and O 1s are listed in Tables S1 and S2, respectively, while the XPS Cu  $L_3M_{4,5}M_{4,5}$  and C 1s spectra of all the three samples are represented in Figure S1b,c in the Supplementary Information document.



**Figure 2.** XPS spectra of (**a**–**c**) Cu 2p<sub>3/2</sub> and Cu 2p<sub>1/2</sub> core peaks and (**d**–**f**) O 1s core peaks for the as-prepared CuM, CuM@200 and SG-CuM@200 samples.

The EDS results (shown in Figure S2) reveal no heavy impurities in our samples. In addition, the results indicate that sample SG-CuM@200 contains more carbon than that adsorbed on pure mesh CuM, as confirmed by the XPS spectra of C 1s core peaks in Figure S1c. We believe that the addition of glycerol to spinach extract (1:3) assisted in a production of a thin carbon layer that is a well-known co-catalyst. Carbon was found not only to enhance the conversion of  $Cu^0$  to  $Cu^+/Cu^{2+}$ , but also to accelerate the electron transfer and endorse the catalytic decomposition of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) to generate •OH radicals [18,28].

The morphology for both pure (CuM) and green synthesized (SG-CuM@200) samples was explored using the SEM images at small and large magnifications. Figure 3a,b reveal that the industrial copper substrate consists of cross-entangled microwires with a diameter of  $\sim$ 50 µm and a mesh opening length of  $\sim$ 200 µm, and its surface contains small fused particles of copper. We have selected this three-dimensional woven substrate here and in our previous report [14] in order to facilitate the passage of the pollutant water through the photocatalytic active materials attached to the copper mesh as a purification filter instead of the two-dimensional flat substrates. In addition, the coated substrate is easier and faster to be installed/removed in/out of the water than the powder form of photocatalytic materials. Annealing the copper mesh at 200 °C, with no treatment with spinach leaf extract and glycerol, did not change the morphology of its surface as it can be noticed in Figure 3c,d. On the other hand, the utilization of spinach extract and glycerol in the synthesis protocol of SG-CuM@200 leads to the successful growth of clear nanocubes with an edge length between 60 and 150 nm, as magnified in Figure 3e,f. Based on the prior XPS analysis of sample SG-CuM@200, these nanoparticles consist of cuprous oxide/copper hydroxide. This thin layer is conformally coating the free-standing copper microwires. Accordingly, we will assign this sample through the remainder of the article as (Cu<sub>2</sub>O)-Cu(OH)<sub>2</sub>@Cu heterogeneous composites.



**Figure 3.** SEM images at low and high magnifications of (**a**,**b**) CuM, (**c**,**d**) CuM@200 and (**e**,**f**) SG-CuM@200 samples.

# 3.2. Catalytic Activity Performance

In general, the mechanism of dye degradation can be divided into two successive parts: the adsorption process and the catalytic reaction [29]. The electrostatic charges that control the adsorption step are very dependent on the pH of the medium and the nature of organic pollutants. Therefore, we will explore the catalytic degradation performance of our green synthesized  $(Cu_2O)/Cu(OH)_2$ @Cu heterogeneous mesh on two different ionic dyes at different initial values of pH.

## 3.2.1. Degradation of Cationic Methylene Blue (MB)

Methylene blue is a well-known cationic, non-azo, aromatic dye with a molecular weight of 319.85 g mol<sup>-1</sup> [2]. In a high pH medium, the catalyst surface appears negatively charged, which enhances the adsorption of positively charged MB molecules and prompts its color removal kinetics [20]. In addition, the adsorption capacity under basic conditions could be improved due to the deprotonation of -COOH and -OH groups by high pH stimulation [19]. Therefore, the photocatalytic activity of  $(Cu_2O)/Cu(OH)_2@Cu$  composites was evaluated at four different initial pH values of MB solution, specifically, 11, 9, 6.5 and 2, under 5 mW/cm<sup>2</sup> of daylight irradiation (see Figure S3). The samples of this batch are symbolized according to the dye type, light condition and pH value as; MBL-11, MBL-9, MBL-6.5 and MBL-2.

