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1 **Unusual, hierarchically structured composite of**  
2 **sugarcane pulp bagasse biochar loaded with Cu/Ni bimetallic**  
3 **nanoparticles for dye removal**

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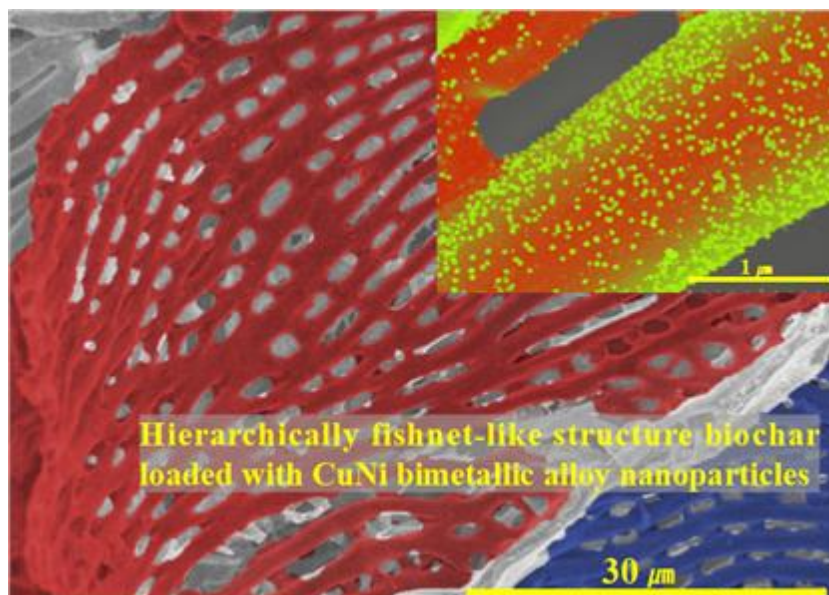
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20

21 **Graphical Abstract**



1 **Abstract**

2 Biochar-supported nanocatalysts emerged as unique materials for environmental  
3 remediation. Herein, sugarcane pulp bagasse (SCPB) was wet-impregnated with  
4  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  and  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , then pyrolyzed at 500 °C, under  $\text{N}_2$ , for 1 hour. We  
5 specifically focused on sugarcane pulp instead of SCB and biochar materials. The  
6 metal nitrate to biomass ratio was set at 0.5, 1, and 2 mmol/g, with Cu/Ni initial ratio  
7 = 1. The process provided hierarchically structured porous biochar, topped with  
8 evenly dispersed 40 nm-sized CuNi alloy nanoparticles (SCPBB@CuNi). The biochar  
9 exhibited an unusual fishing net-like structure induced by nickel, with slits having a  
10 length in the 3-12  $\mu\text{m}$  range. Such a fishing net-like porous structure was obtained  
11 without any harsh acidic or basic treatment of the biomass. It was induced, during  
12 pyrolysis, by the nanocatalysts or their precursors. The CuNi nanoparticles form true  
13 alloy as proved by XRD, and are prone to agglomeration at high initial metal nitrate  
14 concentration (2 mmol/g). Stepwise metal loading was probed by XPS versus the  
15 initial metal nitrate concentration. This is also reflected in the thermal gravimetric  
16 analyses. The SCPBB@CuNi /  $\text{H}_2\text{O}_2$  (catalyst dose: 0.25 g/L) system served for the  
17 catalyzed removal of Malachite Green (MG), Methylene Blue (MB), and Methyl  
18 Orange (MO) dyes (concentration= 0.01 mmol/L). Both single and mixed dye  
19 solutions were treated in this advanced oxidation process (AOP). The dyes were  
20 removed in less than 30 min for MG and 3 h for MB, respectively, but 8 h for MO,  
21 therefore showing selectivity for the degradation of MG, under optimized degradation  
22 conditions. The catalysts could be collected with a magnet and reused three times,  
23 without any significant loss of activity (~ 85 %). AOP conditions did not induce any  
24 nanocatalyst leaching.

25 To sum up, we provide a simple wet impregnation route that permitted to design  
26 highly active Fenton-like biochar@CuNi composite catalyst for the degradation of  
27 organic pollutants, under daylight conditions.

28

29 **Keywords:**

30 *Saccharum officinarum*; biochar; bimetallic nanoalloy; porous materials; Fenton-like  
31 reaction; water treatment.

32

33

34

## 1 **1. Introduction**

2       The world is witnessing unprecedented technological and industrial expansion,  
3 causing real environmental and climate issues that are terrifyingly impacting Human  
4 health and well-being (Liu, Jiang et al. 2015). Meanwhile, many efforts are constantly  
5 devoted to implementing eco-friendly, cost-effective, and sustainable policies in order  
6 to face problems threatening planet Earth, especially those related to water (Ali,  
7 Burakova et al. 2019, Ali, Kon'kova et al. 2021) and air contamination (Hamouma,  
8 Kaur et al. 2019, Huang, Su et al. 2019) organic molecules and gases. Indeed, political  
9 decisions worldwide aim to maintain the balance between ecosystem preservation,  
10 economy, and social benefits (Low and Yee 2021). Convention on Climate Change  
11 (COP) is one of the most important events where politicians and environmental  
12 experts meet to change rules for a safer environment.

13       Taking the sole example of agro-wastes from the agro-industry and the  
14 agricultural activities, their management, recycling, and valorization is a highly  
15 challenging field. Indeed, billions of tons are yearly produced and must be managed,  
16 *e.g.* the World production of raw sugarcane was estimated to be 1.9 billion tons which  
17 once processed generate around 513 million metric tons of lignocellulosic waste (Pan,  
18 Zabed et al. 2022).

19       Besides animal feeding and fertilization, several innovative solutions have  
20 been proposed and employed to convert agro-wastes into green energy with low  
21 carbon dioxide emissions, *e.g.* bioethanol, biofuel or hydrogen (Adewuyi 2020,  
22 Ramlingam, Subramanian et al. 2022, Saravanan, Kumar et al. 2022), and also into  
23 functional bio-sourced material, for example, biochar (Tripathi, Sahu et al. 2016,  
24 Gopinath, Divyapriya et al. 2021, Aoulad El Hadj Ali, Ahrouch et al. 2022).

25       Biochar is a green and carbon-rich material made from the pyrolysis of diverse  
26 biomass wastes, at relatively moderate (400-600 °C) to high temperatures (above 700  
27 °C), under oxygen-free (or low oxygen) conditions. It has emerged as a unique, low-  
28 cost material for agriculture, water treatment, and life sciences, to name but these

1 important domains. Biochar is coined “new black gold” (Nagula and Ramanjaneyulu  
2 2020), for its exceptional physicochemical properties that can be tuned, and enhanced  
3 through modification (Goswami, Kushwaha et al. 2022). Such a modification of  
4 biochar is beneficial for pollutant adsorption (Ali, Afshinb et al. 2020), or for  
5 anchoring nanocatalysts onto the porous material for the complete mineralization of  
6 organic pollutants (Lopes and Astruc 2021, Yameen, AlMohamadi et al. 2023).  
7 Biochar with immobilized nanocatalysts constitute an emerging class of remarkably  
8 efficient advanced materials in water treatment (Shi, Deng et al. 2022), among other  
9 composites (Dihingia and Tiwari 2022) based on metal-organic frameworks (MOFs)  
10 (Xiao, Cheng et al. 2023), zeolites (Wang, Sun et al. 2021), mesoporous silica  
11 (Snoussi, Bastide et al. 2018, Verma, Kuwahara et al. 2020), carbon nitride (Tang,  
12 Cheng et al. 2023), to name but a few. However, biochar platforms are made from  
13 valueless biomass, therefore complying with the concept of *waste-to-wealth*, or *trash-*  
14 *to-treasure*.

15 There is a plethora of biomasses that are thermochemically converted into  
16 biochar, for example, agrowastes and side-products of the food and beverage industry.  
17 Particularly, sugarcane is the main product in the sugar industry; it grows rapidly and  
18 has a high yield worldwide (Aruna, Bagotia et al. 2021). A large amount of sugarcane  
19 bagasse as a by-product is discarded after processing. It follows that the conversion of  
20 SCB into biochar is an appealing strategy to elaborate highly performant catalysts and  
21 adsorbents for water treatment (Lopes and Astruc 2021, Sutar, Patil et al. 2022) and  
22 energy production (Kant Bhatia, Palai et al. 2021).

23 Of relevance to this contribution, the literature shows that bimetallic catalysts  
24 combine high activity and high selectivity metals (Pang, Wang et al. 2012). The  
25 addition of a second metallic component may affect the morphology and the  
26 electronic configuration of the final catalyst. The electronic effect, called also the  
27 ligand effect, results in more binding and active sites, hence a higher catalytic activity  
28 (Liao, Lo et al. 2015, Quiton, Lu et al. 2021, Chen, Liu et al. 2022) .

1 The incipient wet impregnation is most probably the simplest route to incorporate  
2 bimetallic catalysts into/onto the support matrix. The dispersing network is either co-  
3 impregnated with the bimetallic solution or successively impregnated with  
4 monometallic solutions (Quiton, Lu et al. 2021). Wet impregnation has always been  
5 considered a facile, cost-effective, and very efficient method to elaborate composite  
6 catalysts (Deraz 2018, Goswami, Kushwaha et al. 2022).

7 In our previous work, we synthesized several bimetallic biochar@catalyst materials  
8 with different structures by direct pyrolysis method and found that bimetallic  
9 nanoparticle/biochar are more active than the corresponding pure biochar and  
10 monometallic nanocomposites (Khalil, Michely et al. 2021, Omiri, Snoussi et al.  
11 2022, Snoussi, Sifaoui et al. 2023). Transition metal nickel (Ni) is attractive due to its  
12 excellent magnetic properties and high activation ability of C-H and C-C bonds (Liao,  
13 Wang et al. 2018) but can suffer aggregation and consequently decreased catalytic  
14 efficiency (Gong, Ma et al. 2021). Copper is a less active transition metal but exhibits  
15 high selectivity (Hu, Yue et al. 2014). It is worth noting that the catalytic activity of  
16 CuNi is superior to those of the individual monometallic nanocatalysts, and bimetallic  
17 nanocatalysts dispersed on the support can avoid agglomeration and oxidation, hence  
18 the improved catalytic activity (Deka, Borah et al. 2019, Gong, Ma et al. 2021).  
19 Recently, we found that the copper-nickel/biochar served for the degradation of  
20 Methyl Orange and nickel imparted magnetic properties to the biochar (Khalil,  
21 Michely et al. 2021, Omiri, Snoussi et al. 2022). In another application, the group of  
22 Hassan Sheibani successfully synthesized CuNi bimetallic nanoparticles and mixed  
23 them with preformed pomegranate shell biochar to obtain a composite with excellent  
24 catalytic activity for the A3-coupling reactions (Zarei, Saidi et al. 2022). One key  
25 point is that copper precursors are low-cost, which makes CuNi bimetallic  
26 nanocatalyst of interest: cost-effective, catalytically highly active, magnetic, and thus  
27 easy to recover.

