1. Introduction

The inextricable nature of food, energy and water, combined with a growing global population that increasingly taxes these synergistic systems, requires innovative approaches that avoid stressing one system while advancing another. For example, cultivating bioenergy crops with irrigated land that could otherwise be used to grow food increases water withdrawals and may place food supplies at risk.1 Green chemistry and engineering movements call on innovators to reduce hazardous material inputs and outputs as well as process energy requirements whether producing fine chemicals or manufacturing automobiles.2 In an effort to improve the sustainability of nanomaterials production, recent years have brought substantial progress in using biological templates to create “sustainable” nanomaterials without the use of harsh solvents and processing conditions.3 Biotemplates yield nanomaterials with complex structures and high reactive surface areas, and when they are sourced from waste materials, may do so in a more resource-conserving manner than solution-based fabrication techniques.4,5

There are myriad examples in the literature demonstrating procedures for biotemplating nanomaterials and identifying novel templating materials, including biotemplated ZnO on a variety of biomass precursors. For example, Taubert et al. fabricated zincite (ZnO) particles using starch as the crystallization controlling agent.6 They demonstrated the ability to control the morphology of the zincite particles by changing the concentration of the starch in the reactor. Dong et al. used eggshell membrane as template to produce ZnO interwoven nanofiber.7 Other researchers have successfully created ZnO nanoparticles using butterfly wing scales,8 luffa sponges,9,10 and spherobacterium.11 In this paper, we focus on improving the sustainability of zinc oxide fabrication by integrating it with a biomass waste-to-energy conversion using a biomass that would otherwise be considered agricultural waste.

Many studies have shown the potential to use zinc oxide to photocatalytically degrade harmful pollutants, such as commercial dyes, that hamper wastewater treatment.12 Har-ihar test the photocatalytic activity of bulk ZnO, ZnO nanoparticles, and the conventionally used photocatalyst Degussa TiO2. Their study found that ZnO nanoparticles are
comparable or better to both TiO$_2$ and bulk ZnO as a catalytic system.\textsuperscript{12} Chen \textit{et al.} demonstrated that zinc oxide nanorods adhered to the surface of a spinning disc were able to degrade 40\% of methylene orange in 40 minutes.\textsuperscript{14} Similarly, ZnO has been shown to degrade azo dye acid red (AR14), a byproduct of textile manufacturing.\textsuperscript{15} At a neutral pH and optimal concentrations of dye and catalyst, the dye can be completely removed by ZnO in approximately 1 hour. Shen \textit{et al.} compared the effectiveness of ZnO in degrading methylene blue when templated on both starch gel and a silica nanoparticle surface. They found that the ZnO deposited on the silica nanoparticle was more effective, degrading 90\% of methylene blue in 60 minutes, compared to 20\% degradation from the ZnO on starch surface.\textsuperscript{16} Furthermore, hierarchically structured metal oxides could treat water in ways beyond photocatalytic degradation of dissolved compounds. For example, ZnO biotemplated from eggshell membrane demonstrated high adsorption capacity for gold nanoparticles, contaminants of emerging concern as nanomaterials are increasingly incorporated into consumer products.\textsuperscript{17}

In addition to water treatment, ZnO nanomaterials have exhibited photocatalytic antifungal and antibacterial activity as a result of their ability to mediate reactive oxygen species.\textsuperscript{18,19} The sensing applications proposed for ZnO nanomaterials are numerous, including for Schottky ultraviolet photodetectors owing to ZnO’s wide bandgap.\textsuperscript{20} Fatemi \textit{et al.} and Zhou \textit{et al.} demonstrated the use of biomorphic ZnO nanostructures for glucose biosensing.\textsuperscript{21,22} and Zhao \textit{et al.} for enzymatic sensing.\textsuperscript{23} Others have shown the potential for porous ZnO materials to serve as gas sensors for H$_2$S,\textsuperscript{24} NH$_3$, CO and H$_2$,\textsuperscript{25} and acetone.\textsuperscript{26} Biotemplated ZnO also shows promise for aqueous sensing applications, such as acetic acid.\textsuperscript{27} Beyond such sensing and environmental remediation applications, ZnO nanomaterials show promise for use in solar energy conversion,\textsuperscript{28,29} as semiconductor materials,\textsuperscript{30} and as transparent ferromagnets,\textsuperscript{31} among many other applications.