For the sake of comparison, we simultaneously explored the effect of CuM@200 (as a control sample) on the degradation of neutral MB (pH-6.5). The photocatalytic degradation of MB is visualized by a decrease in its optimum absorbance peak which occurs at 665 nm, with no considerable shift in the peaks' positions (see Figure S4a–d). The percentage of color degradation for each sample was calculated according to Equation (1) and is illustrated in Figure 4a.



**Figure 4.** (a) The percentage of the MB dye degradation, (b) the linear fitting of the MB experimental data with the BMG kinetic model and (c) photographs of the degraded MB dye during 90 min by the same catalyst in different pH values under the sunlight and the darkness.

Under a high basic condition (pH-11), when a 20 mL of MB solution was exposed to natural daylight in the presence of a 6 cm diameter of  $(Cu_2O)/Cu(OH)_2$ @Cu heterogeneous mesh, 89.37% of MB was decomposed after 90 min of irradiation. By reducing the pH to 9 and 6.5, the photodegradation percentage through the same duration decreased to 84.36% and 72.32%, respectively. Such dependence of color removal on pH values is expected for a cationic dye such as MB and can be attributed to the effect of both processes: adsorption and photodegradation [20]. It is worth mentioning that the untreated mesh (CuM@200) has no noticeable effect on MB degradation, as shown in Figure S4e.

However, what was unanticipated is the performance of the acidic sample MBL-2 which was conducted at (pH = 2). A lower rate of degradation was expected since numerous of H+ ions will aggressively compete with cationic MB molecules which will decrease the adsorption of the MB molecules on the surface of the acidic catalyst [2]. Yet, as it can be seen from Figure 4a, the dye was removed up to 87.03% after 90 min of irradiation. Such excellent catalytic performance, under the acidic condition of MB, could not be attributed to the normal mechanism of photodegradation. To eliminate the light effect and examine the other pathways of degradation, the measurements of MB with (pH = 2) were repeated in the dark at room temperature. Interestingly, as it is illustrated in Figure 4a, based on data presented in Figure S4f, the degradation activities of MBL-2 and MBD-2 are almost the same. Such outcomes indicate the ability of our  $(Cu_2O)/Cu(OH)_2@Cu$  to behave as a Fenton-like catalyst, although no external H<sub>2</sub>O<sub>2</sub> was added.

It is well-known that conventional Fenton-like reactions require a defined dosage of  $H_2O_2$  to stimulate the initial reaction rate, since the number of hydroxyl radicals (.OH) generated in the solution is directly related to this dosage [9]. However, it has been reported that under aerobic conditions, the copper catalyst can activate molecular oxygen in the water to produce in situ  $H_2O_2$  in both neutral [30] or acidic mediums [18]. Hence, the significant dark catalytic behavior of sample MBD-2 (in the absence of  $H_2O_2$ ) may be attributed to the promoted oxidation of acidic water in the presence of  $(Cu_2O)/Cu(OH)_2$ @Cu composites. Noteworthy, performing the dark measurements for MB under basic condition (MBD-11) shows no noticeable degradation, as in Figure S4g, indicating the necessity for an acidic medium to complete the Fenton-like reaction in the dark.

Another feature of the Fenton-like oxidation is the tendency of the resulting solution toward neutralization [9]. In order to investigate this point, the final values of pH (pH<sub>f</sub>), after 90 min of photodegradation, were measured and found to be 9, 7.5, 6.5 and 5.8, for initial conditions of 11, 9, 6.5 and 2, respectively. By plotting the relation between initial pH values (pH<sub>i</sub>) and the change in pH values ( $\Delta$ pH) (as in Figure S4h), the point of zero charge (pHpzc) of our catalyst was found to be 6.5, indicating that the (Cu<sub>2</sub>O)/Cu(OH)<sub>2</sub>@Cu composite exhibits a neutral characteristic which could be produced by its green synthesis.