28 Despite the rich literature on CuNi bimetallic nanocatalysts, loading CuNi  
29 bimetallic nanocatalysts in- and on the surface of biochar remains sparse (Zhu, Wang

1 et al. 2019). Our ongoing research work consisted of the direct slow pyrolysis of  
2 biomass impregnated by copper and nickel nitrate mixtures under various conditions  
3 (Khalil, Michely et al. 2021, Omiri, Snoussi et al. 2022), instead of the in situ  
4 deposition of CuNi alloy onto pre-fabricated biochar (Zhu, Wang et al. 2019). Post-  
5 modification of biochar by nanocatalysts requires a chemical reductive process to  
6 convert the metal salts into metallic nanocatalysts, whereas mixing of biochar and  
7 CuNi bimetallic catalysts resulted in large immobilized particles (Zarei, Saidi et al.  
8 2022), contrary to the wet impregnation approach before pyrolysis.

9       Returning to sugarcane, most of the research works on its thermochemical  
10 conversion to obtain biochar concerned the total sugarcane bagasse derived from  
11 sugarcane juice making. Instead, we were interested in removing the pulp from the  
12 total sugarcane bagasse to check if there is any interest in terms of physicochemical  
13 properties. Surprisingly, our first results indicated that sugarcane pulp bagasse loaded  
14 with copper and nickel nitrates led to unusual porous structure of the biochar with  
15 even distribution of narrow dispersion bimetallic CuNi nanoparticles (Tang, Snoussi  
16 et al. 2022). This has motivated us to conduct a comprehensive study on the  
17 preparation of new biochar@CuNi materials.

18       In this work, we report a simple and green method to prepare porous  
19 SCPBB@CuNi nanocomposites by slow pyrolysis, under nitrogen, of sugarcane pulp  
20 bagasse mixed with copper and nickel nitrates, through wet impregnation technique.  
21 The materials were characterized by X-ray diffraction (XRD), X-Ray photoelectron  
22 spectroscopy (XPS), Raman spectroscopy, scanning electron microscopy (SEM), and  
23 thermogravimetric analysis (TGA). The initial metal ion/sugarcane pulp has been  
24 monitored and the ratio set to 0.5, 1, and 2 mmol/g. This is an important parameter for  
25 controlling the extent of copper/nickel, the size, and the distribution of the  
26 nanoparticles on the biochar support. Moreover, biochar loaded with single metallic  
27 systems (biochar@Cu and biochar@Ni) served as control composites in order to  
28 understand the effect of each metal on the biochar structure. The biochar samples  
29 loaded with CuNi bimetallic nanoparticles were tested as catalysts of the degradation

1 of model dyes, namely Malachite Green (MG), Methyl Orange (MO), and Methylene  
2 Blue (MB), in the presence of H<sub>2</sub>O<sub>2</sub> (advanced oxidation process, AOP). We have  
3 also tested the performances of the catalytic composites in the degradation of binary  
4 dye mixtures in order to investigate any competitive effects.

5 To the very best of our knowledge, this is the first report on biochar-supported  
6 CuNi bimetallic catalyst obtained by wet impregnation of sugarcane pulp bagasse and  
7 its slow pyrolysis for environmental remediation, *i.e.* dye degradation in water  
8 treatment applications.

9

## 10 **2. Materials and methods**

### 11 ***2.1. Biomass and Chemicals***

12 The used sugarcane bagasse was cultivated and provided from Egypt  
13 (*Saccharum officinarum*). Sugarcane pulp bagasse (SCPB) agricultural was finely  
14 ground before use. Metal nitrate salts Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O and Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O were  
15 purchased from Aldrich and used as received. We used distilled water to dissolve  
16 metal nitrates before pyrolysis.

17

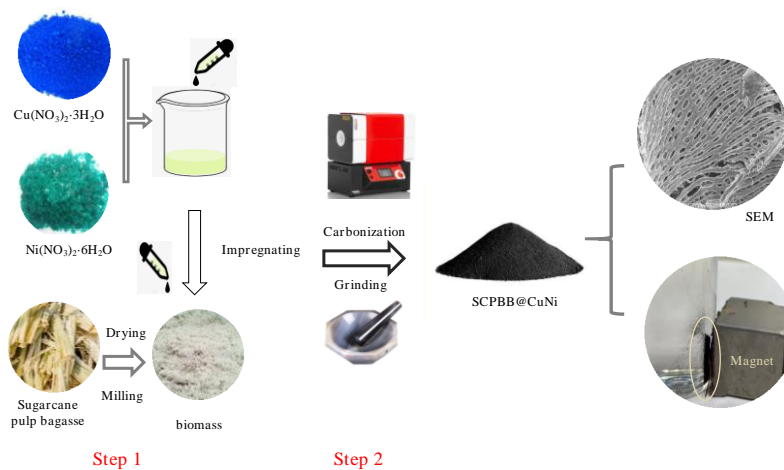
### 18 ***2.2. Synthesis of biochar loaded with Cu/Ni bimetallic nanoparticles***

19 SCPB particles were impregnated with an aqueous solution of copper and nickel  
20 nitrates in the molar mass ratio of 0.5:0.5, 1:1, and 2:2, respectively (see Figure 1).  
21 The powder was mixed on a glass lens and dried at 60 degrees, overnight, until the  
22 powder weight was constant. Subsequently, the mixture containing metal salt-  
23 impregnated particles was transferred into a tubular furnace and pyrolyzed at 500 °C,  
24 under N<sub>2</sub> atmosphere for 1 h, with a heating rate of 20 °C min<sup>-1</sup>. Copper and nickel  
25 nitrates were mixed in the deionized (DI) water. The final bimetallic nanoparticle-  
26 coated biochar samples are labeled SCPBB@CuNi-0.5, SCPBB@CuNi-1, and  
27 SCPBB@CuNi-2, respectively. The same agrowaste SCPB, without any metallic

1 nitrates, was pyrolyzed in the same conditions. We have also prepared SCPBB@Cu-  
 2 0.5 and SCPBB@Ni-0.5 as reference materials.

3

4



5

6 **Figure 1.** Schematic illustration for the copper nickel nanoparticle-loaded biochar  
 7 SCPBB@CuNi by slow pyrolysis.

8

9

10 **Table 1.** Conditions for the preparation of pure and metallic nanoparticle-coated  
 11 biochar by slow pyrolysis.

Materials	P-SCB Mass(g)	Cu(NO <sub>3</sub> ) <sub>2</sub> ·3H <sub>2</sub> O Mass (g)/mmol	Ni(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O Mass (g)/mmol	Distilled water (mL)	Before Pyrolyzed SCB+Metal Ion Mixture(g)	Biochar Mass (g) /Yield (%)	Experimental condition
SCPBB@CuNi-0.5	0.996	120.8/0.5	145.4/0.5	20	1.226	0.352/28.71	Temperature : 500 °C Heating rate: 20 °C · min Residence time: 1 h Gas: N <sub>2</sub> atmosphere N <sub>2</sub> flow rate: 2L · min <sup>-1</sup>
SCPBB@CuNi-1	0.998	241.6/1	290.8/1	20	1.3195	0.441/33.41	
SCPBB@CuNi-2	0.997	483.2/2	581.6/2	20	1.622	0.429/26.45	
SCPBB@Cu-0.5	0.999	120.8/0.5	/	10	1.1089	0.282/25.42	
SCPBB@Ni-0.5	0.997	/	145.4/0.5	10	1.1324	0.297/26.24	
SCPBB	2.143	/	/	/	/	0.504/23.51	

12

### 1            **2.3. Materials characterization**

2            The XRD patterns were recorded in the  $20^\circ \leq 2\theta \leq 80^\circ$  range, using a D8  
3            Advance Bruker diffractometer (Cu  $K\alpha$  radiation) with X-ray generator voltage of 40  
4            kV and the current of 40 mA. The step size and scan rate were set to 0.33  $^\circ\text{C}$  and 1.11  
5             $^\circ\text{C}\cdot\text{s}^{-1}$ , respectively. The data were processed using Highscore Plus software.

6            XPS spectra were recorded using a K Alpha+ apparatus (Thermo, East  
7            Grinstead, UK). The machine is fitted with a mono Al  $K\alpha$  (source energy = 1486.6  
8            eV), and a flood gun for charge compensation build-up. The pass energy was set to  
9            200 eV to record the survey spectra and 80 eV for the acquisition of the narrow  
10            regions. Avantage software version 5.9902 was used for data acquisition and  
11            processing.

12            Raman spectra analysis was conducted by a Horiba HR 800 instrument to  
13            determine the carbon signature at a wavelength of the He–Ne laser beam set to 633  
14            nm. The spectra were acquired in the 800–2700  $\text{cm}^{-1}$  region.

15            We have employed a Hitachi SU 8030 Scanning Electron Microscope (SEM) for  
16            imaging the surface morphology, and ZEISS Gemini SEM 360 for the observation of  
17            the sample morphology and elemental mapping, respectively. No charge  
18            compensation was used, and the source-sample distance was set at 4.2 mm. ImageJ  
19            software was used for SEM image processing.

20            Thermal gravimetric analyses (TGA) were conducted using a Setaram machine  
21            Setsys Evolution model to measure the mass loss kinetics of biochar (with or without  
22            metallic nanoparticles). The experiments were performed under air atmosphere, over  
23            the temperature range RT–800  $^\circ\text{C}$ , and setting the heating rate to 10  $^\circ\text{C}/\text{min}$ .

24            The chemical composition of the prepared materials were analyzed using the  
25            Panalytical MINIPAL4 X-ray fluorescence (XRF) spectrometers analysis with a  
26            rhodium X-ray tube operating at 30 kV and 87  $\mu\text{A}$  current emission.

27

#### 2.4. Catalytic activity investigation

Catalytic tests were performed in a similar manner previously reported by some of us (Omiri, Snoussi et al. 2022). Typically, in each experiment, 5 mg biochar catalyst was added to the dye solution (20 mL, concentration of 0.01 mmol/L ). H<sub>2</sub>O<sub>2</sub> was added to initiate the Fenton-like degradation reaction of the dye. A similar method has been used to study the degradation of dye mixtures. The suspension was filtered to determine the remaining dye concentration, using UV-Vis spectrophotometry at specific time intervals.

The degradation ratio was calculated using the following formulae:

$$\% \text{ degradation efficiency} = ((C_0 - C_t)/C_0) \times 100, \quad (1)$$

where  $C_t$  and  $C_0$  are the concentrations of dye solution at time =  $t$  and  $t = 0$ , respectively.

Based on the experimental data, the kinetic analysis of dye degradation are fitted according to the following zero-order equation (equation 2) and pseudo-first-order (equation 3) reaction kinetic model (equation. 2) equation:

$$C_t/C_0 = -K_0t \quad (2)$$

$$-\ln(C_t/C_0) = -\ln(A_t/A_0) = K_1t, \quad (3)$$

where  $A_t$  and  $A_0$  are the absorbance of the dye at time  $t$  and time  $t = 0$  min, respectively.  $K_0$  and  $K_1$  are the zero-order constant and first-order constant, respectively;  $t$  is the treatment time.

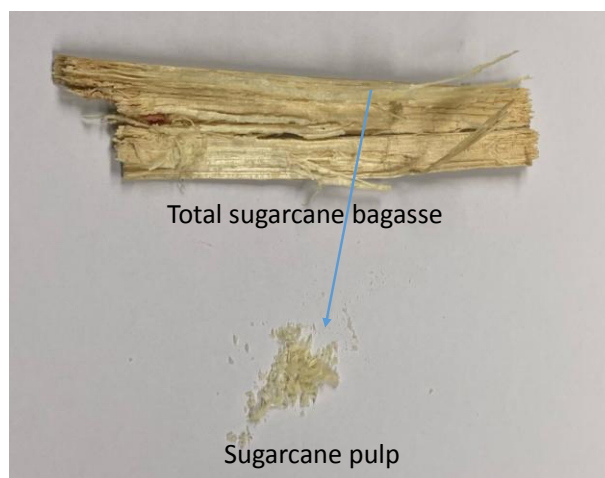
#### 2.5. Recycling experiment

After the catalytic reaction was completed, the SCPBB@CuNi nanomaterials were separated from the solution by an external magnetic field without any washing, and then reused.