Identifying sustainable materials to produce such useful nanomaterials is of paramount importance as we transition to a green economy.\textsuperscript{32} By using nonhazardous materials (biomass) that do not compete for arable land for food supply to biotemplate ZnO nanoparticles, and integrating biofuel production into the waste recovery process, we can strive towards meeting the principles of green engineering.\textsuperscript{2} One such potential biomass source is the banana plant. In 2013, the global banana fruit production topped 100 million tons, with India as the leading producer (over one quarter of worldwide production).\textsuperscript{33} The U.S. produced approximately 6525 tons of bananas in 2013. Despite this tremendous fruit yield, the cultivation of bananas produces a sizeable amount of cellulose waste; only \~12 \text{wt}\% of the banana plant is the edible fruit.\textsuperscript{34} Unfortunately, once the banana hand is picked, the remaining plant matter (pseudo-stems and leaves) dies. Annually, this represents almost one billion tons of agricultural waste, which is often used as in situ fertilizer. The decomposition of this fertilizer releases greenhouse gases and represents a waste of a potentially useable material.

Banana plants are comprised predominantly of water. Parts of the highly cultivated Dwarf Cavendish banana have a moisture content that ranges from 74–94\% by weight water.\textsuperscript{35} As such, converting this cellulosic waste to a byproduct in a sustainable manner requires additional considerations to handle such a wet material. In addition, the relatively high inorganic content of banana stalk biomass represents an interesting challenge for its waste-to-byproduct conversion. For example, the inorganic content negatively impacts kraft pulping, potentially negating the use of this biomass as a raw material for pulp and paper manufacture.\textsuperscript{36} One potential method for byproduct conversion is through hydrothermal carbonization, whereby the biomass is heated with water at elevated pressures and temperatures to extract biofuels. The temperatures required for extraction are lower than traditional pyrolysis temperatures and therefore require less energy for extraction, as well as no energy to pre-dry the biomass.\textsuperscript{37} Rather than a hindrance to conversion, the presence of minerals such as calcium are known to catalytically upgrade bio-oils produced via thermal processes such as hydrothermal liquefaction.\textsuperscript{38,39} However, a substantial amount of solid waste – hydrochar – remains after carbonization. In this work we demonstrate the ability to concurrently produce biofuels from the hydrothermal carbonization of banana stalk, while using the waste hydrochar as a biotemplate for a ZnO water treatment material. ZnO was also templated onto raw banana stalks, and both materials were used to photocatalytically degrade organic water contaminants using methylene blue dye as a model compound.

2. Materials & methods

To demonstrate this holistic approach to the production of sustainable nanomaterials for environmental applications, we used hydrothermal carbonization to produce a bio-oil and hydrochar from the pseudo-trunk of a “Lady Finger” banana, a diploid (AA) cultivar of \textit{Musa acuminata}. The biomass was collected in North Port, Florida following harvest of the banana hand. A section of pseudo-trunk was cut from the center of the trunk, and was air-dried over several days and stored in airtight containers to prevent mold growth. The raw dry banana stalk biomass (termed BR) was ground in a coffee grinder and mechanically sieved to yield a particle fraction between 300 and 500 \text{µm}.

