Electronic Supplementary Material (ESI) for Materials Advances.

Eco-friendly one-shot approach for producing a functionalized nano-torrefied biomass a new application of ball milling technology

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Materials and methods.

Materials

In this study, torrefied biomass and biochar derived from Populus nigra were subjected to prepared at low and high temperatures respectively, along with a slow heating rate of 10 °C/min, within an inert environment enriched with nitrogen gas (N_2= 12 slm). The torrefied biomass sample was labeled B1, indicating torrefaction at 285 °C, and B2, corresponding to biochar prepared at 450 °C. Dodecyl triphenyl phosphonium bromide (DTPPBr), a quaternary phosphonium salt (QPS), with a purity of 98%, and Resazurin were obtained from Sigma-Aldrich.

Feedstock and samples characterization

The biomass Populus nigra (P), and the torrefied biomass and biochar from Populous Nigra treated at low temperature (T= 285°C) and high temperature (450°C) were characterized through proximate analysis using TGA701 LECO using ASTM E870 procedure. Additional TGA analyses for B1 and B2 were performed using Q500 TA Instruments from 10 to 800°C at a heating rate of 10°C, under nitrogen. Ultimate analysis was performed with an elemental analyzer CHN 2000 LECO analyzer, using EDTA as standard based on CEN/TS 15104. The oxygen was obtained by difference considering the measured C, H, N, and ash content calculated on a dry basis (db). The content of inorganic species was determined by dissolving the samples via microwave-assisted acid digestion based on US-EPA Methods 3051 and 3052. A representative sample (200 mg) of biomass was dissolved in 10 ml 65% nitric acid and 1.5 ml H_2O_2. The vessel was sealed and heated in the microwave unit at 140 °C for 10 min, then 180 °C for 30 min (maximum power 1000 W). After cooling the digested samples were analyzed by ICP/MS. The detection limit for all the heavy metals in the biomass is 0.1 mg/kg. Biomass and torrefied biomass pH was evaluated by measuring with a digital pH meter (827 pH LAB, Metrohm) in deionized water using a 1:20 wt/wt ratio following the ASTM D4972-13 standard procedure., whereas the pH pzc was determined following the procedure reported in Mahmood et al., 2011. Torrefied biomass porosity was obtained using an Autosorb-1 (Quantachrome) instrument with N_2 at −196 °C as the adsorbate gas. Before analysis, the samples were degassed at 200 °C for 6 h under vacuum conditions. The surface area was evaluated using the Brunauer–Emmett–Teller equation (BET). Three replicates were conducted for all the analysis and characterization.

Experimental apparatus

Pyrolysis experiments were carried out in a fixed-bed reactor available at STEMS-CNR. The experimental set-up is composed of a fixed bed reactor equipped with a condensation system for the collection of the pyrolysis condensable phase. The system is controlled and monitored with a graphical interphase LABView.

The reactor configuration is flexible with respect to the pyrolysis operating variables (biomass size, pressure, gas flow, heating rate, and temperature).