It is crucial to analyze the obtained data based on different kinetic models to find the most suitable reactor configuration for degrading the organic dye. Three different kinetic models, based on Equations (2)–(4), were utilized for analyzing the decolorization of MB at different initial pH and light conditions. Linear regression analysis based on firstorder, second-order and BMG model reaction kinetics were conducted, and the extracted parameters are listed in Table 1. According to the correlation coefficient values  $R^2$ , the BMG kinetic model was well-fitted to our experimental data. Such a model was found to describe most of catalytic degradation based on Fenton [24] or Fenton-like [18] chemistry. Figure 4b, represents the kinetic rates according to BMG model for the photodegradation of MB at different initial pH values, while other kinetic rate models are plotted in Figure S5a,b. Although our green synthesized composites show acceptable photodegradation for the MB in both basic and acidic mediums, a faster kinetic rate (1/m) of 0.0945 min<sup>-1</sup> was obtained at pH = 11, compared to 0.0614 min<sup>-1</sup> at pH = 2. Moreover, when the degradation was performed in the dark, the kinetic rate of the acidic MB sample (MBD-2) was found to slow down to  $0.0443 \text{ min}^{-1}$ . On the other hand, considering the oxidation capacity parameter (1/b) obtained from the BMG model, it was observed that the photodegradation reaction was capable of occurring at both extremes (i.e., pH = 11 and pH = 2) with the same efficiency. These results indicate that our  $(Cu_2O)/Cu(OH)_2@Cu$  composites are very effective at photodegrading MB dye under both alkali and basic conditions. Furthermore, they have the ability to degrade the color of acidic MB, in the dark, via the Fenton-like chemistry with no addition of  $H_2O_2$ . The photocatalytic performance of  $(Cu_2O)/Cu(OH)_2@Cu$  composites on MB solution with different initial pH values can be visualized in Figure 4c.

**Table 1.** Linear regression parameters for the photodegradation of MB extracted based on first-order, second-order and BMG model reaction kinetics were conducted and extracted.

Sample	BMG			First-Order		Second-Order	
	1/ <i>m</i> (min <sup>-1</sup> )	1/b	<i>R</i> <sup>2</sup>	K <sub>1</sub> (min <sup>-1</sup> )	<i>R</i> <sup>2</sup>	$K_2 \ (mg^{-1} \ min^{-1})$	<i>R</i> <sup>2</sup>
MBL-11	0.09451	0.99285	0.99739	0.02299	0.88911	0.06369	0.98638
MBL-9	0.08126	0.97133	0.99730	0.02011	0.83615	0.04422	0.95285
MBL-6.5	0.05466	0.84792	0.99918	0.01336	0.85724	0.01803	0.95686
MBL-2	0.06145	1.05001	0.99123	0.0228	0.88867	0.05304	0.92921
MBD-2	0.04431	1.23779	0.98668	0.02860	0.95796	0.0825	0.94967
Control Sample	0.00118	0.83838	0.02102	0.00134	0.91223	$8.89  imes 10^{-4}$	0.90903

3.2.2. Degradation of Anionic Methyl Orange (MO)

Methyl orange is an anionic, aromatic, azo dye with a molecular weight of 327.33 g mol<sup>-1</sup> [31]. As with any other azo dye, the nitrogen double bond (N=N) in MO is the chromophoric group responsible for its color [32]. Since MO molecules are negatively charged, the adsorption capacity for this dye would only be pronounced in acidic medium. In basic conditions, the electrostatic repulsion between MO and the adsorbent will prohibit the adsorption. Therefore, the photocatalytic activity of  $(Cu_2O)$ -Cu(OH)<sub>2</sub>@Cu composites was evaluated (under 5 mW/cm<sup>2</sup> of daylight intensity) at three different acidity levels of MO solution, namely at pH of; 2, 4 and 6 (see Figure S6). Correspondingly, samples of this experiment are represented as; MOL-2, MOL-4 and MOL-6.

Because MO is a pH indicator dye, its maximum absorption band, which represents the (N=N) bond, shows a red shift from 464 to 507 nm with a decrease in the initial pH values from 6 to 2, as illustrated in Figure S7a. This shift in the MO absorption band is commonly related to proton transfer to the dye, indicating its acidic character and color changing from yellow to red [32].