### 1 3. Results and Discussion

#### 2 3.1. General aspects

3 In previously published reports on biochar@CuNi, the focus has been on the  
4 method of preparation and catalytic activity of the designed biochar composites  
5 obtained from olive stones in environmental remediation (Khalil, Michely et al. 2021,  
6 Omiri, Snoussi et al. 2022) and pistachio shell or pomegranate peels for catalyzing  
7 organic chemical reactions (Zarei, Mohammadzadeh et al. 2022, Zarei, Saidi et al.  
8 2022). Herein, we investigate the effect of CuNi bimetallic nanoparticle loading on  
9 the dispersion and catalytic activity of the final biochar@CuNi. Moreover, we have  
10 employed sugarcane pulp bagasse as a biomass for making biochar, which is rather  
11 not explored in the literature compared to the total sugarcane bagasse. The sugarcane  
12 bagasse was dried after juice making and scratched in order to obtain the dried pulp  
13 bagasse. The latter was further ground, impregnated with metal ions, and pyrolyzed.



14

15 **Figure 2.** Digital photographs of total sugarcane bagasse, and the pulp obtained  
16 after scratching.

17

#### 18 3.2. SEM /EDX study

19 The SEM micrographs of bare and NP-coated biochar are shown in Figure 3. The  
20 biochar SCPBB@CuNi-0.5 (Figure 3 a-d) is observed at various magnifications; it  
21 forms the ordered arrangement with uniform pores, similar to fishing net. The pores  
22 are elongated, almost like slits with length in the 3 to 12  $\mu\text{m}$  range and  $\sim 1 \mu\text{m}$  slit

1 width (Figure 3a). The pores are of smaller size, which is ascribed to dehydration of  
2 the cell structure. Nanoparticles are visible in Figure 3b but are very well  
3 distinguished in Figure 3c, which is at a higher magnification. The NPs are densely  
4 and homogenously dispersed over the surface, without any evidence of aggregation.  
5 This conforms again with our previous findings on CuNi bimetallic NPs loaded on  
6 olive stone powder biochar (Khalil, Michely et al. 2021). The protocol is therefore  
7 very well reproducible and yields similar results on a different biomass (herein  
8 sugarcane pulp bagasse). From Figure 3d, one could estimate the average CuNi  
9 nanoparticle size to  $40\pm 3$  nm, meaning that the bimetallic nanoparticles are in the  
10 nanoscale regime ( $< 100$  nm). Oppositely, the SCPB-derived biochar exhibits an  
11 almost featureless surface (Figures 3 e-g), with only fewer micrometer-sized pores.  
12 The latter seem to be at the origin of the slits displayed by the composite  
13 nanomaterials. It further follows that the activation of the biomass with copper and  
14 nickel nitrates favours the formation of slits and the highly porous structure, without  
15 using any harsh acidic or basic media. At this stage, it is important to note that neither  
16 olive pit (Khalil, Michely et al. 2021), nor pomegranate (Zarei, Saidi et al. 2022)  
17 biochar loaded with CuNi exhibited such a fishing net-like structure.

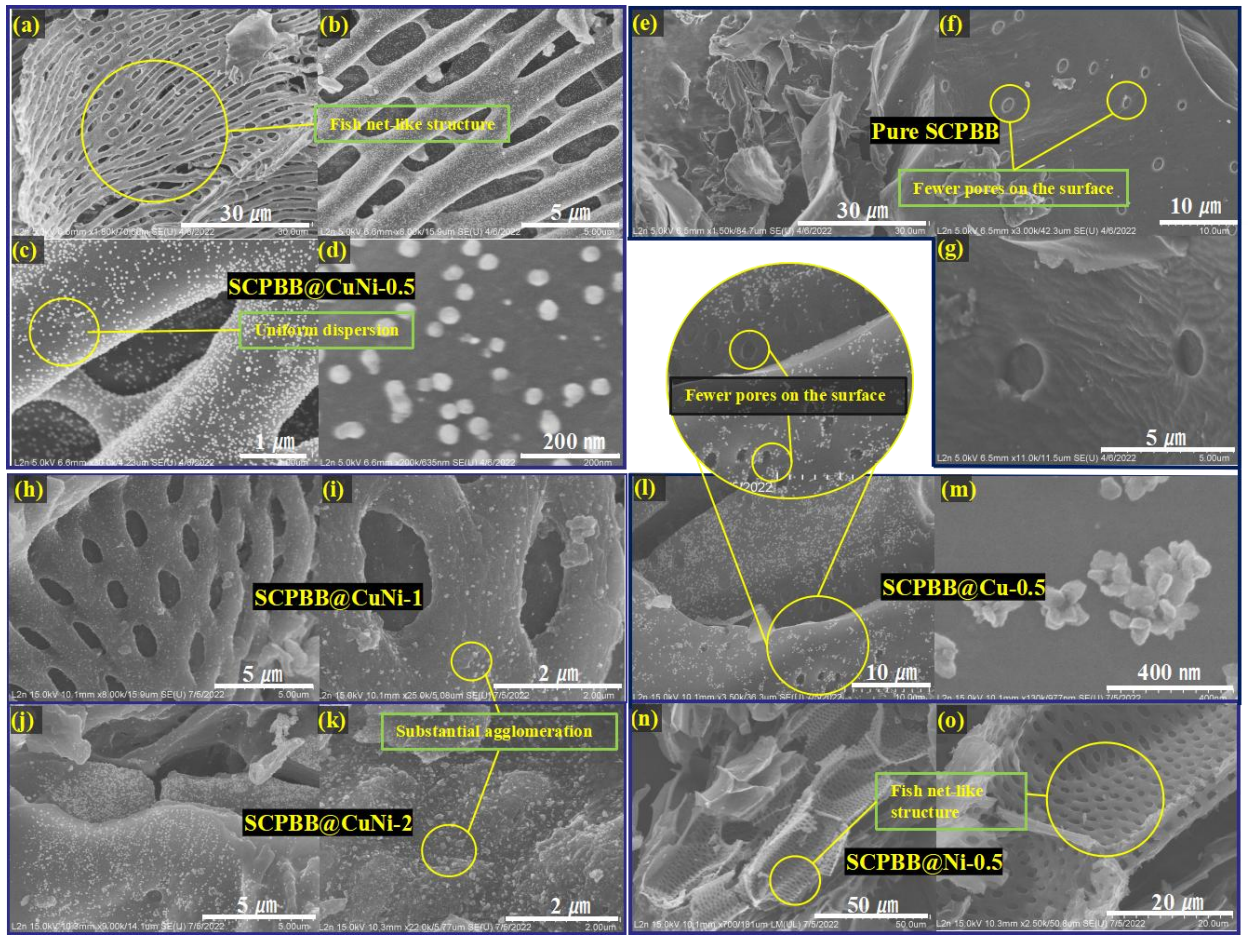
18 Figures 3 (h-k) shows the SEM images of SCPBB@CuNi biochar prepared with  
19 various metal ion loading. The porous structure has been changed, showing even  
20 smaller pores at higher nanoparticle loading. For SCPBB@CuNi-2, it was difficult to  
21 find any porous structure as the one noted for SCPBB@CuNi-0.5. Moreover, at high  
22 metal ion loading during the impregnation stage, the pyrolysis process led to  
23 substantial agglomeration of CuNi NPs all over the SCPBB surface. A higher content  
24 of nanoparticles aggregated on the biochar substrate, leading to possible lower surface  
25 area.

26 SCPBB@Ni-0.5 and SCPBB@Cu-0.5 surface morphologies could be compared  
27 in Figures 3 l-o. The SEM images of SCPBB@Cu-0.5 showed just a few pores on the  
28 featureless surface, and copper nanoparticles appear flower-shaped. In contrast,  
29 SCPBB@Ni-0.5 nanocomposite morphology is almost identical to that obtained with

1 SCPBB@CuNi. One could then argue that the formation of the highly porous  
2 structure is attributed to the addition of nickel, which is known to catalyze the  
3 transformation of  $sp^3$  to  $sp^2$  carbon as well as it catalyzes the formation of the porous  
4 structure by consuming carbon (Li, Zhao et al. 2021). These structural characteristics  
5 could hypothesize the catalytic enhancement due to the fishing net-like structure of  
6 SCPBB@CuNi, which exhibits abundant adsorption sites for removing organic  
7 pollutants.

8         Additionally, EDX mapping confirmed the presence of all the desired elements  
9 of the SCPBB@CuNi sample at the surface in EDX spectra. Figure 4 shows that  
10 SCPBB@CuNi mainly contains C, O, Cu, and Ni, which accounts for the effective  
11 loading of copper and nickel on the surface of biochar SCPBB through the simple wet  
12 impregnation method. Moreover, the elements simultaneously present in the biochar  
13 SCPBB correspond to the C, O, N, Ca, Mg, and Si peaks. The results of EDX analysis  
14 were confirmed by analyzing different regions (Table 2); the ratio of Cu/Ni is almost  
15 1:1 with an atomic ratio of 3.66 and 3.56 % copper and nickel, respectively.

1



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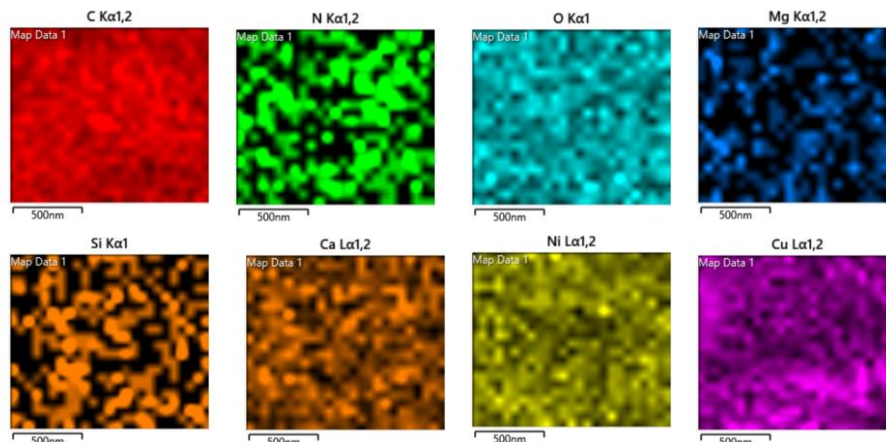
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**Figure 3.** SEM images of SCPBB@CuNi (a-d), SCPBB (e-g) SCPBB@CuNi-1(h,i), SCPBB@CuNi-2 (j,k), SCPBB@Cu (l,m) and SCPBB@Ni (n,o) at various magnifications.

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**Figure 4.** Chemical mapping of SCPBB@CuNi-0.5 at the spots probed for the acquisition of EDX spectra.

1 **Table 2.** EDX-determined surface elemental analysis of SCPBB@CuNi-0.5 catalyst.