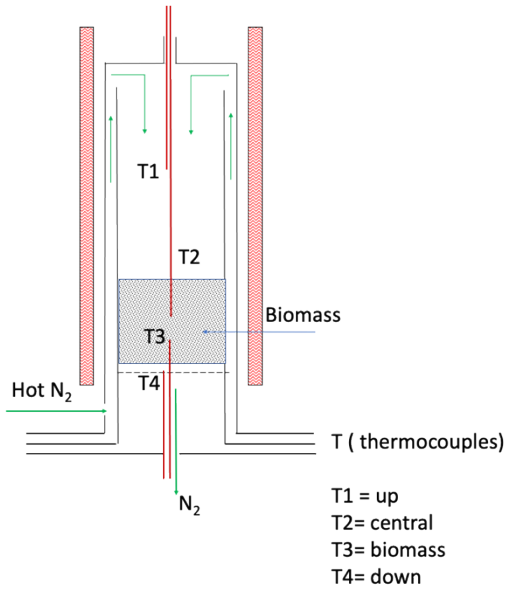

Figure 1. Pyrolysis reactor: Cross-section of the reaction chamber

The reactor consists of a cylindrical jacketed chamber (H= 465 mm; D= 134 mm for the internal cylinder; D= 160 mm for the external cylinder). N_2 flows into the jacket heated at the desired rate. Then the flow is reversed and enters the pyrolysis chamber that can host a biomass fixed bed, 9 cm height, corresponding to about 750 g of biomass in the pellet with size L and Ø: 1 x 0.5 cm. Along the chamber's longitudinal axis, four N-type thermocouples monitor the temperature. From the top of the reaction chamber, two thermocouples are positioned for the inlet N_2 temperature and the temperature in the biomass bed. At the outlet, the other two N-type thermocouples are allocated to measure the temperature in the lower section of the biomass bed, whereas the second one allows monitoring of outlet gas temperature. The condensable vapors pass through the biomass/char bed and exit the reactor. Then they are condensed in a water-cooled heat exchanger and collected in a flask, following the tar protocol procedure.
Pyrolysis tests were conducted at a constant flow of N_2 = 12.5 slm, heating rate (HR= 10 °C/min), and pressure (P= 5 x 10^5 Pa) heated up to the final temperature (T_{max}= 285 °C; T_{max}= 450 °C).

Preparation of Compounds by Ball Milling.

The ball-milling experiments were conducted using the planetary ball mill Pulverisette 7 Premium manufactured by Fritsch GmbH in Germany, operating at room temperature. The specific milling parameters employed for the experiments are outlined in Table 1. To carry out the procedures, an 80ml silicon nitride jar was utilized, along with silicon nitride balls measuring 10mm in diameter. The rotational frequency of the mill was set at 300 rpm, and the milling duration was fixed at 30 minutes. For the samples, they were denoted as B1/DTPP with weight ratios of 1/0.5, 1/1, 1/2, and 1/3. The temperature inside the milling jar was continuously monitored using the Easy-GTM system from Fritsch GmbH. During the 30-minute milling process, the temperature gradually rose

to 32 °C from the initial room temperature and remained stable throughout due to the milling procedure. The same methodology was applied to B2/DTPP with a weight ratio of 1/2.

Table 1. Experimental Conditions of the Ball Milling Experiments with Silicon Nitride Balls.

rotation frequency [min^{-1}]	300
ball-to-powder weight ratio	100
ball size [mm]	10
total balls weight [g]	15
milling tool material	Silicon nitride
beaker volume [cm^3]	80
B1+DTPP [mg]	150

Table 2. Experimental Conditions of the Ball Milling Experiments with Zr and TS balls.

	Zirconium Balls	**Tempered Steel Balls**
ball-to-powder weight ratio	160	214
rotation frequency [min^{-1}]	300	300
ball size [mm]	10	10
total balls weight [g]	24	32
beaker volume [cm^3]	80	80
B1+DTPP [mg]	150	150

B1/DTPP and B2/DTPP Characterization

Scanning electron microscope (SEM/EDS). SEM apparatus coupled with energy-dispersive X-ray spectroscopy (EDS) analysis (Phenom ProX with EDS detector-Phenom-World BV, Netherlands) was adopted for morphological characterization and element identification. All results were acquired using the ProSuite software integrated with Phenom Element Identification software, allowing for the quantification of the concentration of the elements present in the samples. Before the analysis, samples were covered with a thin film of gold by sputtering. SEM micrograph was imported and processes to evaluate the mean size of aggregates. Segmentation analysis allowed for separate the particles from the background. Automatic particle analysis requires a “binary”, black and white, image. A threshold range is set. Detected particles with circularity ranging from 0 to 1 were highlighted in black color. Area values were recorded while mean radius was calculated as $r=(area/\pi)^{0.5}$.

