SUPPORTING INFORMATION

The Role of Small Nanoparticles on the Formation of Hot Spots under Microwave-Assisted Hydrothermal Heating

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Description of the LC-DAD-MS/MS experimental conditions.

All chromatographic experiments were carried out through an HPLC Agilent Technologies 1200 Series (Agilent Technologies, Santa Clara, USA) configured with a degasser (G1322A), a quaternary pump (G1311A), an auto-sampler (G1329A), a column oven (G1316A) and a DAD detector. Dye and degraded products were analyzed by Welch Materials Xtimate column (150 mm × 4.6 mm, 5μm particle size). The mobile phase for a gradient procedure consisted of 0.1 mol L^{-1} ammonium acetate buffer and acetic acid (pH 5.3) and acetonitrile. The gradient elution was 5% (v/v) to 95% (v/v) in 30 min at 35°C, the flow rate was 0.8 mL min^{-1}, and the injection volume was 20 μL. The detection system by DAD was performed monitoring wavelengths between 200 and 700 nm. The acquired detector signal was recorded by Analyst software 1.5.2. After separation, the HPLC flow was directed to the MS inlet after 1:10 splitting. MS and MS/MS analyses were carried out through an API 2000 (AB/MDS Sciex, Framingham, MA, USA) with a Turbo Ion Spray electrospray ionization source operating in MS scan positive mode (ESI+). The mass range was between *m/z* 100 and 500; capillary voltage of 3.5 kV; cone voltage of 40 V; sheath gas (N_2) flow rate of 800 L h^{-1}; heated capillary temperature of 350°C; source temperature of 150°C. Nitrogen was used as the carrier, heater, and collision gases. The software Analyst v.1.5.2 (AB/MDS Sciex, Framingham, MA, USA) was used to control the equipment for data acquisition and analysis.

MB showed high sensitivity to the positive ionization mode by electrospray (ESI+) and the identification of the main stable compounds in the degradation process was performed by analyzing molecular ion peaks [M]+.