2.1. Hydrothermal conversion of banana stalk biomass

The banana stalk hydrochar (BH) was prepared in a 200 mL stainless steel hydrothermal autoclave (ColTech International). 10.71 g of raw biomass was combined with 150 mL of deionized water and heated at an average rate of 1.8 \textdegree\text{C} min$^{-1}$, to a final temperature of 225 \textdegree\text{C} and 2.8 MPa, and held at these conditions for 1 h under constant stirring at 110 rpm. The mixture was cooled to 50 \textdegree\text{C} before the autoclave was vented, and the liquid and solid contents removed. The hydrochar and liquid was separated \textit{via} vacuum filtration. The hydrochar was washed with 30 mL of methanol and the filtrate collected to analyze non-aqueous phase bio-oil components. A second wash was
performed with acetone and the filtrate again collected for analysis. The hydrochar was washed one additional time with methanol, and dried overnight in a 75 °C oven.

20 mL of the aqueous filtrate was mixed with 20 mL of n-hexane (Acros Organics, HPLC grade) in a glass vial on a shaker table at 150 rpm overnight to separate the condensable bio-oil components. A 100 µL aliquot of the hexane layer was added to 1.0 mL of dichloromethane (DCM, Acros Organics, HPLC grade) in a glass vial. Likewise, 100 µL aliquots of the methanol and acetone extracted fractions were added to 1.0 mL of DCM. Analysis of the bio-oil components was performed using an Agilent 7890B gas chromatograph-mass spectrometer (GC-MS). The instrument was run in split mode with a split ratio of 10 : 1, an injection temperature of 250 °C, using helium as a carrier gas. For the hexane fraction, the GC program started at 40 °C, held for 10 minutes, then the oven temperature was raised to 2.5 °C min⁻¹ to 170 °C, held for 6 min, heated at 5 °C min⁻¹ to 250 °C, held for 10 min, then heated at 15 °C min⁻¹ to 300 °C and held for 10 minutes. For the acetone and methanol fractions, GC conditions started at 40 °C with a hold time of 10 min, followed by heating at 3 °C min⁻¹ to 170 °C, held for 5 min, then raised at 4 °C min⁻¹ to 270 °C, held for 10 min, and finally heated to 300 °C at 12 °C min⁻¹ and held for 10 minutes. An initial 6.5 min solvent delay was used for both methods to prevent saturation of the MS filaments. The interface temperature was set at 325 °C. Mass spectra were recorded under electron ionization mode using an m/z range of 50 to 300 amu. A semiquantitative analysis was performed by integrating the 25 largest (by area) gas chromatograms peaks. Peaks are only reported if their NIST-library identification similarity was greater than 90%. Given the heterogeneity of biomass sample and difficulty in separating and quantifying these mixtures, we note that this is a qualitative bio-oil analysis and the products here are reported for comparative purposes against other hydrothermal bio-liuids.

2.2. Biotemplating with ZnO
Both raw biomass and hydrochar were used as sacrificial bio-templates for ZnO production in a three-step impregnation, washing and calcination procedure. Briefly, a 0.15 g mL⁻¹ suspension of BR or BH in a zinc acetate solution was mixed for one hour. The zinc acetate solution was 0.1 M Zn(II) solution (zinc acetate dihydrate, Acros Organics, ACS reagent 98%) prepared in 1 : 1 200-proof EtOH : deionized (DI) water. The suspension was vacuum filtered followed by a wash with 1 : 1 EtOH : DI H₂O, and the resulting material was dried overnight in an oven at 75 °C. Zn-impregnated raw biomass and hydrochar are referred to as BRZ and BHZ, respectively. The samples were then calcined in a tube furnace under air at 100 mL min⁻¹. They were heated up to 550 °C at 5 °C min⁻¹ and held for two hours. Calcined, Zn-impregnated raw biomass and hydrochar are referred to as BRZC and BHZC, respectively.