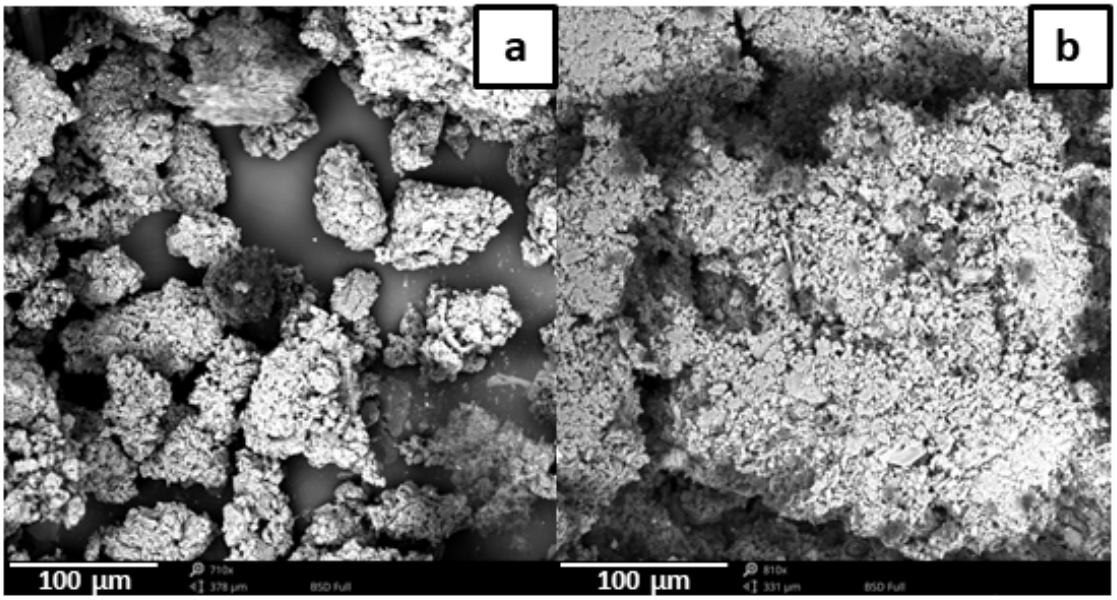

Figure 2. Sem images of B1/DTPP adduct obtained by a) Zr and b) TS balls.

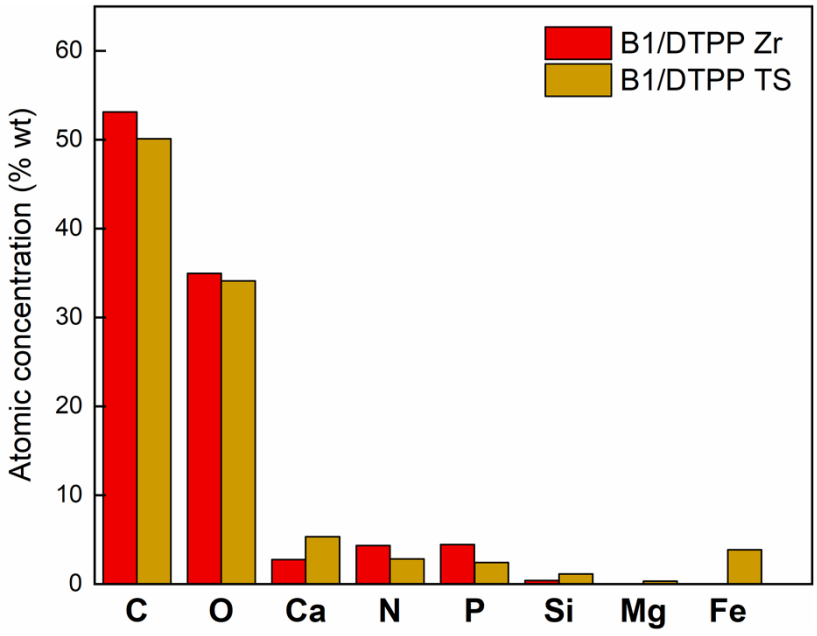

Figure 3. EDX maps of B1/DTPP adduct obtained by a) Zr and b) TS balls.

UV-vis Spectroscopy and Release Properties of B1/DTPP

UV-vis spectra were obtained using a PerkinElmer Lambda 800 UV-vis spectrophotometer. The release of DTPP+ from B1/DTPP in both neutral (10wt% NaCl) and acid (0.05 M HCl) aqueous solutions were measured over various soaking time intervals. To conduct the experiments, a nitrocellulose filter containing 8 mg of B1/DTPP was immersed in 20 ml of aqueous solution at room temperature with stirring. At different time points, aliquots of the solution were withdrawn using a syringe, and the concentration of released $DTPP^+$ was determined using a UV-vis spectrophotometer.

UV-vis Spectroscopy and photocatalytic properties of B1/DTPP

An aqueous solution of resazurin was prepared at a concentration of 1.5 µg/mL Coated cotton fabrics (COTTON-B1 and COTTON-B1/DTPP) were immersed in the resazurin solution and irradiated with a UV lamp (350 nm). Absorption spectra were recorded at regular time intervals.