The photocatalytic degradation of MO is visualized by the time-dependent absorption measurement (see Figure S7b–d). It is clear that the pH = 2 condition is favorable for the MO adsorption due to the high electrostatic attraction between the anionic dye and the catalyst surface which is positively charged under a high acidic medium [31]. On the contrary, adsorption, and hence degradation, is remarkably inhibited at initial pH values of 4 or 6. The photodegradation percentage for sample MOL-2 was calculated according to Equation (1) and is illustrated in Figure 5a. During the first 40 min, there was a noticeable decrease in the intensity of the absorption band at 507 nm, which represents the chromophoric group, indicating the cleavage of the azo bond. However, after that period the formation of aromatic products, or the probably produced  $H_2O_2$ , is indicated by the appearance of strong absorption in the UV region with a tail spread out until 700 nm. Similar behavior was observed for some catalysts that follow Fenton-like chemistry in the presence of  $H_2O_2$  [33]. As a result, the MO band at 495 nm cannot be followed and does not reach zero even after the complete removal of color. The photodegradation percentage was then calculated at 40 min as 92.95% with a kinetic rate as fast as  $0.12658 \text{ min}^{-1}$  and an oxidation capacity of 0.9046.





In order to confirm the Fenton-like capability of our composites, the degradation of acidic MO was then repeated in the dark and is referred to as MOD-2. Although the degradation rate and oxidation capacity were almost the same for both illumination cases (as listed in Table 2 and plotted in Figure 5b), there was not a tail that hid the MO band at 495 nm, and measurements were recorded until 90 min with a degradation efficiency of 64.5% as shown in Figure 5a. The effect of our  $(Cu_2O)-Cu(OH)_2@Cu$  composites on removing the color of MO under different conditions is shown in Figure 5c.

	BMG			First-Order		Second-Order	
Sample	1/ <i>m</i> (min <sup>-1</sup> )	1/b	<i>R</i> <sup>2</sup>	<i>K</i> <sub>1</sub> (min <sup>-1</sup> )	<i>R</i> <sup>2</sup>	$K_2$ (mg <sup>-1</sup> min <sup>-1</sup> )	R <sup>2</sup>
MOL-2	0.1265	0.9046	0.9949	0.0735	0.9779	0.1890	0.9770
MOD-2	0.0701	0.9046	0.9802	0.0332	0.9628	0.0412	0.9895
MOL-4	-0.0024	-0.3662	0.3800	-0.0020	0.9933	-0.0023	0.9929
MOL-6	-0.0021	-0.1303	0.7934	-0.0014	0.9864	-0.0016	0.9852

**Table 2.** The main extracted parameters for the photodegradation of MO based on the three kinetic models.

Compared to other reported  $Cu_xO@Cu$  composites [13,14,34–38] (see Table S3), our ( $Cu_2O$ )- $Cu(OH)_2@Cu$  catalysts demonstrated excellent photocatalytic degradation of MB and MO with high kinetic rates under a low light intensity.

## 3.2.3. Selective Degradation of (MB) and (MO)

As both MB and MO have shown an excellent response to our catalyst under acidic condition, we decided to investigate the selective catalytic activity on a solution contain-

ing a (1:1) mixture of both MB and MO with an initial pH of 2. Samples MBOL-2 and MBOD-2 were employed to examine the selective separability under sunlight and in the dark, respectively.

It is worthwhile to mention that at pH = 2, the color of the MB/MO mixture was purple with peaks at 665 nm and 507 nm that refer to the characteristic absorption of MB and MO, respectively. As shown in Figure S8a, the degradation of MB/MO binary dyes under natural daylight irradiation is confirmed by a persisting and equal decrease in both peaks. However, after 40 min of irradiation, strong absorption in the UV region with an expanding tail to the IR region is observed, hence our recorded data were limited to 30 min. Conversely, sample MBOD-2 in the dark shows a steady and clear degradation for the two peaks until 90 min (see Figure S8b). The percentage of dye removal was then determined for each color individually by recording its intensity at different intervals as presented in Figure 6a.



**Figure 6.** (a) The percentage of the MB/MO mixed dye degradation, (b) the linear fitting of the MB/MO experimental data with the BMG kinetic model and (c) photographs of the degraded MB/MO mixed dye during 90 min by the same catalyst in different pH values under sunlight and in darkness.

The obtained data were analyzed based on the three mentioned kinetic models. The BMG model, outlined in Figure 6b, is found to be the most suitable configuration representing the MB/MO binary dye degradation. The extracted degradation rate (1/m) and oxidation capacity (1/b) are listed in Table 3.

**Table 3.** Extracted kinetic parameters for the photodegradation of the orange peak (O) and the blue peak (B) in the mixture of MB/MO binary dye.