2.3. Materials characterization
The carbon contents of the raw and hydrochar biomasses were determined via thermogravimetric analysis (TGA, Mettler Toledo TGA-DSC-1) with a 0.1 µg balance and sensitivity of ±0.1 °C. 5 to 10 mg samples were placed in 70 µL alumina crucibles. Under a constant flow of nitrogen at 50 mL min⁻¹, with a 20 mL min⁻¹ N₂ balance protective gas flow, samples were heated at 10 °C min⁻¹ to 110 °C and held for 30 min to remove residual moisture. Samples were then heated to 910 °C and held for 60 min; the mass loss between 110 and 910 °C was attributed to volatile carbon. To determine the fixed carbon, the samples were then heated from 910 °C to 950 °C at 10 °C min⁻¹ under air and held for 60 min. Residual mass is considered to be mineral matter. For all TGA experiments, an empty crucible run at the same experimental conditions was used as a baseline to account for buoyancy. The differential scanning calorimeter (DSC) feature was calibrated using NIST-traceable gold and indium at 5 °C min⁻¹. To gauge the relative reactivity of the impregnated biomass samples, and insure that all bulk samples would be oxidized as described in Section 2.2, a 5–10 mg sample of each impregnated biomass was placed in the TGA. These impregnated samples were heated in air flowing at 50 mL min⁻¹ to 110 °C at a rate of 5 °C min⁻¹ (to mimic tube furnace conditions) and held for 30 min, then heated to 550 °C at the same rate and held for two hours.

Calcined and non-calcined banana stalk materials (BRZ, BHZ, BRZC and BHZC) were analyzed for the presence of crystalline phases by X-ray powder diffraction (XRD, Bruker D8 Discover) using Cu Kα radiation at 40 kV and 40 mA with a step size of 0.05° and dwell time of 0.5 s. Powder samples were affixed to the sample holder using Kapton tape, and a background Kapton tape spectrum taken at the same conditions was subtracted from all spectra.

Raw and hydrochar banana stalk templated materials were analyzed by scanning electron microscopy (SEM, Zeiss Supra55 with field emission gun) operated at 3 or 10 kV for imaging and 10 kV for energy dispersive spectroscopy (EDS). Material powder was sprinkled onto double-sided copper tape and coated with a ~10 nm layer of gold (Cressington 108 sputter-coater) to reduce the charging of nonconductive materials.

Surface areas were determined by the Brunauer–Emmett–Teller (BET) method of monolayer N₂ adsorption isotherms at 77.35 K (Quantachrome Instruments Autosorb-1). Under vacuum, BR and BH were outgassed at 80 °C while BRZC and BHZC were outgassed at 180 °C. Samples were weighed immediately after degassing. Surface areas were calculated from an 11-point analysis over a partial pressure range of 0.05 to 0.3.

2.4. Application of biotemplated ZnO to water treatment
To test the efficacy of the biotemplated ZnO photocatalysts (BRZC and BHZC) to degrade organic contaminants, methylene blue (MB) dye was used as a model compound and degradation kinetics under UV light exposure were determined. De-ionized (DI) water was used for all solutions and dilutions. A working stock suspension of 50.0 mg L⁻¹ methylene blue dye and 35.0 mg BRZC or BRHC was prepared, covered with aluminum foil, and stirred with a magnetic stir bar while equilibrating for 30 min. This equilibration time between the dye and the photocatalytic material was suggested by Shen et al., and we found...
that it is critical to obtaining consistent UV-degradation results.\textsuperscript{16} 1 mL of equilibrated suspension was aliquoted into 1.5 mL glass vials, and exposed to UV light (UVP, 8 watt, 0.20 amp) at a wavelength of 365 nm with agitation via an IKA horizontal shaker table at 150 rpm. The distance between the level of the solution and the UV source was 5.5 cm. Control samples included BRZC or BHZC in the dark. Vials were sacrificed over a period of 1.5 hours, syringe-filtered (0.45 μm, hydrophilic PTFE) and diluted in triplicate. UV-Vis spectroscopy (Shimadzu UV-1800) was used to quantify the MB concentration over time by measuring the absorbance at a wavelength of 664 nm.