Coating on cotton fabrics

Cotton fabrics (150 m^2/g) were cut into square samples (2cm x 2cm) and were immersed in B1 and B1/DTPP aqueous solutions (2%wt) under stirring. After 3 hours, the fabrics were taken from the solutions and washed with distilled water to remove excess of torrefied biomass from the surface. The obtained samples (named COTTON-B1 and COTTON-B1/DTPP) were allowed to dry at room temperature for 24 hours. The amount of torrefied biomass deposited on cotton (W_{BC}) was evaluated gravimetrically by employing the formula:

$$W_{BC} = W_f - W_i$$

Where W_i is the initial weight of the cotton fabric and W_2 is the final weight of the torrefied biomass-coated cotton fabric.

W_{B1} = 6.09 mg (+12% respect to uncoated cotton fabric)

$W_{B1/DTPP}$ = 7.95 mg (+16.5% with respect to uncoated cotton fabric)

Photocatalytic activity (Test with resazurin)

An aqueous solution of resazurin was prepared at a concentration of 1.5 µg/mL Coated cotton fabrics (COTTON-B1 and COTTON-B1/DTPP) were immersed in the resazurin solution and irradiated with a UV lamp (350 nm). Absorption spectra were recorded at regular time intervals.

DECONVOLUTION CURVES for COTTON-B1/DTPP

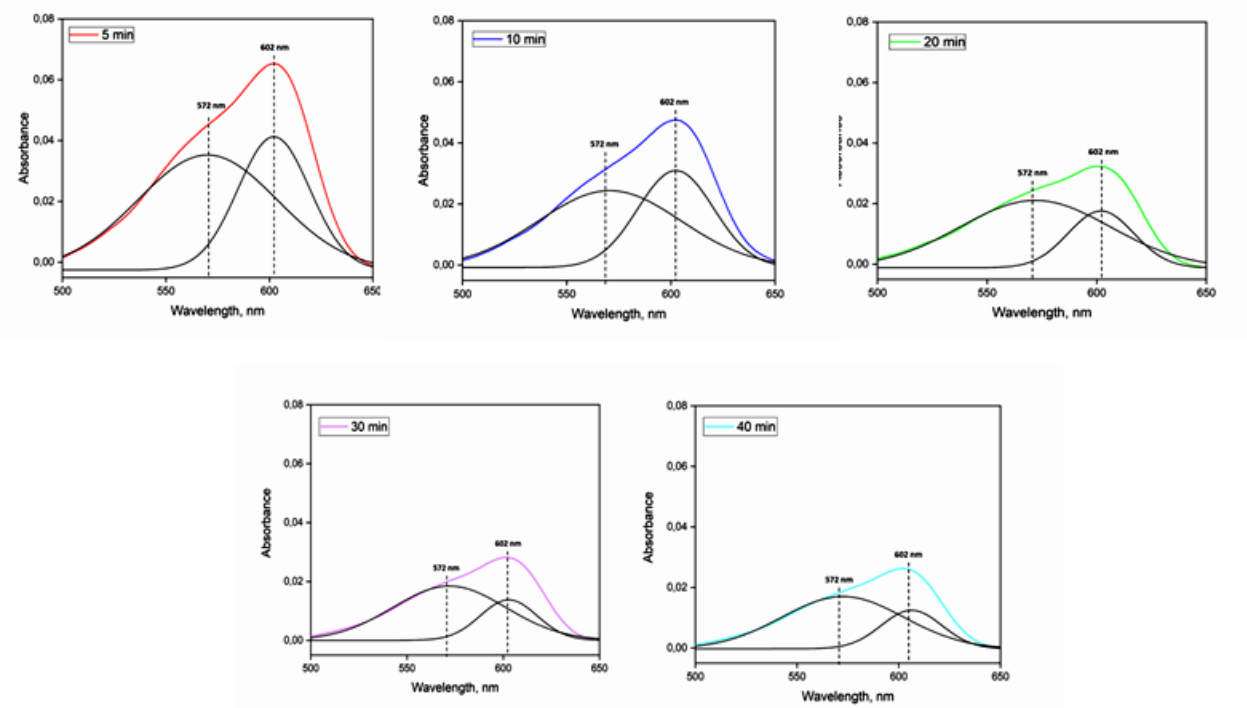

Figure 4. Deconvoluted spectra after 5,10,20,30 and 40 min of reaction in the presence of Resazurin.