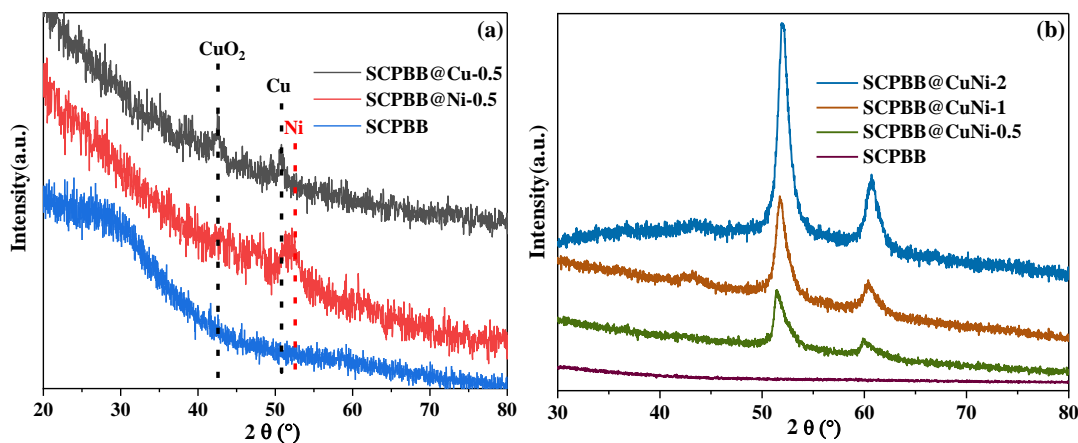
Catalyst	Elemental Atomic %									
SCPBB@CuNi-0.5	C	N	O	Mg	Si	P	S	Ca	Ni	Cu
	81.39±4.31	0.30±0.4	10.14±2.19	0.14±0.4	0.36±0.29	0.08±0.02	0.11±0.01	0.23±0.05	3.56±0.17	3.66±2.46
	Weight %									
	Cu		Ni		O	Mg	Si	P	S	K
31.25±0.25		31.91±0.26		29.71±0.19	0.73±0.07	2.50±0.09	0.40±0.10	0.46±0.13	3.04±0.34	

2

3

### 4 **3.3. XRD**

5 The XRD analyses were conducted on bare SCPBB, and copper and nickel  
6 nitrate-impregnated biochar. As shown in Figure 4a, it is worth noting that there is no  
7 corresponding diffraction peak for SCPBB after biomass calcination. The diffraction  
8 peak exhibited by SCPBB@Cu at 50.7 ° corresponds to the Cu(111) reflection planes  
9 of Cu<sup>0</sup> species (ICSD 98-0050-3757), whereas the diffraction peak at 51.9 ° exhibited  
10 by SCPBB@Ni is attributed to the Ni(111) reflective surface of the Ni<sup>0</sup> species (ICSD  
11 98-007-6667). The diffractogram corresponds to SCBPP@CuNi and reference  
12 biochar in Figure 4b. The XRD pattern does not show any single metal copper or  
13 nickel, and two new diffraction peaks are displayed at 51.5 ° and 59.8 ° are assigned  
14 to structures of copper and nickel metals (111), (002) crystallographic planes,  
15 respectively (ICSD 98-062-8543). In addition to the Cu peak, Cu<sub>2</sub>O also appears at 2θ  
16 = 42.3°. This indicates that SCBPP@CuNi showed the presence of a crystalline  
17 structure of copper-nickel alloy on biochar.



**Figure 5.** XRD patterns of SCPBB, SCPBB@Cu and SCPBB@Ni (a); and SCPBB@CuNi composites at various CuNi loadings (b).

### 3.4. XPS surface chemical analysis

XPS was employed to investigate the surface chemical composition of biochar and its nanocatalyst-decorated counterparts. Figure 6 displays the survey spectra of bare SCPBB (Figure 6a) and the SCPBB@CuNi samples (Figures 6b-d). Cu2p and Ni2p are very clearly visible and account for the fine dispersion of the nanoparticles as imaged by SEM. Interestingly, one could note the gradual increase in the relative Cu2p and Ni2p peak intensity versus the initial impregnation rate of the biomass with the metal nitrates. Concerning the monometallic nanocatalyst systems, the survey spectra are displayed in Figure 6e and Figure 6f for SCPBB@Ni and SCPBB@Cu, respectively. In either the mono- or the bimetallic system, XPS testifies for the presence of these elements in the metallic states as noted in the inset of Figure 6a-d (Ni2p<sub>3/2</sub> at ~852.1 eV; sharp Cu2p<sub>3/2</sub> peak centred at 932.1 eV). The Cu2p<sub>3/2</sub> spectrum has two overlapping features at 932.7 and 934.4 eV, assigned to Cu<sup>0</sup> and CuO, respectively (Biesinger 2017). In addition, small shake-up satellites are located in the 938-948 eV region, indicating the presence of Cu<sup>2+</sup> species in the SCPBB@CuNi (Jha, Jeong et al. 2015, Biesinger 2017). The Ni2p<sub>3/2</sub> narrow region exhibits a sharp peak at 852.7 eV, and a broad region at 854-861 eV attributed to Ni and nickel oxides, respectively. The binding energy values reported for metallic copper and nickel in the alloy fit in well with those reported by the NIST XPS database

1 (<https://srdata.nist.gov/xps/>) for pure copper and nickel, taken separately. Probably,  
2 this is due to the equal electronegativity of copper and nickel (~1.9). Elsewhere, no  
3 major shift was found for CuNi compared to pure copper or nickel (Wolfbeisser,  
4 Kovács et al. 2017).

5 Table 3 reports the apparent surface composition determined by XPS for the  
6 biochar and the corresponding mono- and bimetallic systems. A few trends could be  
7 noted from the data reported in Table 3: (i) there is a monotonous increase in the  
8 (Cu+Ni)/C atomic ratio versus the total initial impregnation rate, defined as the total  
9 number of metal salt millimoles per gram of sugarcane pulp bagasse (Figure 6g).  
10 Interestingly, the monometallic system fits in well with the plotted data for the  
11 bimetallic system, which rules out any synergetic effect of copper and nickel on the  
12 (Cu+Ni)/C atomic ratio. This chemical descriptor accounts for the gradual changes in  
13 the surface morphology as imaged by SEM. (ii) Moreover the N/C atomic ratio  
14 increases monotonously with the initial impregnation rate.

15 N/C atomic ratio could be considered a chemical descriptor of the nitrogen-  
16 doping of the carbonaceous structure. It could be due to the nickel catalytic effect  
17 resulting in the loss of carbon, which led to the biochar porous structure (see above,  
18 section 3.2). The increase in N/C could also be due to the nitrates as a nitrogen source  
19 for doping the carbonaceous biochar structure. Elsewhere, ammonium nitrate  
20 impregnation was reported to induce nitrogen doping of the biochar (Kasera, Kolar et  
21 al. 2022).

22

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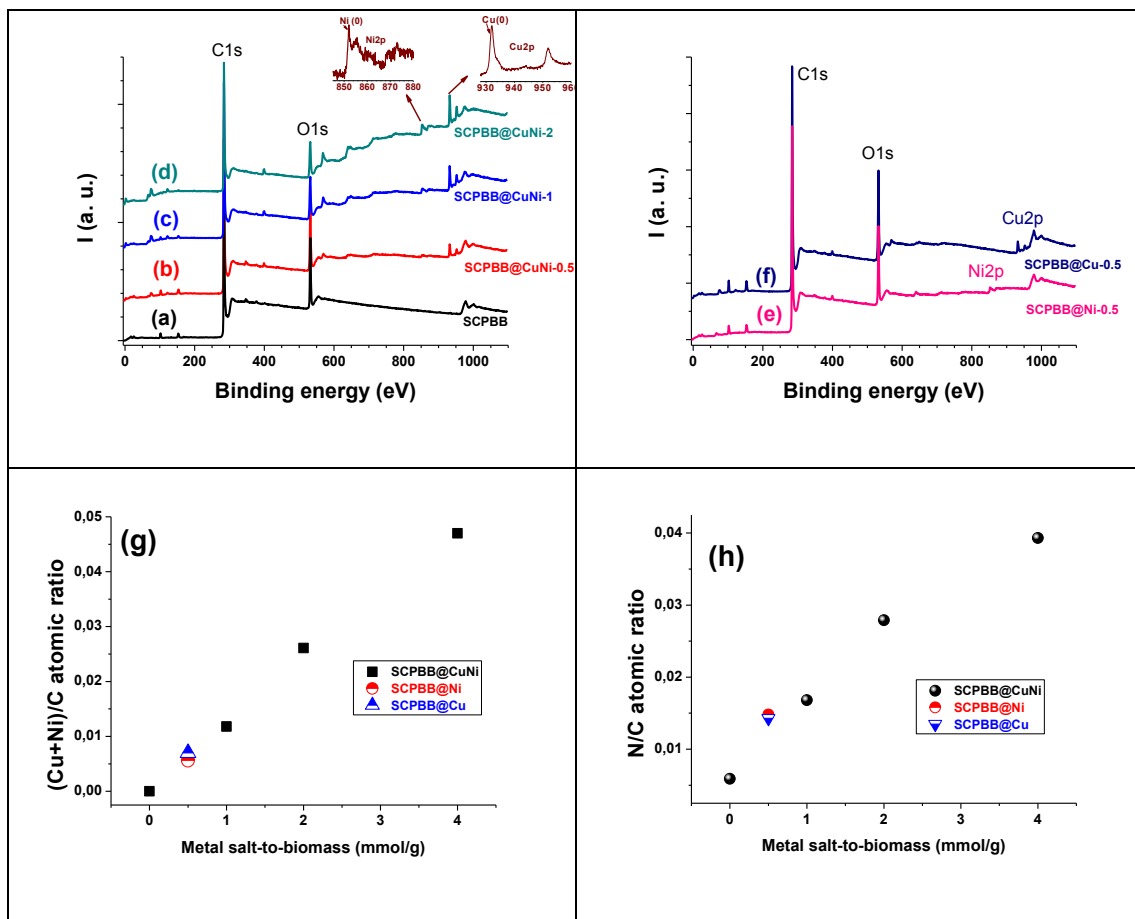
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**Table 3. XPS-determined surface chemical composition of biochar samples**

Materials	C	O	N	Ni	Cu
SCPBB	84.6	14.9	0.5	-	-
SCPBB@CuNi-0.5	81.6	15.8	1.37	0.31	0.65
SCPBB@CuNi-1	82.3	13.3	2.30	0.71	1.44
SCPBB@CuNi-2	79.7	13.4	3.13	1.61	2.11
SCPBB@Ni-0.5	82.6	15.6	1.22	0.46	-
SCPBB@Cu-0.5	81.8	16.3	1.17	-	0.57