3. Results & discussion

To address the sustainable manufacture of photocatalytic water treatment materials, we selected banana stalk, a biomass that is readily available across the world and does not compete with food supply. As shown in Table 1, the volatile carbon content of the dried biomass was 82.8 wt%, with a fixed carbon content of 2.8 wt% with the remainder being mineral matter. The surface area of the raw biomass was 6.3 m\(^2\) g\(^{-1}\). We first subjected this wet biomass to hydrothermal carbonization to extract biofuels and produce a biochar for templating of the zinc oxide photocatalysts.

3.1. Hydrothermal carbonization of banana pseudo-stalk

The raw banana biomass (BR) was carbonized at 225 °C for 1 hour at 2.8 MPa. The gas chromatograms (available in Fig. S1 of ESI\textsuperscript{†}) of the aqueous bio-oil extracted with hexane, and the methanol and acetone fractions extracted via washing the hydrochar, are typical of hydrothermal biofuels, showing a myriad of compounds. As expected with a cellulosic biomass, the primary aqueous bio-oil constituents that were identified with a minimum 90% library match were furfurals, alkanes and phenols (Table 2). The acetone and methanol extracted components (those that initially partitioned to the hydrochar and not water) were predominantly higher molecular weight substituted aromatic ring compounds. Common substituent groups noted were methyl, phenyl, and carbonyl groups. These results mimic the bio-oils recovered from hydrothermal carbonization of cherry pits\textsuperscript{40} and rice husks.\textsuperscript{41}

The hydrothermal treatment increased the relative volatile carbon concentration of the hydrochar as compared to the raw biomass. As shown in Table 1, the volatile carbon content (dry basis) increased to 87.5 wt%, while the mineral matter content

<table>
<thead>
<tr>
<th>Sample</th>
<th>Volatile carbon (wt% dry basis)</th>
<th>Fixed carbon (wt% dry basis)</th>
<th>Mineral matter (wt% dry basis)</th>
<th>Surface area (m(^2) g(^{-1}))</th>
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<tbody>
<tr>
<td>BR</td>
<td>82.8</td>
<td>2.8</td>
<td>14.5</td>
<td>6.3</td>
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<tr>
<td>BH</td>
<td>87.5</td>
<td>1.3</td>
<td>11.3</td>
<td>28.3</td>
</tr>
<tr>
<td>BRZC</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BHZC</td>
<td></td>
<td></td>
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</table>

<table>
<thead>
<tr>
<th>Bio-oil fraction</th>
<th>Retention time (min)</th>
<th>Area%</th>
<th>Compound</th>
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<tr>
<td><strong>Aqueous extraction</strong></td>
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<td></td>
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<td>Hexane</td>
<td>6.68</td>
<td>3.08</td>
<td>2-Furanmethanol</td>
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<td>1.59</td>
<td>Phenol</td>
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<td>8.88</td>
<td>1.27</td>
<td>Decane</td>
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<td>10.92</td>
<td>6.02</td>
<td>Furfural</td>
</tr>
<tr>
<td>Hexane</td>
<td>11.01</td>
<td>1.68</td>
<td>Phenol, 4-ethyl or 3-ethyl</td>
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<td>Hexane</td>
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<td>0.29</td>
<td>((E)-2-(But-2-enyloxy)butan-2-one)</td>
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<td>12.97</td>
<td>5.72</td>
<td>2-Amino-4-methyl-2-pentenitrile</td>
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<td>Hexane</td>
<td>15.06</td>
<td>0.95</td>
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<td>Hexane</td>
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<td>2.15</td>
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<tr>
<td>Hexane</td>
<td>28.36</td>
<td>0.22</td>
<td>(trans)-3-Methoxy-5-(4-methoxyphenyl)-1,2,4-trioxolane</td>
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<td><strong>Hydrochar extraction</strong></td>
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<tr>
<td>Acetone</td>
<td>18.15</td>
<td>6.37</td>
<td>Phenol</td>
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<td>Acetone</td>
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<td>10.95</td>
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<td>Acetone</td>
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<td>6-Phenylhexanal</td>
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<td>3.52</td>
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<td>1.06</td>
<td>Ethanone, 1-(2-furanyl)-</td>
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<tr>
<td>Methanol</td>
<td>18.15</td>
<td>2.17</td>
<td>Phenol</td>
</tr>
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</table>
decreased from 14.5 wt% for BR to 11.3 wt% for BH. This is likely due to the dissolution and/or degradation of minerals present in the biomass into the process water during the high temperature and pressure treatment. The resulting hydrochar had a specific surface area of 28.3 m² g⁻¹, a three-fold increase over the raw biomass.