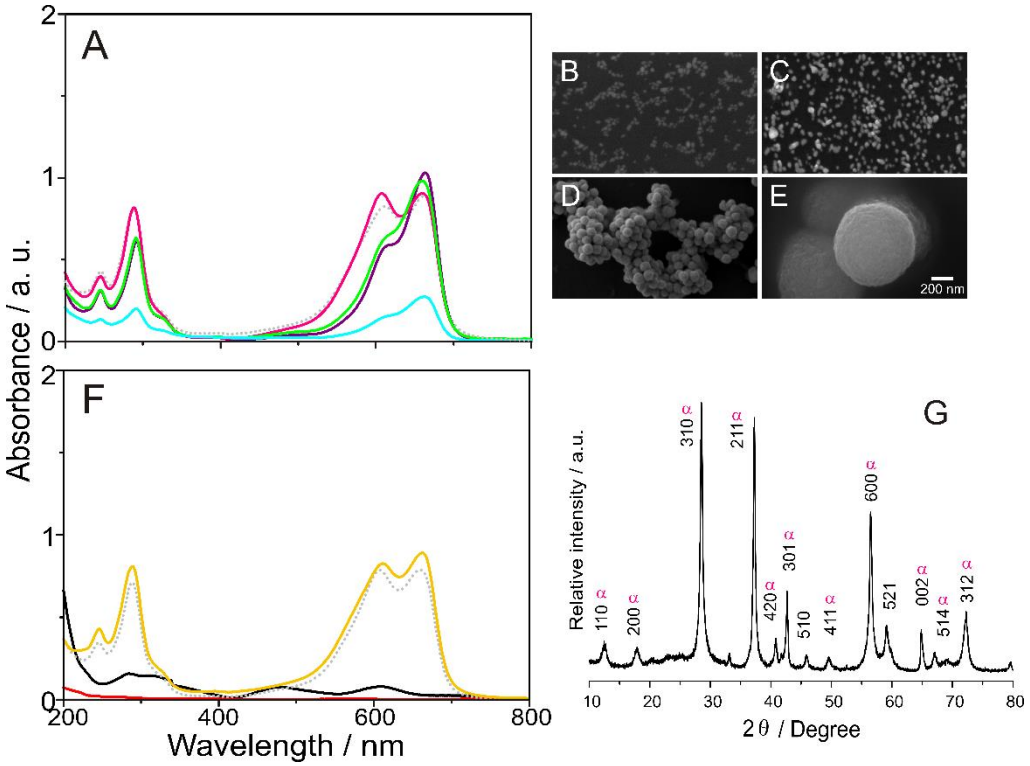

Figure S1. (A) UV/vis absorption spectra of methylene blue, after microwave heating at 200 °C for 180 min in the presence of TiO_2 NPs: (blue) 25 nm; (green) 50 nm; (purple) 100 nm and (pink) 700 nm, diameter. The dotted grey line corresponds to microwave heating at 200 °C for 180 min in the absence of TiO_2 particles, for comparison. (B-E) SEM images of TiO_2 NPs of 25 nm, 50 nm, 100 nm and 700 nm diameter, respectively. (F) Absorption spectra of methylene blue, after microwave heating at 200 °C for 180 min in the presence of: (black) 5 nm MnO_2; (yellow) 5 nm SiO_2 NPs. The dotted grey and the red lines correspond to the spectra of methylene blue after microwave heating at 200 °C for 180 min, in the absence and in the presence of 2 nm TiO_2 particles, respectively. (G) XRD pattern of 5 nm of highly crystalline α-MnO_2. (JPCDS #44-141).

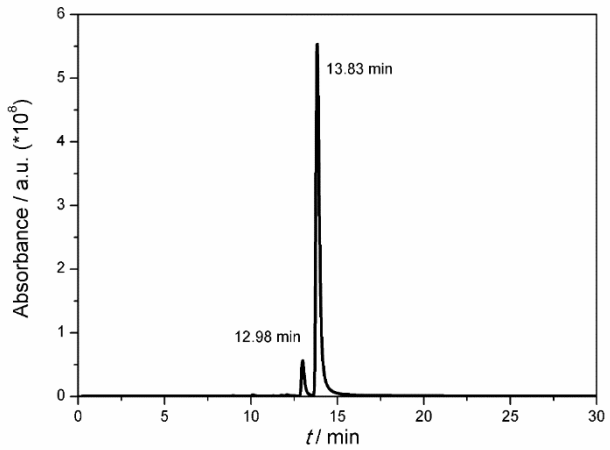

Figure S2. Typical chromatographic profile of MB.

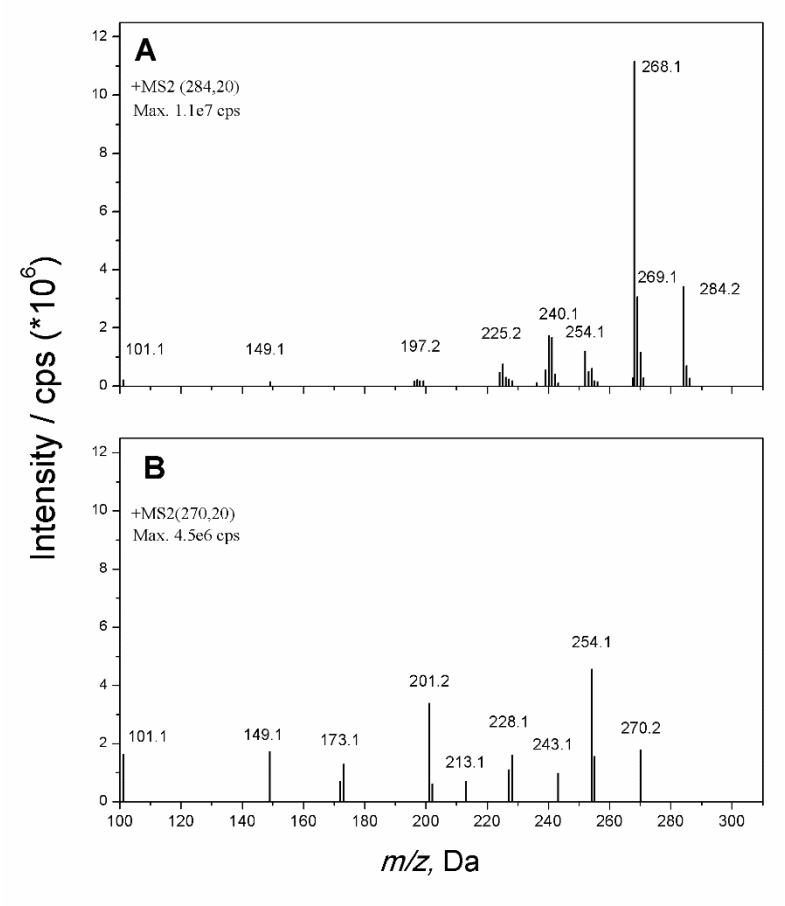

Figure S3. Mass spectra of detected intermediates in MB (blank) at (A) 13.9 min and (B) 13.0 min RT.