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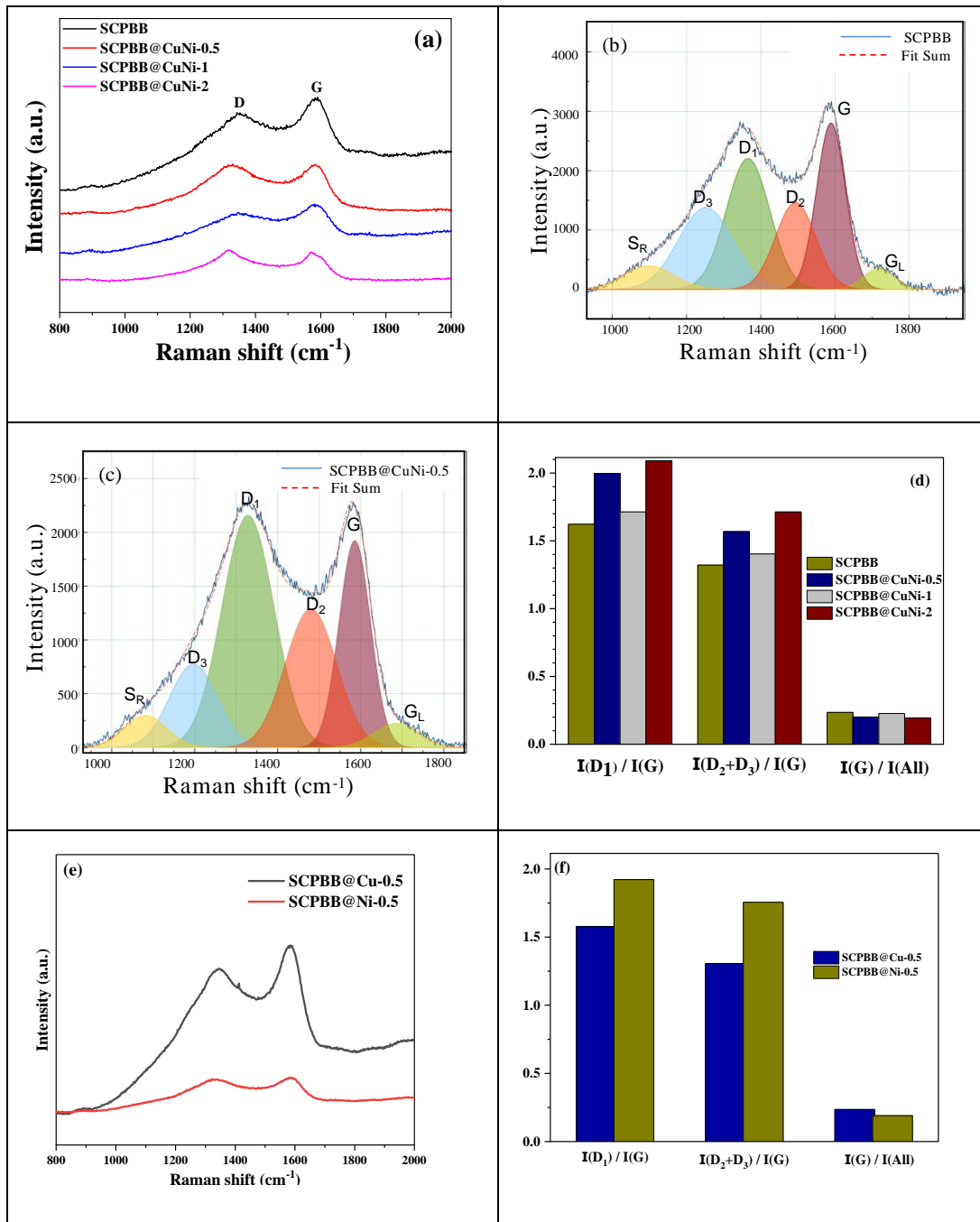
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**Figure 6.** XPS analysis of biochar samples: survey spectra of SCPBB (a), SCPBB@CuNi-0.5 (b), SCPBB@CuNi-1 (c), SCPBB@CuNi-2 (d), SCPBB@Ni-0.5 (e), and SCPBB@Cu-0.5 (f). High resolution Cu2p and Ni2p spectra are shown in inset of Figure 6a-d. Atomic ratios are plotted versus the initial metal impregnation rate in mmol nitrate per gram of biomass: (Cu+Ni)/C (g) and N/C (h).

1

### 3.5. Raman characterization of biochar D and G bands



2 **Figure 7.** Raman spectra of bare SCPBB biochar and SCPBB@CuNi  
 3 composites(a), curve-fitted Raman spectra of bare SCPBB biochar(b) and  
 4 SCPBB@CuNi composites(c), the band area ratio of  $I(D_1)/I(G)$ ,  $I(D_2 + D_3)/I(G)$  and  
 5  $I(G)/I(All)$  obtained from the peak splitting(d), Raman spectra(e) and the band area  
 6 ratio (f) of SCPBB@Cu and SCPBB@Ni.

7

1 To have further insights into the structural transformations of bare SCPBB and to  
2 infer the presence of graphitic characteristics (da Silva Veiga, Schultz et al. 2020,  
3 Dong, Yang et al. 2021), biochar was characterized by Raman spectroscopy with a  
4 633 nm laser to assess the degree of carbonation of carbonaceous materials (da Silva  
5 Veiga, Cerqueira et al. 2021). The spectral curve fitting of Raman spectra from 950 to  
6 1950  $\text{cm}^{-1}$  is shown in Figure 7. Six main Gaussian peaks are centred at 1081, 1197,  
7 1328, 1480, 1585, and 1685  $\text{cm}^{-1}$ , and assigned to  $S_R$ ,  $D_3$ ,  $D_1$ ,  $D_2$ ,  $G$ , and  $G_L$  bands,  
8 respectively (Li 2007, Cao, Yuan et al. 2021). The peak of  $S_R$  at 1081  $\text{cm}^{-1}$  is  
9 attributed to the C–H on aromatic rings, and the D band centered at 1328  $\text{cm}^{-1}$  referred  
10 to disorder and defective carbonaceous material, and aromatics with not less than 6  
11 benzene rings. The G band mainly represents aromatic ring quadrant breathing with  
12 graphite  $E_{2g_2}$  structures. The  $D_2$  centred at 1480  $\text{cm}^{-1}$  is mainly attributed to the semi-  
13 circle breathing of aromatic rings and amorphous carbon structures (Cao, Yuan et al.  
14 2021). The  $S_R$  and  $D_3$  bands can be ascribed to the C–H on aromatic rings and the  
15 aryl–alkyl ether. The broad  $G_L$  band originated from the carbonyl group of biochar  
16 catalysts.

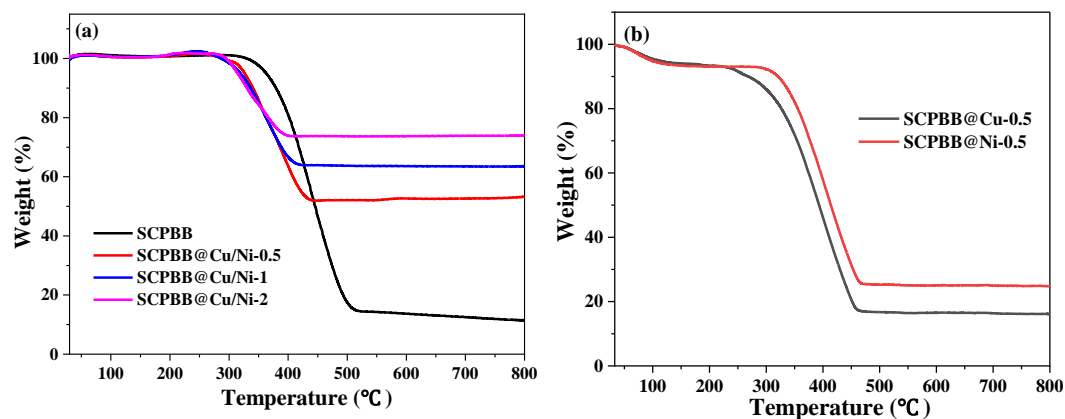
17 There is a significant change of D-G doublet with the loading of copper and  
18 nickel; D/G becoming higher than 1 (NB: peak area ratio, and not peak height ratio is  
19 considered), thus indicating that loading nanoparticles onto the biochar may impede  
20 the formation of the graphitic structure of the biochar during pyrolysis (Cao, Yuan et  
21 al. 2021, Sun, Feng et al. 2022). The evolution of catalysts crystalline structure was  
22 investigated using band area ratios  $I(D_1)/I(G)$ ,  $I(D_2 + D_3)/I(G)$ , and  $I(G)/I(\text{All})$ , as  
23 displayed in Figure 7d. The  $I(D_1)/I(G)$  ratio and  $I(D_2 + D_3)/I(G)$  ratio of  
24 SCPBB@CuNi increased consistently compared to pure SCPBB, while the  $I(G)/I(\text{All})$   
25 ratio showed a contrasting trend. The results suggested that the concentration of  
26 carbon structures (not less than 6 benzene rings) containing defects and heteroatoms  
27 increases as a result of the dehydrogenation of hydroarenes (Cao, Yuan et al. 2021).  
28 As far as the monometallic systems are concerned,  $I(D_1)/I(G)$ ,  $I(D_2 + D_3)/I(G)$ , and  
29  $I(G)/I(\text{All})$  values for SCPBB@Ni-0.5 (Figure 7e,f) match those of SCPBB@CuNi-

1 0.5, which indicates that nickel only has a profound effect on the carbon structure of  
2 the biochar.

3

### 4 3.6. Thermogravimetric analysis of biochar samples

5 The thermogravimetric (TG) curves for the bare biochar and SCPBB@CuNi are  
6 shown in Figure 8a. Thermal analysis was conducted in air to monitor the thermal  
7 stability and determine the mass loading. These curves show the residual weight % of  
8 CuNi-decorated biochar is higher than that of SCPBB at a high temperature; the  
9 weight loss of SCPBB is about 90% at 800 °C. Adding copper and nickel to biochar  
10 resulted in a significantly higher residual weight %, which accounts for the initial  
11 metal ion loading at the wetness impregnation step before pyrolysis. Copper and  
12 nickel from the bimetallic NPs convert to metallic oxides, hence SCPBB@CuNi  
13 yields slightly higher weight % due to oxygen in CuO and NiO. Similarly, the residual  
14 weight % of SCPBB@Cu-0.5 and SCPBB@Ni-0.5 are higher than those of pure  
15 biochar but lower than that of SCPBB@CuNi-0.5. There is clear control over the  
16 preparation procedure adopted in this work for the fabrication of biochar loaded with  
17 bimetallic nanocatalysts.



18

19 **Figure 8.** TG curves of SCPBB and SCPBB@CuNi samples (a), SCPBB@Cu-  
20 0.5 and SCPBB@Ni-0.5 (b). Analysis in air; heating rate = 10 °C min<sup>-1</sup>.