3.2. Biotemplated nanomaterials

Both BR and BH were impregnated with a zinc acetate ethanol/water solution and the resulting biomass calcined to remove the carbonaceous templates and to form metal oxides. Samples (5–10 mg) of the impregnated biomasses were placed in the TGA and heated at 5 °C min⁻¹ to 550 °C to (1) insure the bulk calcination procedure would remove the carbonaceous template and (2) determine the impact of carbonization on the resulting thermal reactivities of the impregnated samples during oxidation. The yield after calcination for the BRZC samples was 8.9 wt% (of impregnated weight) and for the BHZC samples was 12.9 wt%. Fig. 1A shows the mass fraction of the oxidized portion of the sample (the 91.1 wt% and 87.1 wt% of the sample lost, respectively) converted as a function of temperature. From this plot, we confirm that the sample was fully calcined at approximately 475 °C, such that calcination at 550 °C for one hour was sufficient to remove the carbonaceous template.

From Fig. 1B, we note higher reactivity of the BRZ sample as compared to the impregnated hydrochar. Though both impregnated biomasses see a large portion of sample oxidized between 280 and 300 °C, the rate of oxidation for the raw impregnated biomass is considerably higher (more than twice as high) at lower temperatures. The derivative thermogravimetric (DTG) curve for BHZ shows a second peak around 415 °C with slightly higher mass loss rate than the first peak at 280 °C. This behavior corresponds to the changes in slope of the mass fraction conversion plot of Fig. 1A. The higher reactivity of the raw biomass versus the hydrochar can be explained by the
carbonization process itself. During hydrothermal treatment, the more volatile compounds are forced out of the raw biomass, concentrating the higher molecular weight, more condensed components in the biomass. Thus, the remaining compounds are more “difficult” to oxidize. The carbonization step, as it is known to do, produces an “energy concentrated” biomass. As shown in Fig. 1C, the differential scanning calorimeter data, the peak exotherm of the hydrochar impregnated sample occurs at a lower temperature and higher heat value than the raw biomass.

The mineral content of any plant matter depends upon the composition of the soil in which the plant is grown; given the high water content of the biomass, which is drawn into the plant from the soil, the appearance of minerals throughout the biomass is logical. The ash fractions of a Dwarf Cavendish banana plant harvested in Funchal, Portugal contained between

![XRD spectra of Zn²⁺-impregnated banana stalk materials](image)

**Fig. 2** XRD spectra of Zn²⁺-impregnated banana stalk materials (plotted on left y-axis), zincite (R060027) and calcite (R050048) (plotted on right y-axis). The Background signal from the instrument and Kapton tape was subtracted.