	BMG			First-Order		Second-Order	
Sample	1/ <i>m</i> (min <sup>-1</sup> )	1/b	<i>R</i> <sup>2</sup>	<i>K</i> <sub>1</sub> (min <sup>-1</sup> )	<i>R</i> <sup>2</sup>	$K_2$ (mg <sup>-1</sup> min <sup>-1</sup> )	<i>R</i> <sup>2</sup>
MBOL-2-O Peak	0.20441	0.97327	0.99756	0.05964	0.90114	0.22334	0.97356
MBOL-2-B Peak	0.16763	1.08389	0.99889	0.07269	0.96155	0.34561	0.98960
MBOD-2-O Peak	0.11858	1.08389	0.99969	0.00747	0.91776	0.05371	0.94129
MBOD-2-B Peak	0.11565	1.0221	0.99771	0.01621	0.76927	0.17357	0.80569

In darkness, both dyes are degraded with the same efficiency and rate. However, under sunlight irradiation, the rates are faster for both peaks indicating the synergetic effect of light for the proposed Fenton-like degradation pathway. Additionally, compared with the dye degradation rate in the single scheme, MB/MO binary scheme shows a much-enhanced efficiency of color removal, especially with MB where its rate increases by a factor of 16. The color fading at different time intervals under daylight and in darkness is shown in Figure 6c. These remarkable results highlight the promising potential of our green synthesized  $Cu_2O/Cu(OH)_2@Cu$  mesh composites in the field of dye selective separability under sunlight and in darkness. It is worth mentioning that fresh leaves are not necessary to create the catalysts, so the required spinach leaves could be taken from the market surplus. This could lead to a considerable increase in the global water supply using a much smaller amount of the consumable food supply.

## 4. Conclusions

In summary, both phases of Cu<sub>2</sub>O and Cu(OH)<sub>2</sub> nanoparticles were synthesized on Cu mesh using a simple, low-cost and eco-friendly route using spinach leaf extract and glycerol. The Cu<sub>2</sub>O/Cu(OH)<sub>2</sub>@Cu mesh, annealed at 200 °C, was proven to have excellent photocatalytic activity for degradation of azo-free dye methyl blue, azo dye methyl orange and a mixture of both dyes. The effect of changing the pH value of the dye on the photodegradation process was explored. This work contributes to providing a new way of green synthesis of Cu-based catalysts that have the capability of dye removal under sun light or in darkness with no addition of H<sub>2</sub>O<sub>2</sub>.

# 5. Patents

This study is an extension of our previous work that was patented on the 5 July 2022 from USPTO-Patent number: US11376570.

**Supplementary Materials:** The following supporting information can be downloaded at: https: //www.mdpi.com/article/10.3390/cryst12101328/s1. Figure S1: (a) XRD spectra, (b) XPS spectra of Cu L3M4,5M4,5 and (c) XPS spectra of C 1s core peaks for as-prepared CuM, CuM@200 and SG-CuM@200 samples; Figure S2: (a,b) SEM images of the as-prepared CuM and SG-CuM@200 samples, respectively, with photographs of the samples in the insets and (c,d) EDS spectra of both samples, respectively, with tables of the elemental and atomic weight percentages; Figure S3: Photographs of (a) the experiments setup with the photodetector and samples exposed to natural sunlight in a shaded area and (b) the initial and final visualized color of the MB dyes on the disks and their final degraded dyes in the beakers; Figure S4: (a-g) UV-Vis absorption spectra of MBL-11, MBL-9, MBL-6.5, MBL-2, control sample MBL-6.5, MBD-2, and MBD-11, respectively, during 90 minutes and (h) the change between the final and initial pH values ( $\Delta$ pH) for all these samples; Figure S5: The linear fitting of the MB experimental data with (a) the first-order kinetic model, and (b) the second-order kinetic model; Figure S6: Photographs of (a) the experiments setup with the photodetector and samples exposed to natural sunlight in a shaded area and (b) the initial and final visualized color of the MO and MB/MO dyes on the disks and their final degraded dyes in the beakers; Figure S7: (a) UV-Vis absorption spectra at initial pH values and (b-e) UV-Vis absorption spectra of MOL-2, MOL-4, MOL-6, and MOD-2, respectively, during 90 minutes and (f) the change between the final and initial pH values ( $\Delta$ pH) for all these samples; Figure S8: (**a**,**b**) UV-Vis absorption spectra of MBOL-2 and MBOD-2, respectively, during 90 minutes; Table S1: Peak centers and peak areas of the Cu 2p for Cu M@200 and SG-Cu M@200 samples; Table S2: Peak centers and peak areas of O 1s for Cu M@200 and SG-Cu M@200 samples; Table S3: Brief comparison between our results and other reported CuxO@Cu composites.