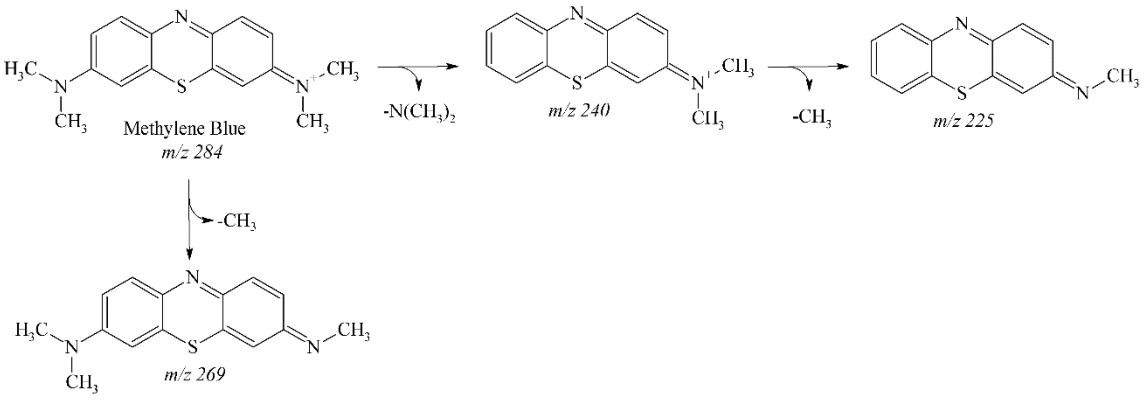

Figure S4. Principal fragments of MB, blank under positive ionization mode by electrospray (ESI+).

Table S1. Retention times and molecule correlation for peaks in Figure 4.

	Peak 1	Peak 2	Peak 3	Peak 4	Peak 5	Peak 6
MB (blank)	15.5 min	13.82 min				
30 min	15.5 min	14.0 min	13.3 min	13.0 min	12.1 min	11.8 min
60 min	15.5 min		13.3 min	12.9 min	12.3 min	11.8 min
120 min			13.3 min	12.9 min		11.8 min
	Oxidized Azure A	Methylene blue	Azure B isomer	Azure B	Azure A isomer	Azure A
	Oxidized Azure A		Oxidized Azure C	Oxidized Thionine		Oxidized thionine
	Oxidized Azure A		Oxidized Azure C	Oxidized Thionine		Oxidized Thionine

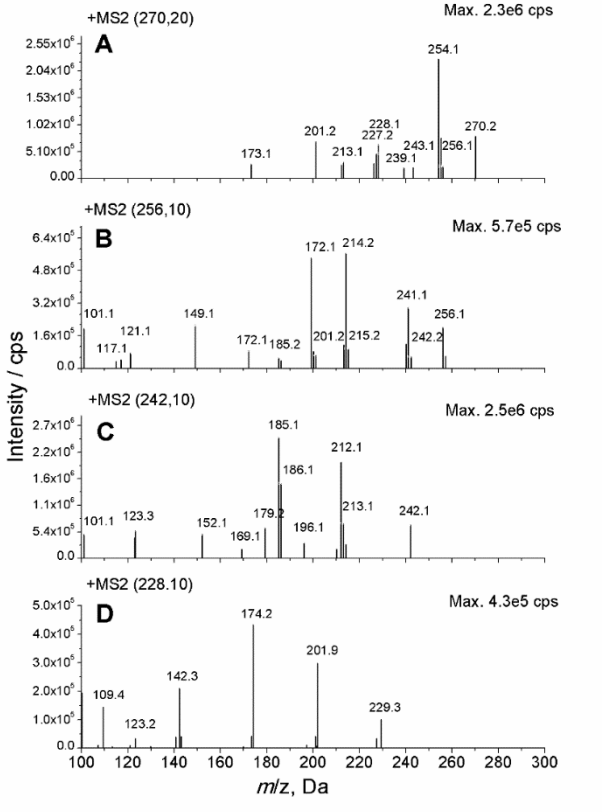

Figure S5. Mass spectra of MB molecular ion peaks: (A) Azure B, $C_{15}H_{16}N_3S$, m/z 270.2 Da; (B) Azure A, $C_{14}H_{14}N_3S$, m/z 256.1 Da; (C) Azure C, $C_{13}H_{12}N_3S$, m/z 242.1 Da; (D) Thionine, $C_{12}H_{10}N_3S$, m/z 229.3 Da, after microwave-assisted hydrothermal heating at 200 °C for 30 min, 60 min, 120 min and 180 min, respectively.