It is evident from the deconvoluted spectra that as the exposure time increases, the intensity of the peak at 572 nm increases. To confirm that the dye was reduced through the photocatalytic activity of the B1/DTPP and not simply adsorbed by the cotton, a further test was conducted without UV irradiation. In this case, there is a slight decrease in the peak at 602 nm (probably due to physical adsorption), and above all no appearance of the peak at 572 nm. This is further confirmation of the sample's photocatalytic activity.

TEST ON COTTON-B1/DTPP (without lamp)

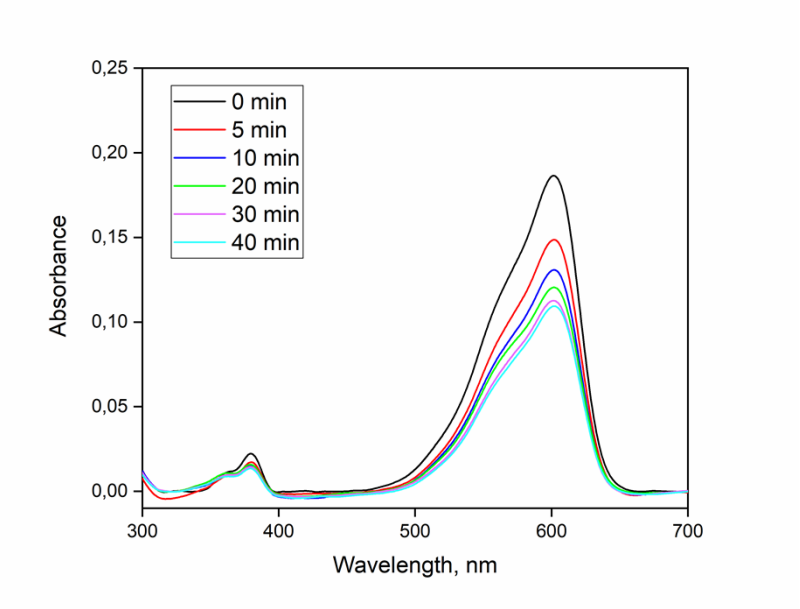

Figure 5. Photocatalytic activity of COTTON-B1/DTPP in resazurin aqueous solution without UV irradiation

DISPERSION AND PHOTOCATALYTIC TESTS ON COTTON/DTPPBr (with lamp)

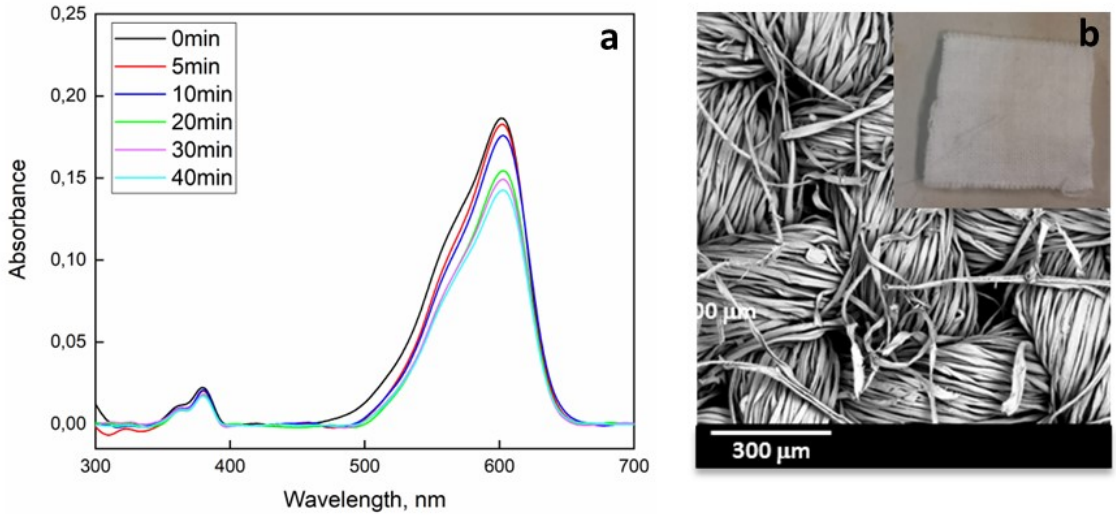

Figure 6. a) Photocatalytic activity of COTTON/DTPP in resazurin aqueous solution with UV irradiation and b) picture and SEM image of COTTON/DTPPBr.