**Author Contributions:** Conceptualization, methodology, validation and investigation, H.A.A.-J. and N.A.A.; resources, H.A.A.-J.; data curation, N.A.A.; writing—original draft preparation, H.A.A.-J.; writing—review and editing, N.A.A.; visualization, N.A.A.; supervision and project administration, H.A.A.-J. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

**Conflicts of Interest:** The authors declare no conflict of interest.

# References

- Al-Tohamy, R.; Ali, S.S.; Li, F.; Okasha, K.M.; Mahmoud, Y.A.; Elsamahy, T.; Jiao, H.; Fu, Y.; Sun, J. A critical review on the treatment of dye-containing wastewater: Ecotoxicological and health concerns of textile dyes and possible remediation approaches for environmental safety. *Ecotoxicol. Environ. Saf.* 2022, 231, 113160. [CrossRef] [PubMed]
- Khan, I.; Saeed, K.; Zekker, I.; Zhang, B.; Hendi, A.H.; Ahmad, A.; Ahmad, S.; Zada, N.; Ahmad, H.; Shah, L.A.; et al. Review on Methylene Blue: Its Properties, Uses, Toxicity and Photodegradation. *Water* 2022, 14, 242. [CrossRef]
- 3. Hussain, S.; Aneggi, E.; Goi, D. Catalytic activity of metals in heterogeneous Fenton-like oxidation of wastewater contaminants: A review. *Environ. Chem. Lett.* **2021**, *19*, 2405–2424. [CrossRef]
- 4. Thangaraj, S.; Bankole, P.O.; Sadasivam, S.K. Microbial degradation of azo dyes by textile effluent adapted, Enterobacter hormaechei under microaerophilic condition. *Microbiol. Res.* **2021**, 250, 126805. [CrossRef] [PubMed]
- Islam, A.; Teo, S.H.; Taufiq-Yap, Y.H.; Ng, C.H.; Vo, D.-V.N.; Ibrahim, M.L.; Hasan, M.M.; Khan, M.A.R.; Nur, A.S.M.; Awual, M.R. Step towards the sustainable toxic dyes removal and recycling from aqueous solution- A comprehensive review. *Resour. Conserv. Recycl.* 2021, 175, 105849. [CrossRef]
- Khan, S.; Sayed, M.; Sohail, M.; Shah, L.A.; Raja, M.A. Chapter 6—Advanced Oxidation and Reduction Processes. In Advances in Water Purification Techniques; Ahuja, S., Ed.; Elsevier: Amsterdam, The Netherlands, 2019; pp. 135–164. [CrossRef]
- 7. Luo, B.; Liu, G.; Wang, L. Recent advances in 2D materials for photocatalysis. Nanoscale 2016, 8, 6904–6920. [CrossRef]
- 8. Sadeghfar, F.; Ghaedi, M.; Zalipour, Z. Chapter 4—Advanced oxidation. In *Interface Science and Technology*; Ghaedi, M., Ed.; Elsevier: Amsterdam, The Netherlands, 2021; Volume 32, pp. 225–324.
- Walling, S.A.; Um, W.; Corkhill, C.L.; Hyatt, N.C. Fenton and Fenton-like wet oxidation for degradation and destruction of organic radioactive wastes. NPJ Mater. Degrad. 2021, 50, 1–20. [CrossRef]
- 10. Dong, S.; Feng, J.; Fan, M.; Pi, Y.; Hu, L.; Han, X.; Liu, M.; Sun, J.; Sun, J. Recent developments in heterogeneous photocatalytic water treatment using visible light-responsive photocatalysts: A review. *RSC Adv.* **2015**, *5*, 14610–14630. [CrossRef]
- 11. Meyer, B.; Polity, A.; Reppin, D.; Becker, M.; Hering, P.; Klar, P.J.; Sander, T.; Reindl, C.; Benz, J.; Eickhoff, M.; et al. Binary copper oxide semiconductors:From materials towards devices. *Phys. Status Solidi B* **2012**, *249*, 1487–1509. [CrossRef]