![SEM image of raw banana stalk biomass](image)

**Fig. 3** SEM image of raw banana stalk biomass, impregnated with Zn²⁺ and calcined at 550 °C (BRZC), with approximate area of EDS spectra indicated by letters (A–D). Aggregates of finer-grained particles are ZnO, while hexagonal plates and corrugated fiber structures are CaCO₃. Au peak is from the sputter-coated conductive coating.
0.6 and 32.3 (elemental) percent calcium;\textsuperscript{35} the sandy soil where the present banana stalk was harvested is known to contain elevated amounts of calcium, silicon and sulfur (from groundwater). As such, the presence of both ZnO (from the impregnation) and CaCO\textsubscript{3} (naturally present in the biomass) in both the BRZC and BHZC is expected. XRD confirms that both zincite (ZnO) and calcite (CaCO\textsubscript{3}) phases co-exist in both types of bio-templated BRZC and BHZC materials (Fig. 2), and we note relatively higher concentrations of calcite in the BHZC. These zincite crystalline phases are not present in the raw biomass or hydrochar samples (BRZ, BHZ) prior to calcination. While the overall mineral matter decreased during carbonization (as noted in Section 3.1.), it is possible – given the XRD peak – that a small amount of inorganic minerals initially present crystallized; XRD peaks for BHZ qualitatively suggest that this is a possibility, but the spectral match cannot be confirmed. Zinc acetate, cellulose and lignin were ruled out as possibilities based on lack of spectral match.

The SEM images of BRZC and BHZC in Fig. 3 and 4 confirm the heterogeneity observed in the XRD results. At least four different particle morphologies are present. Aggregates of finer-grained material are primarily ZnO (e.g. areas 3B, 3D), as porous lattice type structures (e.g. area 4C). These ZnO particles likely form from oxidation of the zinc-impregnated biomasses, but we cannot rule out the possibility of some level of solution growth possible during carbonization, given the many examples of solution-growth crystalline ZnO microtubes\textsuperscript{43} and nanotubes\textsuperscript{44} in the literature. Hexagonal plates up to tens of nanometers in diameter are CaCO\textsubscript{3} (e.g. areas 3C, 3D, 4A), as are “corrugated” fibers (e.g. areas 3A, 3B). Such hollow CaCO\textsubscript{3} structures are known to precipitate in the presence of biomass templates such as starch.\textsuperscript{45} The ZnO particles generally appear to be coating the

![Fig. 4 SEM image of banana stalk hydrochar, impregnated with Zn\textsuperscript{2+} and calcined at 550 °C (BHZC), with approximate area of EDS spectra indicated by letters (A–D). Aggregates of finer-grained particles are ZnO, while hexagonal plates and corrugated fiber structures are CaCO\textsubscript{3}. Au peak is from the sputter-coated conductive coating.](image-url)
CaCO_3 particles. CaCO_3 is formed during the calcination as calcium naturally taken up by the biomass reacts with organic carbon and oxygen. In addition to forming separate hexagonal plates, the CaCO_3 appears to have biotemplated on the banana stalk fibers themselves. However, even the plates were porous and appear to have formed from smaller calcite crystals fused together. Proteins naturally present in the banana plant likely promote the growth of CaCO_3 crystals. The calcite form is thermodynamically more stable than the aragonite or vaterite forms of CaCO_3, and given the presence of large organic molecules in both the raw and hydrochar biomass, the calcite form is favored over aragonite.

We note from the SEM images and EDS analysis that few carbon-based fibers from the raw biomass (4D) remain, indicating complete calcination as suggested by the TGA data in Fig. 1. Table 1 shows the surface areas for the resulting ZnO materials. Though hydrothermal processing significantly increased the surface area of the banana stalk biomass, once impregnated and calcined, both BRZC and BHZC materials had similar surface areas, with that of the hydrochar’s particles slightly lower than those templated on the raw biomass. Our surface areas are higher than those reported in the literature for ZnO templated on fir wood, which showed a surface area of between 1.28 and 16.09 m² g⁻¹. The surface area results complement the SEM images (Fig. 3 and 4), which show similar composition and degree of heterogeneity of the calcined materials. To determine whether the carbonization has a significant effect on the efficacy of these particles, in addition to the physical characteristics, we turned to photocatalytic water treatment experiments.