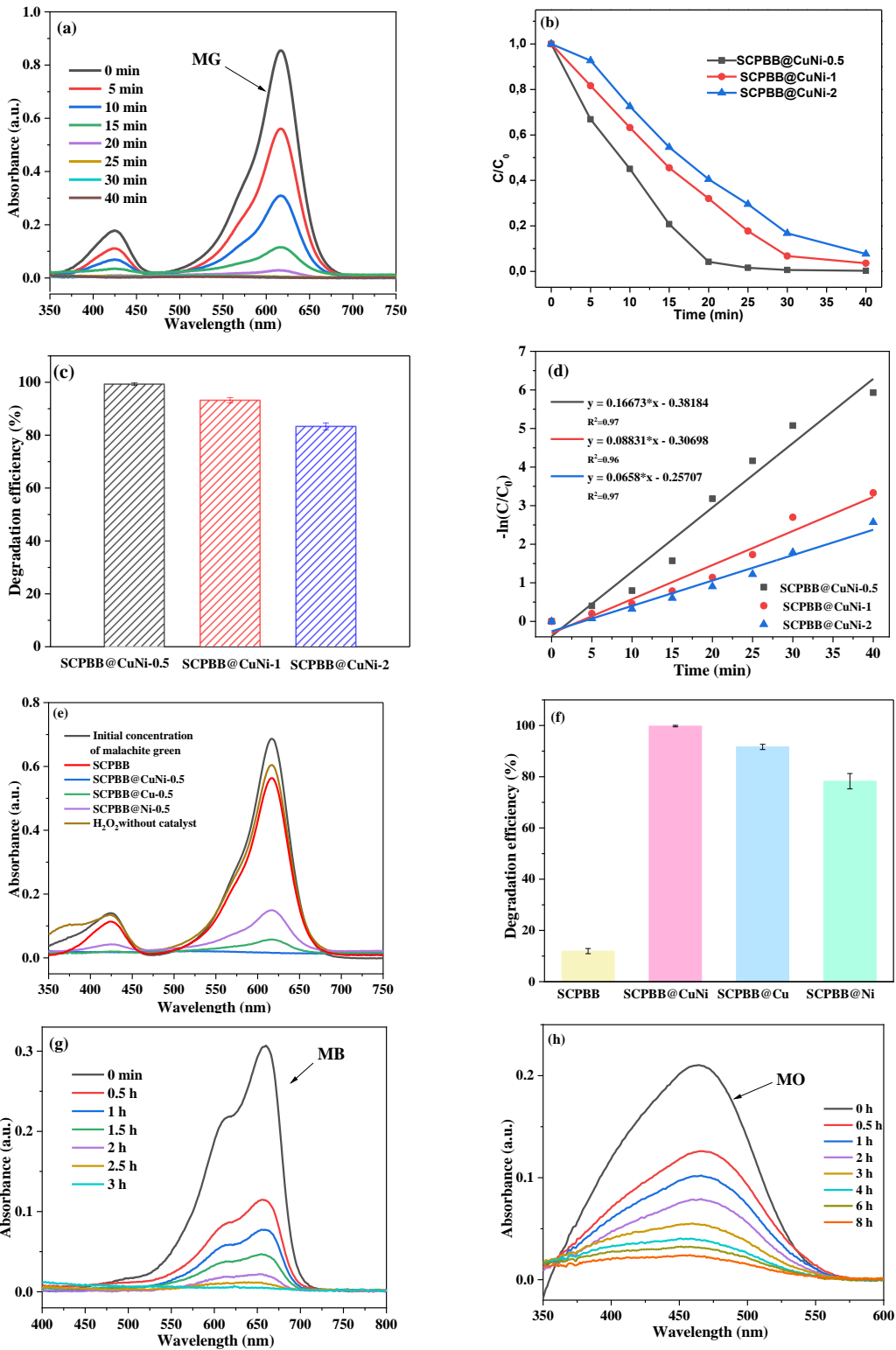
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1

### 3.7. Catalytic oxidation of dye solution using biochar@CuNi

2

#### 3.7.1. Removal of single dyes from aqueous solutions



1 Figure 9. UV-vis spectra of dye solutions during the catalysis degradation reactions  
2 of Malachite Green (a), Methylene Blue (g), and Methyl Orange (h).  $C/C_0$ -vs-time  
3 plots for MG degraded using biochar@CuNi catalysts (b) and the corresponding  
4 removal % after 30 min (c). Pseudo first order kinetic model for MG catalytic  
5 reaction with different metal mass loading samples of SCPBB@CuNi (d). UV-vis  
6 spectra of Malachite Green dye solutions in 30 min (e), the corresponding removal %  
7 after 30 min for Malachite Green dye solutions (f).

8

9 Figures 9 (a)–(d) show that the degradation of Malachite Green (MG) dye varied with  
10 Cu and Ni loadings. The order of MG dye solution degradation is: SCPBB@CuNi-0.5  
11 > SCPBB@CuNi-1 > SCPBB@CuNi-2, and the degradation efficiency of MG over  
12 SCPBB@CuNi 0.5, 1, and 2 nanocomposites in 20 min, was 99.3, 93.2 and 83.3%,  
13 respectively. To better understand the kinetic behaviour of different catalysts for MG  
14 degradation, the pseudo-first order kinetic model of MG dye removal was applied  
15 (Figure 9c). As shown in the linear relationship between time and  $-\ln(C/C_0)$ ; all the  
16 prepared samples exhibit good linear correlations, and their  $R^2$  values were close to 1  
17 for SCPBB@CuNi-0.5, 1, 2 nanocomposites. From the above, the degradation  
18 activity of metal nanoparticle-doped SCPBB is best obtained for the minimum metal  
19 loading, in the decreasing order SCPBB@CuNi-0.5 > SCPBB@CuNi-1 >  
20 SCPBB@CuNi-2. This trend accounts for the excellent dispersion of CuNi  
21 nanoparticles over the biochar surface when the initial metal ion to biomass ratio is set  
22 to 0.5 mmol/1g. It follows that the catalytic activity of the materials prepared so far  
23 correlates very well with the state of dispersion of the NPs as observed by SEM.

24 Subsequently, we further performed the degradation of MG dye in 30 min on  
25 pure SCPBB, single metal-supported SCPBB@Cu and SCPBB@Ni, and the presence  
26 of  $H_2O_2$  without catalyst in Figures 9(e)-(f). We found that both pure SCPBB and  
27  $H_2O_2$  alone could only remove a small number of dye molecules, whereas the removal  
28 efficiencies of SCPBB@Cu-0.5 and SCPBB@Ni-0.5 were 91.6 and 78.2 %,  
29 respectively, indicating that copper and nickel played important role in the dye  
30 degradation, respectively. Note, however, that SCPBB@Cu-0.5 is more efficient as

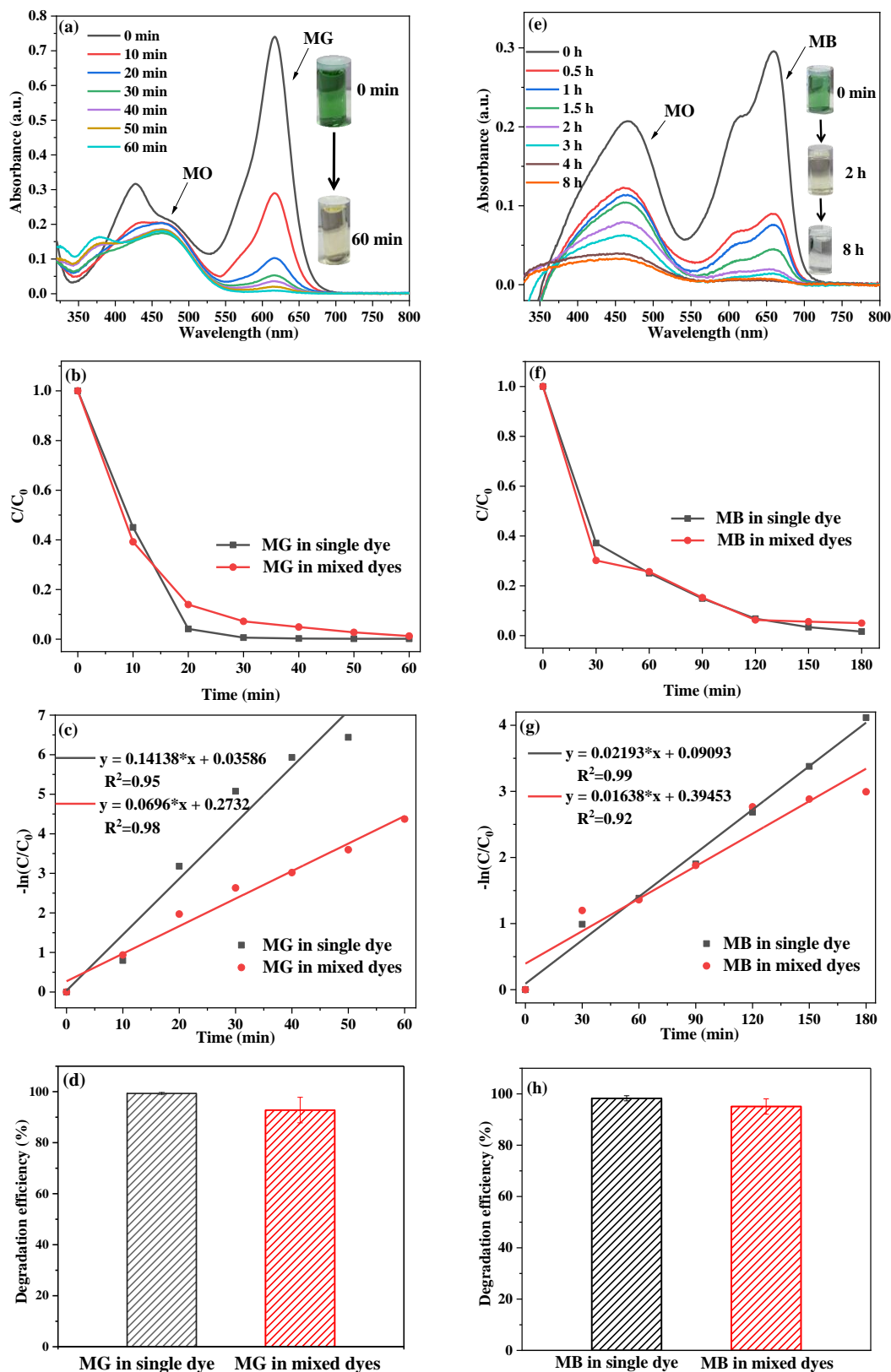
1 Fenton-like composite catalyst than SCPBB@Ni-0.5 (Wang, Ma et al. 2018) (Radji,  
2 Bettahar et al. 2022).

3 The discoloration of single MB and MO with SCPBB@CuNi-0.5 reached 98%  
4 and 74% in 3 h, respectively. The complete discoloration of MO occurred after 8 h.  
5 The superior activity exhibited by SCPBB@CuNi-0.5 can be attributed to the  
6 activation of H<sub>2</sub>O<sub>2</sub> by the metallic species loaded on the biochar to generate more  
7 hydroxyl radicals, which attack the dye molecules to generate water, dinitrogen, and  
8 carbon dioxide (Nidheesh, Gandhimathi et al. 2013, Wang, Sun et al. 2021, Rani,  
9 Nayak et al. 2022).

10

1 **3.7.2. Degradation process of mixed dye solutions**

2



3

1 **Figure 10.** (a) UV-vis spectra, (b) degradation, (c) Pseudo first order kinetic model  
2 and (d) degradation efficiency for simultaneous degradation of binary mixture of dyes  
3 MO and MG, ( I) MG change of individual dye, ( II)MG change of multiple dyes. (e)  
4 UV-vis spectra, (f) degradation, (g) Pseudo first order kinetic model and (h)  
5 degradation efficiency for the binary mixture of dyes MO and MB, (III) MB change of  
6 individual dye, (IV)MB change of multiple dyes. Operation condition: MG initial  
7 concentration= 0.02 mmol/L, MB initial concentration= 0.02 mmol/L, MO initial  
8 concentration= 0.02 mmol/L, biochar dosage = 0.25 g/L.