- 12. Sun, S. Recent advances in hybrid Cu<sub>2</sub>O-based heterogeneous nanostructures. Nanoscale 2015, 7, 10850–10882. [CrossRef]
- 13. Al-Jawhari, H.; Al-Murashi, R.; Abu Saba, L.; Alhebshi, N.; Altuwirqi, R. Effective degradation of MB under natural daylight using green synthesized Cu-Cu<sub>2</sub>O composite films. *Mater. Lett.* **2019**, *254*, 233–236. [CrossRef]
- Alhebshi, N.; Huang, H.; Ghandour, R.; Alghamdi, N.K.; Alharbi, O.; Aljurban, S.; He, J.-H.; Al-Jawhari, H. Green synthesized CuxO@Cu nanocomposites on a Cu mesh with dual catalytic functions for dye degradation and hydrogen evaluation. *J. Alloys Compd.* 2020, 848, 156284. [CrossRef]
- 15. Murugadoss, G.; Rajesh Kumar, M.; Kuppusami, P. Synthesis of Cu<sub>2</sub>O-Cu(OH)<sub>2</sub> nanocomposite from CuSCN precursor by a facile chemical precipitation method. *Mater. Lett.* **2021**, *284*, 128866. [CrossRef]
- 16. Hu, L.; Wang, Z.; Hu, Y.; Liu, Y.; Zhang, S.; Zhou, Y.; Zhang, Y.; Liu, Y.; Li, B. The preparation of Janus Cu(OH)<sub>2</sub>@Cu<sub>2</sub>O/Cu mesh and application in purification of oily wastewater. *Mater. Res. Bull.* **2020**, *126*, 110815. [CrossRef]
- Mamba, G.; Pulgarin, C.; Kiwi, J.; Bensimon, M.; Rtimi, S. Synchronic coupling of Cu<sub>2</sub>O(p)/CuO(n) semiconductors leading to Norfloxacin degradation under visible light. *J. Catal.* 2017, 353, 133–140. [CrossRef]
- Sun, B.; Li, H.; Li, X.; Liu, X.; Zhang, C.; Xu, H.; Zhao, X.S. Degradation of Organic Dyes over Fenton-Like Cu<sub>2</sub>O–Cu/C Catalysts. *Ind. Eng. Chem. Res.* 2018, 57, 14011–14021. [CrossRef]
- 19. Wang, G.; Li, G.; Huan, Y.; Hao, C.; Chen, W. Acrylic acid functionalized graphene oxide: High-efficient removal of cationic dyes from wastewater and exploration on adsorption mechanism. *Chemosphere* **2020**, *261*, 127736. [CrossRef] [PubMed]
- Salleh, M.A.M.; Mahmoud, D.K.; Karim, W.A.W.A.; Idris, A. Cationic and anionic dye adsorption by agricultural solid wastes: A comprehensive review. *Desalination* 2011, 280, 1–13. [CrossRef]
- Zheng, J.Y.; Van, T.-K.; Pawar, A.U.; Kim, C.W.; Kang, Y.S. One-step transformation of Cu to Cu<sub>2</sub>O in alkaline solution. *RSC Adv.* 2014, 4, 18616–18620. [CrossRef]
- 22. Liu, Y.; Chu, Y.; Li, M.; Li, L.; Dong, L. In situ synthesis and assembly of copper oxide nanocrystals on copper foil via a mild hydrothermal process. *J. Mater. Chem.* 2006, *16*, 192–198. [CrossRef]
- 23. Behnajady, M.A.; Modirshahla, N.; Ghanbary, F. A kinetic model for the decolorization of C.I. Acid Yellow 23 by Fenton process. J. Hazard. Mater. 2007, 148, 98–102. [CrossRef] [PubMed]
- 24. Santana, C.S.; Nicodemos Ramos, M.D.; Vieira Velloso, C.C.; Aguiar, A. Kinetic Evaluation of Dye Decolorization by Fenton Processes in the Presence of 3-Hydroxyanthranilic Acid. *Int. J. Environ. Res. Public Health* **2019**, *16*, 1602. [CrossRef] [PubMed]
- 25. National Institute of Standards and Technology. *NIST X-ray Photoelectron Spectroscopy Database*; National Institute of Standards and Technology: Gaithersburg, MD, USA, 2000; Volume 20899.