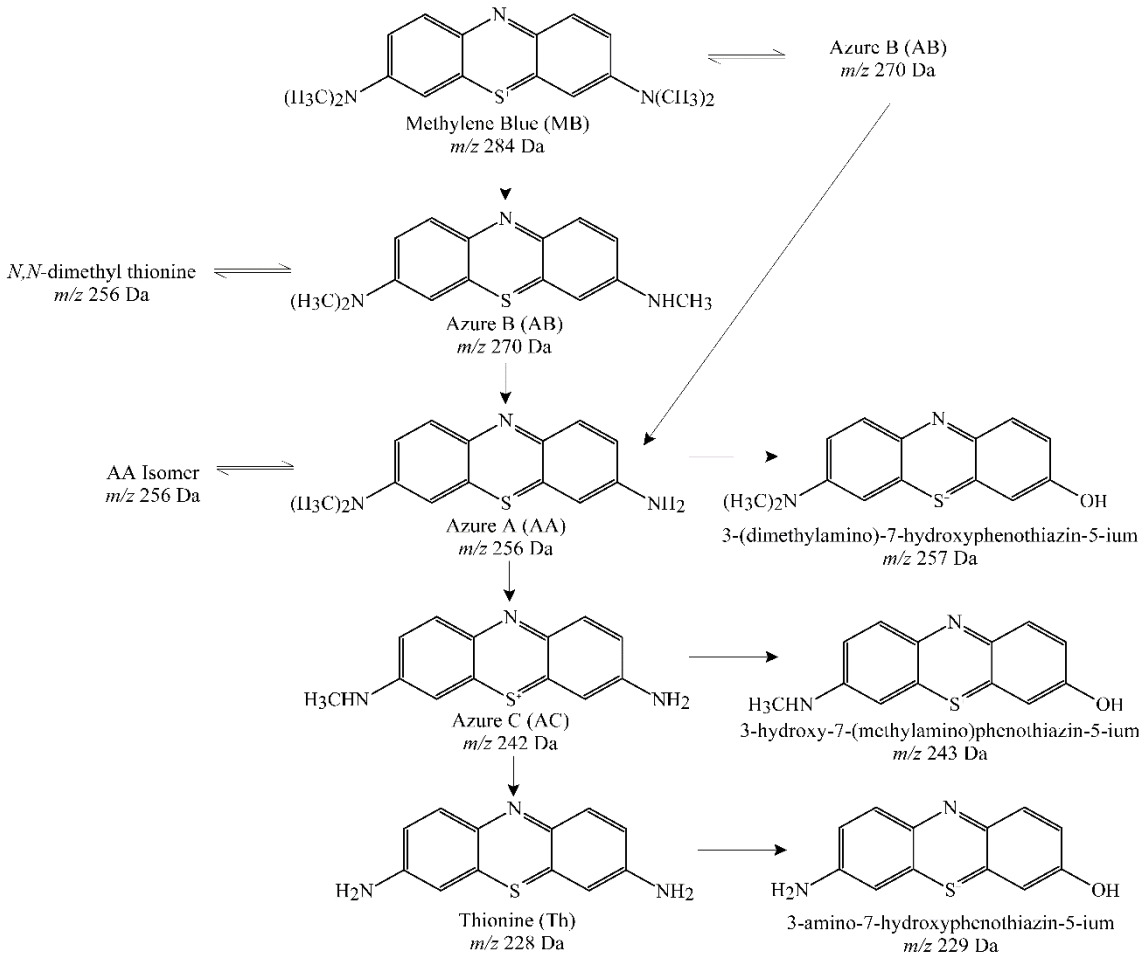

Figure S6. Proposed demethylation pathway of methylene blue under microwave-assisted hydrothermal heating at 200 °C for 180 min.