9 Preliminary tests showed that SCPBB@CuNi-0.5 could optimally degrade  
10 individual dye solutions under natural light in the presence of H<sub>2</sub>O<sub>2</sub>, which  
11 prompted us to study its catalytic performance for mixed dyes. Recently, some of us  
12 have tried to study brewer's spent grain Biochar@Ag-Cu for Methyl Orange and  
13 Methylene Blue mixed dye solution, and the degradation rates were excellent after  
14 6 hours (Boubkr, Bhakta et al. 2022). For this study, two different types of  
15 equimolar dye mixtures (MG+MO and MB+MO mixtures) were prepared to  
16 understand how the SCPBB@CuNi catalyst would still maintain the significant  
17 degradation rate of single organic dye pollutant in complex binary dye solutions.

18 After the selective degradation spectra of the two mixtures were established  
19 using the same conditions, the catalytic degradation reaction of the three dyes MG,  
20 MB, and MO (equimolar mixture) with the catalyst was investigated, and then  
21 compared with the degradation performance in the corresponding single dye  
22 systems. As shown in Figure 10a, MG dye in the MG+MO mixture showed an  
23 obvious sharp decrease to completely disappear at 616 nm, the absorbance drop of  
24 MO at 464 nm was very slight; the mixture's color gradually changed from green to  
25 yellow after 60 min. It took longer for MO to completely degrade.

26 In the MB+MO system, we have also noted faster degradation of MO, thus  
27 leading to a change of color from green (MB+MO mixture) to light yellow due to  
28 complete degradation of MB while there were persistent MO molecules in the  
29 solution. Complete discoloration of the MB+MO system was reached after 8 h. The

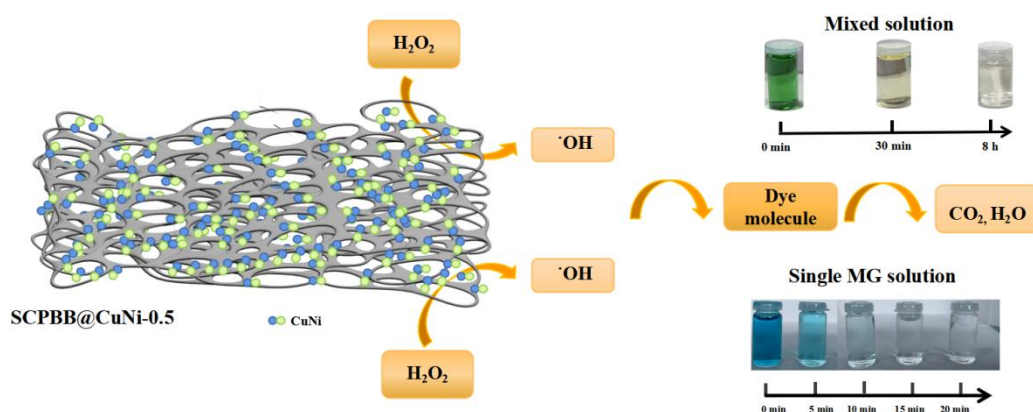
1 degradation rates of MB and MO were 95% (after 3 h) and 84% (after 8 h),  
2 respectively.

3 In addition, the degradation rate and first-order reaction kinetics of  
4 SCPBB@CuNi in the single dye solution and dye mixture system are also explored.  
5 The  $C/C_0$ -vs-time plots for MG and MB dye degradation in mixed dyes using  
6 SCPBB@CuNi catalyst are shown in Figure 10(b,f): faster degradation of the dye  
7 solution occurs during the first 30 minutes (Rani, Nayak et al. 2022). We found that  
8 the degradation rate of an individual dye in the mixed solution was slightly reduced  
9 within 5% and the kinetics versus reaction time plot clearly showed that all MG  
10 degradation processes followed a pseudo-first-order kinetic model (linearization  
11 coefficient  $R^2 > 0.90$ ). The SCPBB@CuNi catalyst retains its performance in the  
12 degradation of the dyes, and the dye mixtures do not seem to significantly alter its  
13 efficiency.

### 14 **3.7.3. Mechanism**

15 The plausible dyes degradation mechanism by the catalytic oxidation of  
16 SCPBB@CuNi/H<sub>2</sub>O<sub>2</sub> system follow adsorption and Fenton-like reactions (Liu, Liu et  
17 al. 2022). Its characterizations confirmed the particular pore structure, graphitic  
18 carbon, and metallic states of copper and nickel loaded on the underlying biochar.  
19 Heterogeneous Fenton-like reactions played a dominant role in the catalytic  
20 degradation process, and adsorption played a minor role in dye removal. The  
21 bimetallic species loaded on the biochar in SCPBB@CuNi provided active sites for  
22 activating H<sub>2</sub>O<sub>2</sub> to generate hydroxyl radicals (Liu, Liu et al. 2022). SCPBB created  
23 an excellent support for metallic species. In order to further understand whether metal  
24 leaching from catalyst into the solution causes secondary pollution, the loss of metal  
25 copper/nickel was detected by XRF technology. Firstly, the XRF analysis of the  
26 carbonaceous catalyst SCPBB@CuNi-0.5 showed that the alloy represents  $\approx 13.7\%$   
27 from the total mass. Also, it revealed that Cu alone represents  $\approx 93\%$  from the total  
28 mass of the alloy. For catalytic performance testing, we used 5 mg of catalyst

1 containing 685 ng CuNi, 637 ng Cu, and 48 ng Ni. After completing the catalyzed  
 2 reaction under natural light, no copper and/or nickel leaching into the solution were  
 3 observed by XRF technique, meaning their absence from the solution, or their  
 4 quantity is below the detection limit of the apparatus. This is strong supporting  
 5 evidence that either metal lixiviation was negligible or did not occur at all from the  
 6 catalyst. One could thus conclude that heterogeneous Fenton-like catalysis reaction  
 7 dominates the whole process. For this reason, the catalyst surface does not undergo  
 8 significant surface chemical composition, retains its active sites, therefore ensuring  
 9 high catalytic performances (Soon and Hameed 2011, Liu, Jiang et al. 2022). Robust  
 10 anchoring of the CuNi nanoparticles is essential, and this point will be tackled below  
 11 (see section 3.9). Meanwhile, organic pollutants can be completely mineralized into  
 12 carbon dioxide and water, simultaneously, elucidating that dye degradation mainly  
 13 ascribe to surface catalysis of heterogeneous Fenton-like reactions rather than  
 14 homogeneous Fenton-like reactions in solution (Xavier, Gandhimathi et al. 2015).  
 15 Under  $H_2O_2$  conditions, pH effect was reported to be crucial for the control of the  
 16 catalytic activity (Bokare and Choi 2014). Particularly, both copper/ $H_2O_2$  (Radji,  
 17 Bettahar et al. 2022) and nickel/ $H_2O_2$  (Akram, Ikhlaiq et al. 2021) systems are active  
 18 over a broad pH range.

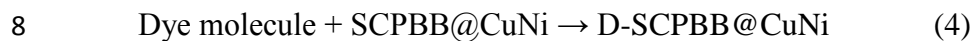


19  
 20 **Fig. 11.** Proposed possible reaction mechanism for dye degradation in  
 21 SCPBB@CuNi/ $H_2O_2$  system.

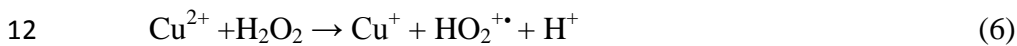
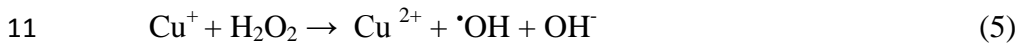
22  
 23 Therefore, based on these results, SCPBB@CuNi can effectively degrade  
 24 individual dye solutions and mixtures with  $H_2O_2$  may be attributed to the following

1 aspects: (1) The special fishnet-like porous structure of substrate SCPBB material is  
2 easy to adsorb, resulting in dye molecules being concentrated around the metal  
3 nanoparticles to increase their degradation. (2) More hydroxyl radicals and metal ions  
4 are produced to attack the dye molecules, which are mineralized into carbon dioxide  
5 and water to achieve discoloration.

6 In summary, the whole process of Fenton-like degradation could occur through  
7 the following pathways.



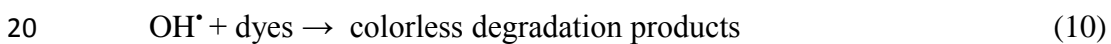
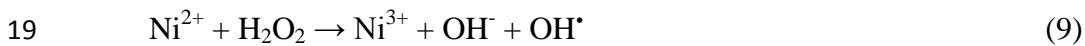
9 Biochar and metal ions in the catalyst accelerate the generation of hydroxyl  
10 radicals, as shown in the following formula (Wang, Liu et al. 2021)



13 Degradation of dye solution via the attack of the hydroxyl radicals plays the  
14 dominant role in dye solution discoloration.



16 Similarly, nickel could participate in the Fenton-like degradation of the dyes. As  
17 suggested, by Bhaumic *et al.* (Bhaumik, Maity et al. 2022):



21 If the role of copper is restricted to catalysis only, nickel has dual properties: catalysis  
22 and magnetic properties that permits collection of the biochar with a magnet, after use.

23

24

25

### 1 **3.8. Comparison with other biochar-based catalytic systems**

2           Table 4 compares the catalytic performance of SCPBB@CuNi to other  
3 biochar-based systems.

**Table 4.** Comparison of the catalytic performances of SCPBB@CuNi to other biochar-base materials.

Catalyst	Experimental conditions	Contact Time(min)	Degradation (%)	Recovery  (cycle times, degradation)	References
<b>Malachite Green</b>					
Mn/SRBC (KMnO <sub>4</sub> / biochar)	Catalyst 2 g/L, H <sub>2</sub> O <sub>2</sub> 5 m mol/L, MG 8000 mg/L, pH 3, temperature 30°C	90	100	3rd cycles, 62%	(Zhu and Zou 2022)
PBC@ $\delta$ -MnO <sub>2</sub>	Catalyst 0.2 g/L, PDS 1 mmol/L, pH 5, MG 200 mg/L, temperature 30 °C	120	92.6	4th cycles 75%	(Xia, Li et al. 2023)
BMFH/Fe <sub>3</sub> O <sub>4</sub>	Catalyst 1.0 g/L, MG 50 mg/L, H <sub>2</sub> O <sub>2</sub> 50 mmol/L, pH 6, temperature 30 °C	60	99	10 cycles 81%	(Chen, Lin et al. 2022)
Fe@BCFAK	Catalyst 0.2 g/L, MG 20 mg/L, H <sub>2</sub> O <sub>2</sub> 2 mmol/L, pH 3, temperature 30 °C	30	98	/	(Xia, Shen et al. 2022)
Fe NPs/tea extract	Catalyst 50 mg/L, MG 50 mg/L, H <sub>2</sub> O <sub>2</sub> 7.4 mmol/L, pH 4, temperature 35°C	60	78.2	/	(Wu, Zeng et al. 2015)
ZnO@BC	Catalyst 0.4 g/L, MG 400 mg/L, 300 W xenon lamp (no mention)	60	98.4	/	(Jing, Ji et al. 2021)
Algal biochar@La/Cu/Zr	Catalyst 0.4 g/L, MG $2 \times 10^{-6}$ mmol/L, solar light	240	90	4 cycles 71%	(Sharma, Bhogal et al. 2019)
CuFe <sub>2</sub> O <sub>4</sub> @biochar	Catalyst 0.2 g/L, PS 2.5 mmol/L, MG 100 mg/L, pH 8, temperature 55°C	90	98.5	5 cycles 90%	(Huang, Chen et al. 2021)
SCPBB@CuNi	Catalyst 0.25 g/L, H <sub>2</sub> O <sub>2</sub> 48 mmol/L, MG 9.3 mg/L, room temperature	30	>99	4 cycles 87±3%	This work