- Moulder, J.F. Standard XPS Spectra for Elements. In *Handbook of X-ray Photoelectron Spectroscopy: A Reference Book of Standard Spectra for Identification and Interpretation of XPS Data*, 1st ed.; Chastain, J., Ed.; Perkin-Elmer Corporation: Eden Prairie, MN, USA, 1992.
- 27. Biesinger, M.C. Advanced analysis of copper X-ray photoelectron spectra. Surf. Interface Anal. 2017, 49, 1325–1334. [CrossRef]
- 28. Zhu, G.; Jin, Y.; Ge, M. Simple and green method for preparing copper nanoparticles supported on carbonized cotton as a heterogeneous Fenton-like catalyst. *Colloids Surf. A Physicochem. Eng. Asp.* **2022**, *647*, 128978. [CrossRef]
- Dong, C.; Zhong, M.; Huang, T.; Ma, M.; Wortmann, D.; Brajdic, M.; Kelbassa, I. Photodegradation of methyl orange under visible light by micro-nano hierarchical Cu<sub>2</sub>O structure fabricated by hybrid laser processing and chemical dealloying. *ACS Appl. Mater. Interfaces* 2011, *3*, 4332–4338. [CrossRef]
- 30. Dong, G.; Ai, Z.; Zhang, L. Total aerobic destruction of azo contaminants with nanoscale zero-valent copper at neutral pH: Promotion effect of in-situ generated carbon center radicals. *Water Res.* **2014**, *66*, 22–30. [CrossRef]
- Abdulrahman Hanoon, M.; Ahmed, M.J. Adsorption of Methyl Orange from Wastewater by using Biochar. *Iraqi J. Chem. Pet. Eng.* 2019, 20, 23–29. [CrossRef]
- Sha, Y.; Mathew, I.; Cui, Q.; Clay, M.; Gao, F.; Zhang, X.J.; Gu, Z. Rapid degradation of azo dye methyl orange using hollow cobalt nanoparticles. *Chemosphere* 2016, 144, 1530–1535. [CrossRef]
- Trotte, N.S.F.; Aben-Athar, M.T.G.; Carvalho, N.M.F. Yerba Mate Tea Extract: A Green Approach for the Synthesis of Silica Supported Iron Nanoparticles for Dye Degradation. J. Braz. Chem. Soc. 2016, 27, 2093–2104. [CrossRef]
- Li, H.; Su, Z.; Hu, S.; Yan, Y. Free-standing and flexible Cu/Cu<sub>2</sub>O/CuO heterojunction net: A novel material as cost-effective and easily recycled visible-light photocatalyst. *Appl. Catal. B* 2017, 207, 134–142. [CrossRef]
- Baghriche, O.; Rtimi, S.; Pulgarin, C.; Kiwi, J. Polystyrene CuO/Cu<sub>2</sub>O uniform films inducing MB-degradation under sunlight. *Catal. Today* 2017, 284, 77–83. [CrossRef]
- Kamazani, M.; Zarghami, Z.; Rahmatolahzadeh, R.; Ramezani, M. Solvent free synthesis of Cu-Cu<sub>2</sub>O nanocomposites via green thermal decomposition route. *Adv. Powder Technol.* 2017, *28*, 2078–2086. [CrossRef]
- Xu, L.; Srinivasakannan, C.; Peng, J.; Zhang, L.; Zhang, D. Synthesis of Cu-CuO nanocomposite in microreactor and its application to photocatalytic degradation. J. Alloys Compd. 2017, 695, 263–269. [CrossRef]
- Jiang, D.; Xue, J.; Wu, L.; Zhou, W.; Zhang, Y.; Li, X. Photocatalytic performance enhancement of CuO-Cu<sub>2</sub>O heterostructures for photodegradation of organic dyes—Effects of CuO morphology. *Appl. Catal. B* 2017, 211, 199–204. [CrossRef]