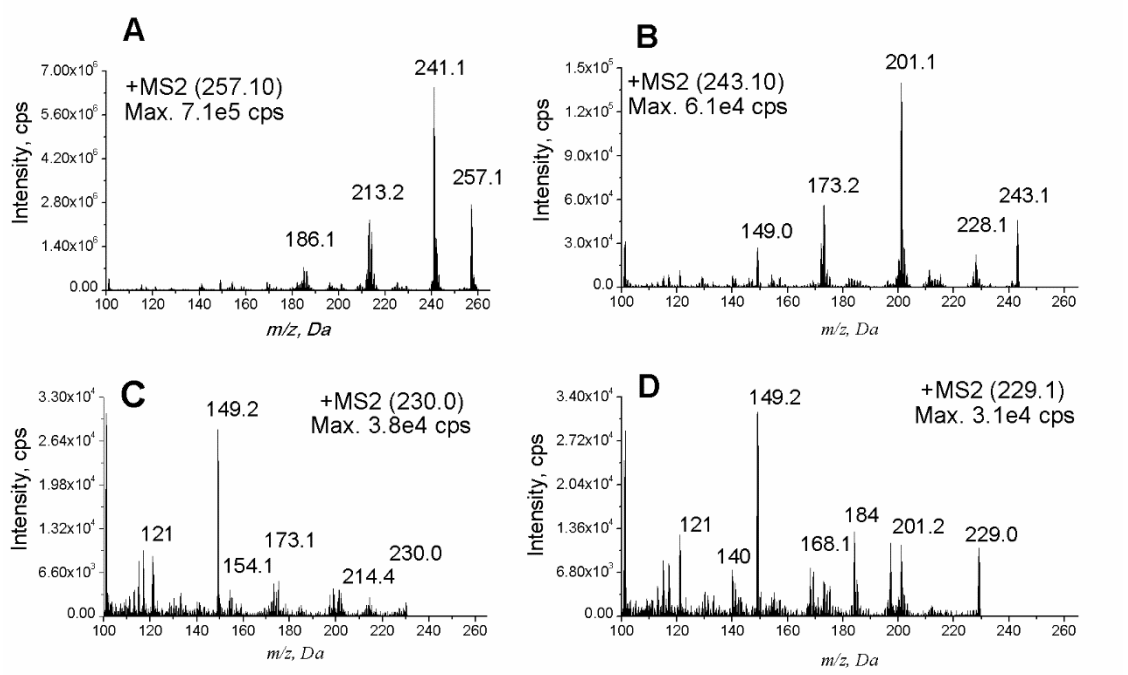

Figure S7. Mass spectra of intermediates after O_2 oxidation, eluting at (A) 15.5 min, oxidized azure A; (B) 13.3 min, $C_{13}H_{11}N_2OS$; (C) 12.9 min, $C_{12}H_8NO_2S$; (D) 11.8 min, $C_{12}H_9N_2OS$.

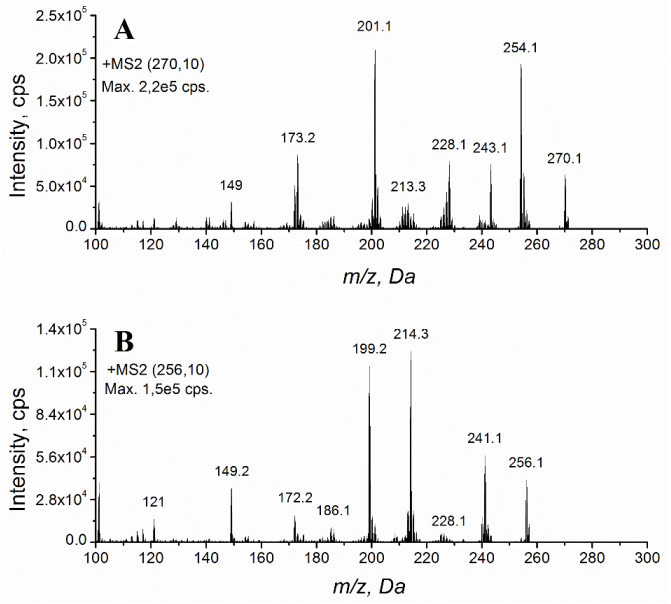

Figure S8. Mass spectra of methylene blue molecular ion peaks after microwave-assisted hydrothermal heating at 200 °C. (A) Azure B isomer, m/z 270.2 Da; (B) Azure A isomer, m/z 256.1 Da.

Table S2. Efficiency comparison with other results in literature. (MB = methylene blue; MO = methyl orange; X-3B = active brilliant red; CR = Congo red).