### 3.3. Applicability of biotemplated ZnO–CaCO_3 materials to water treatment

Methylene blue dye was used as a model compound to simulate organic water pollutants in a test photocatalytic degradation experiment with BRZC and BHZC. As shown in Table 3, the raw biomass templated ZnO removed almost 50% of the MB from solution, while the hydrochar template biomass removed only 13%. From Fig. 5, we see that the concentration of MB in the vials exposed to UV light and biotemplated materials equilibrates after only 20 minutes.

Initially, the dye degradation appears to follow pseudo first order degradation kinetics (with respect to dye concentration), through the data at 15 minutes, such that:

\[
\ln \left( \frac{[MB]_0}{[MB]_t} \right) = k_{psf} t
\]

where \([MB]_0\) is the concentration of methylene blue in mg L⁻¹, \(t\) is the time in minutes, and \(k_{psf}\) is the observed pseudo first order rate constant, determined from Fig. 6. The \(k_{psf}\) for BRZC is 0.0122 ± 0.0018 min⁻¹ and for BHZC is 0.0262 ± 0.0018 min⁻¹ as shown in Table 3. These values are similar to those found for the photocatalytic degradation of acid orange 7 using ZnO nanopowder as a catalyst. However, a pseudo-first order equation does not fit data beyond 15 minutes of UV light exposure. This is likely attributed to the decrease in the

### Table 3

<table>
<thead>
<tr>
<th>Material</th>
<th>Removal efficiency</th>
<th>Pseudo first order kinetics (k_{psf}) (\text{min}^{-1}) (over 0–15 min)</th>
<th>(R^2)</th>
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<tbody>
<tr>
<td>BRZC</td>
<td>48.8%</td>
<td>0.0122 ± 0.0018</td>
<td>0.9904</td>
</tr>
<tr>
<td>BHZC</td>
<td>13.0%</td>
<td>0.0262 ± 0.0018</td>
<td>0.9593</td>
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</tbody>
</table>
number of active sites available on the catalyst surface over time, which could be a function of dye surrounding the catalyst particles, especially because of the CaCO₃ present in the heterogeneous material. Though both materials have similar surface areas, the raw banana biotemplated particles removed more than twice the amount of dye from solution, suggesting the BRZC has more active photocatalytic surface area. This, combined with the semi-quantitative XRD results showing a greater concentration of CaCO₃ in the BHZC versus the BRZC, suggests that the hydrochar retains a large portion of its initial calcium, which can occlude the photocatalytic treatment.

However, the presence of the CaCO₃ nanostructures opens then potential for treatment of complex contaminant mixtures of both organics, that can be degraded photocatalytically via ZnO as demonstrated here, as well as heavy metals such as Cd²⁺, Pb²⁺, Cr³⁺, Fe³⁺, and Ni²⁺ that have been shown to be removed from water using stabilized amorphous calcium carbonate nanoparticles. Calcium carbonates act as coagu-lants and buffers for acid mine wastewater treatment and to remove heavy metals from groundwater. Further studies are recommended to determine the possibility of removing both organics and inorganics from wastewaters using these heterogeneous materials.

4. Conclusions

This work demonstrates an integrated concept for the conversion of banana stalk, an agricultural waste with little intrinsic value, to liquid bio-fuels and solid biochar via hydrothermal carbonization. Zinc oxide nanostructures biotemplated onto the biomass and biochar demonstrated photocatalytic activity to degrade an aqueous organic dye. Calcium present in the banana plant was converted to calcite during oxidation of the impregnated biomass. This calcite appears to limit the photo-degradation degradation capacity of the zincite on the hetero-geneous biotemplated material. However, the calcium present may be beneficial to the remediation of water contaminated by both organic and heavy metals. It is recommended that future work explore the capacity of this calcite to treat mixed contaminant systems, as well as the impact of any additional (unidentifiable) mineral matter present on the overall water treatment system.

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