<b>Methylene Blue</b>					
BGT-NPs	Catalyst 0.25 g/L, H <sub>2</sub> O <sub>2</sub> 16 mmol/L, MB 10 mg/L, UV-light, wide pH range	120	96–99%	4 cycles 96%	(Ashraf, Rasool et al. 2021)
P-GBC (H <sub>3</sub> PO <sub>4</sub> activation)	Catalyst 0.1 g/L, H <sub>2</sub> O <sub>2</sub> 0.2 mmol/L, PMS 4 mmol/L MB 100 mg/L, temperature 298.15 K	360	94.9%	3 cycles 79%	(Ding, Tong et al. 2023)
MnO <sub>2</sub> @SBC	Catalyst 0.3 g/L, pH 7 PMS 0.5 mmol/L MB 35 mg/L, temperature 25 °C	180	100%	5 cycles 0.02084 min <sup>-1</sup> (degradation rate)	(Li, Liu et al. 2022)
SCPBB@CuNi	Catalyst 0.25 g/L, H <sub>2</sub> O <sub>2</sub> 4.8 mol/L, MB 3.2 mg/L, room temperature	180	>98%	/	This work
<b>Methyl Orange</b>					
<b>H<sub>2</sub>SO<sub>4</sub> biochar</b>	Catalyst 1 g/L, H <sub>2</sub> O <sub>2</sub> 25 mmol/L, MO 50 mg/L, 1000 W Xe arc light temperature 50 °C;	60	92%	5 cycles >80%	(Rangarajan and Farnood 2022)
Biochar@Cu <sub>2</sub> O	Catalyst 0.1 g/L, MO 20 mg/L, UV light, pH 4, temperature 50 °C;	140	94.5 %	/	(zhang, Li et al. 2023)
SCPBB@CuNi	Catalyst 0.25 g/L, H <sub>2</sub> O <sub>2</sub> 4.8 mol/L, MO 3.2 mg/L, room temperature	480	>90%	/	This work

BCFAK acid-precipitated black liquor of poplar kraft pulp; BMFH magnetic biochar fungal hyphae (*Trichoderma reesei*); PBC the phosphoric acid modified millet husk biochar; P-GBC P-GBC was prepared by H<sub>3</sub>PO<sub>4</sub> assisted pyrolysis over camellia shell powder; PMS: peroxymonosulfate PMS; SRBC spirulina residue biochar.

1 Concerning the degradation of MG, the biochar composites catalysed the removal of MG with  
2 efficiency in the 78–99 wt.% range, within 30 to 240 min. It is worth noting that, under natural  
3 pH conditions, the degradation of dyes remains difficult. The degradation efficiency of  
4 Fe@BCFAK (Xia, Shen et al. 2022) and Mn/SRBC (Zhu and Zou 2022) is over 98% within 60  
5 minutes, which is very similar to SCPBB@CuNi, but under acidic pH. The ZnO@BC catalysed  
6 the removal of MG within 60 min under xenon lamp irradiation (Jing, Ji et al. 2021). The actual  
7 SCPBB@CuNi/H<sub>2</sub>O<sub>2</sub> system catalyzed the removal of MG cationic dyes to an extent of 99%  
8 within 30 min only, under natural light and neutral pH. In addition, no acidic or alkali treatment  
9 was applied to obtain highly porous biochar.

10 Magnetic biochar (BMFH/Fe<sub>3</sub>O<sub>4</sub>) (Chen, Lin et al. 2022) was synthesized by the bio-assembly  
11 property of fungal hypha; the removal rate of MG remained above 80% after 10 cycles, but the  
12 catalyst was washed and carbonized before the next cycle.

13 The degradation performance of CuFe<sub>2</sub>O<sub>4</sub>@biochar is always maintained at 90% after five  
14 reactions (Huang, Chen et al. 2021). The catalyst/PS system also possesses promising prospects  
15 for treating wastewater. Even if four-time reactions, compared with the PBC@ $\delta$ -MnO<sub>2</sub> (Xia, Li et  
16 al. 2023) and Algal biochar@La/Cu/Zr (Sharma, Bhogal et al. 2019) catalysts, the degradation  
17 performance of SCPBB@CuNi was found to be as high as 87% after four cycle tests, no washing  
18 and drying steps were done and the catalyst was directly re-used for a new catalysed degradation.  
19 This is of practical application importance.

20  
21 Concerning the Fenton-like process, the literature reported large amounts of H<sub>2</sub>O<sub>2</sub>, or extra  
22 oxidants or light irradiation could significantly improve the effect of the catalytic system, which  
23 contrasts with our much simpler conditions consisting in using low H<sub>2</sub>O<sub>2</sub> amounts, under daylight  
24 exposure. Ashraf *et al.* (Ashraf, Rasool et al. 2021) on the one hand, and Rangarajan *et al.*  
25 (Rangarajan and Farnood 2022), on the other hand, used UV light source to the catalyst/H<sub>2</sub>O<sub>2</sub>  
26 system to increase the degradation rate of the dye. P-GBC (Ding, Tong et al. 2023) and  
27 MnO<sub>2</sub>@SBC (Li, Liu et al. 2022) catalytic systems were combined with peroxymonosulfate  
28 (PMS), as an alternative to H<sub>2</sub>O<sub>2</sub> to produce active species. To further know whether H<sub>2</sub>O<sub>2</sub>  
29 suffices to remove the dyes and plays a major role in their degradation, reactions were conducted  
30 in the absence of catalyst, but the degradation efficiency was only about 30%, with only H<sub>2</sub>O<sub>2</sub>

1 and under the same condition. It can thus be confirmed that the degradation rate of MB and MO  
2 can reach 98% and 90% only when the catalyst and H<sub>2</sub>O<sub>2</sub> coexist.

3 These dye degradation experiments suggest that SCPBB@CuNi not only has advantages in  
4 degrading MG but also has catalytic performance in degrading MB and MO under the synergistic  
5 effect of H<sub>2</sub>O<sub>2</sub>, under daylight.

6  
7 This comparative study shows that SCPBB@CuNi is a very competitive catalytic composite  
8 compared to other biochar-based catalyst systems employed to remove MG, MB, and MO dyes,  
9 as well as their mixtures.

10

### 11 ***3.9. Stability and recovery of the catalyst***

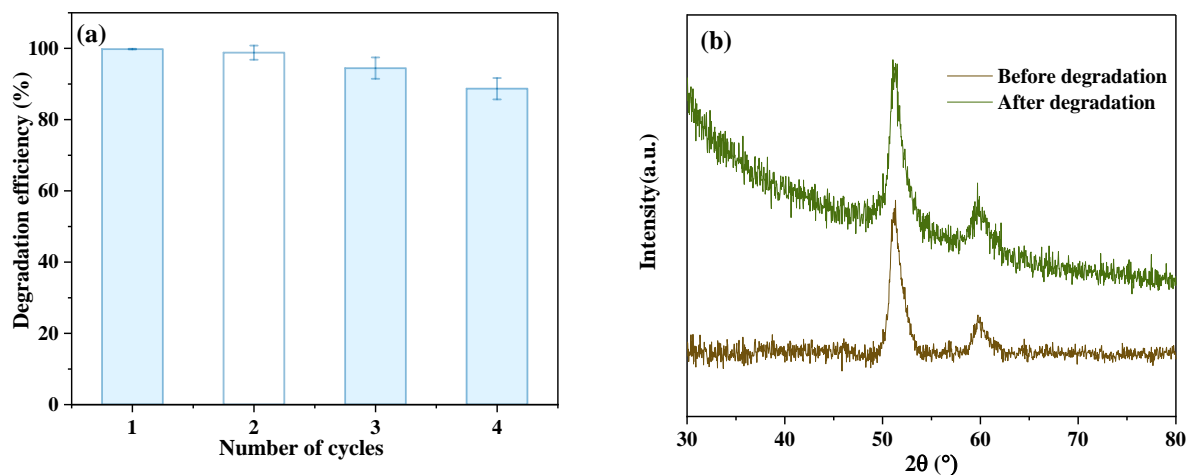
12 Due to the presence of Ni species in the catalyst, after each catalytic reaction, the catalyst was easily  
13 separated by an external magnet, and then used for the next catalytic testing, without any washing  
14 treatment.

15

16 We recollected SCPBB@CuNi-0.5 material by an external magnet to evaluate reusability  
17 and stability, without any cleaning treatment, then the catalyst was reused under the same  
18 conditions for the MG degradation. Figure 12(a) shows that discoloration occurred at 87±3% and  
19 can still be maintained within 20 mins after four times. It is worth noting that the catalyst can be  
20 reused without any secondary washing, and retains high catalytic efficiency. This simple  
21 recycling method, without any washing step, shows that SCPBB@CuNi is a green and cost-  
22 effective catalyst. The crystalline structure of the catalyst after many times of usage was analyzed  
23 by XRD (Fig. 12b). Comparing the XRD patterns of the original and the used SCPBB@CuNi  
24 catalyst hardly show any significant change, hence the stability of the immobilized bimetallic  
25 CuNi NPs.

26

1



2 **Figure 12.** (a) The degradation efficiency of MG dye solution after 4 times with  
3 SCPBB@CuNi, (b) XRD patterns of reused and fresh SCPBB@CuNi.

4

#### 5 **4. Conclusion**

6 In this contribution, sugarcane pulp bagasse biochar samples, loaded with bimetallic copper-  
7 nickel alloy nanoparticles, were prepared by pyrolysis at 500 °C, during 1 hour, under dinitrogen  
8 stream. SEM images reveal the unusual hierarchical micro/nanostructure resembling to a fishing  
9 net, with evenly dispersed and immobilized ~40 nm-sized nanoparticles. The fishnet-like  
10 structure of the underlying biochar is shown to be induced by nickel, which also endows the  
11 biochar with magnetic properties. Copper and nickel are mostly present in the metallic state but  
12 undergo surface oxidation as probed by XPS. Their loading on the biochar gradually increased  
13 with initial metal ion impregnation. The unique textural properties and evenly dispersed  
14 bimetallic nanoparticles over the optimized biochar SCPBB@CuNi contribute to the superior  
15 catalytic activity for removing organic contaminants. The biochar/H<sub>2</sub>O<sub>2</sub> system was tested for the  
16 degradation of model dyes and their mixtures at RT and under daylight conditions. The  
17 SCPBB@CuNi-0.5 catalyzed the total degradation of MG and MB dyes within 30 min and 3 h,  
18 respectively, and could be recycled without a significant decrease in its catalytic performance.  
19 Even in complex dye mixtures, the catalyst maintained a high ability to remove organic pollutants.  
20 For higher initial loading of 1 and 2 mmol metal ions per gram of biomass, the catalytic  
21 efficiency decreased due to significant agglomeration of the CuNi nanoparticles.

1 From the above, this work obviously opens avenues for its application to the treatment of  
2 complex wastewaters containing organic pollutant mixtures, therefore contributing to address  
3 UNs 6<sup>th</sup> SDG related to Clean Water & Sanitation.

4

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#### 16 **Conflict of Interest**

17 The authors declare no conflict of interest

18



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