Method	Catalyst	Dye	Degradation / efficiency	ref
MW-assisted heating 40 W, 2.45 GHz	2 nm TiO_2 1 mg mL^{-1}	100 ppm MB	3 h, 92%	Ours
Microwave-photodegradation 700 W, 2.45 GHz	180–250 μm TiO_2 4 g L^{-1}	100 ppm X-3B	3 h, 92%	35a
MW-electroFenton	Fe(III)/Fe(II) redox cycles	300 ppm MO	3 h, 80%	35b
MW-assisted heating 300 W, 2.45 GHz	MnO_2 2 g L^{-1}	10 ppm MB	10 min, 92%	11
Microwave-photodegradation 800 W, 2.45 GHz λ > 420 nm, 88 W	RGO/Mn_3O_4	20 ppm MB	1 h, 60%	33
Photodegradation 6 W, λ = 365 nm	Chitin–TiO_2 composite	10 ppm MB	4 h, 98%	35c
Photodegradation 60 μW cm^{-2}, λ = 365 nm;	TiO_2 film 50 mm^2	116 μM MB	6 h, 80%	31a
Photodegradation. sunshine (21 June 2016; north latitude 26°08′, east longitude 119°30′)	Polyoxo-Ti clusters 70 mg mL^{-1}	200 ppm MB	8 min, 35%	35d
Photodegradation 12 W, λ = 365 nm	Ta-TiO_2 nanofibers 1 mg mL^{-1}	40 μM MB	4 h, 90%	35e
Photodegradation 15 W, λ = 365 nm	N-TiO_2 1 mg mL^{-1}	25 ppm MB	80%	35f
Electrochemical	K^+-MnO_2	35 ppm CR	16 h, 60%	35g

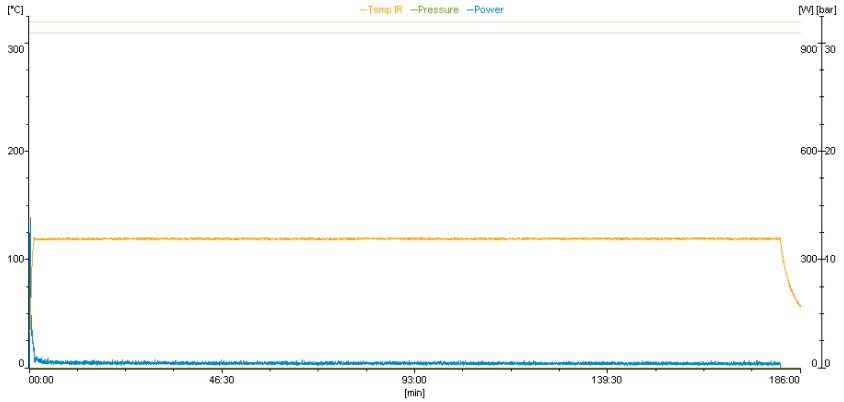

Figure S9. Registered temperature (orange line), pressure (green line) and output power (blue line) during the degradation of MB under microwave-assisted hydrothermal heating at 120 °C.

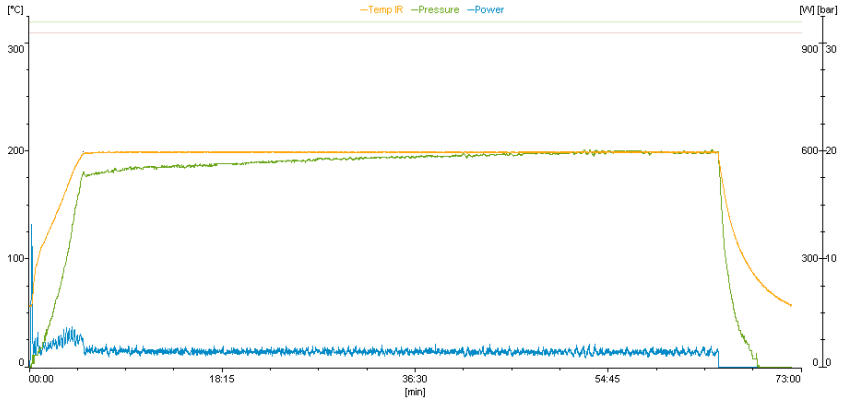

Figure S10. Registered temperature (orange line), pressure (green line) and output power (blue line) during the degradation of MB under microwave-assisted hydrothermal heating at 200 °C.