Supplementary Data

Electroactive biochar outperforms highly conductive carbon materials for biodegrading pollutants by enhancing microbial extracellular electron transfer

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Cyclic voltammetry analysis

The characterization by cyclic voltammetry was carried out in an H-type electrochemical cell (Fig. S5). The anodic and cathodic chambers were separated by a proton exchange membrane (Nafion). Single granules of the three different conductive materials (G, C and BQ) were used as working electrodes, all in the same anodic chamber (under similar environment). The granules of each material (of ca. 1 cm^2) were attached to a wire for external connection. An Ag/AgCl/Cl-(sat.) reference electrode was also placed in this chamber. A graphite plate (3.0 x 1.5 cm) was used as a counter electrode.

The anodic chamber had a volume of 200 mL of Fresh Water Medium (FWM) with 20 mM acetate as electron donor. This medium was inoculated with 20 mL of Geobacter sulfurreducens pure culture with an OD=0.6. Immediately after inoculation, a cyclic voltammetry of each of the granules was made (experiment referred to as t=0). Next, the granules were simultaneously polarized at 0.2 V (vs. Ag/AgCl/Cl-) for 7 days to promote biofilm growth. After this time, a cyclic voltammetry of each of the granules was made again (experiment referred to as t=7).

The voltammetric analysis of the granules was performed sequentially, one by one, using a potentiostat (Nanoelectra NEV-4). The scan rate was 10 mV/s and the potential range -0.6V - +0.6V (vs Ag/AgCl/Cl-). For the potentiostatic polarization, the three conductive granules were simultaneously connected to the same potentiostat. Despite the different electrical resistances of the different materials, the successful polarization (at the same potential) of each granule was confirmed by using a multichannel multimeter (Keithley 2700) connected in series between each granule and the reference electrode.
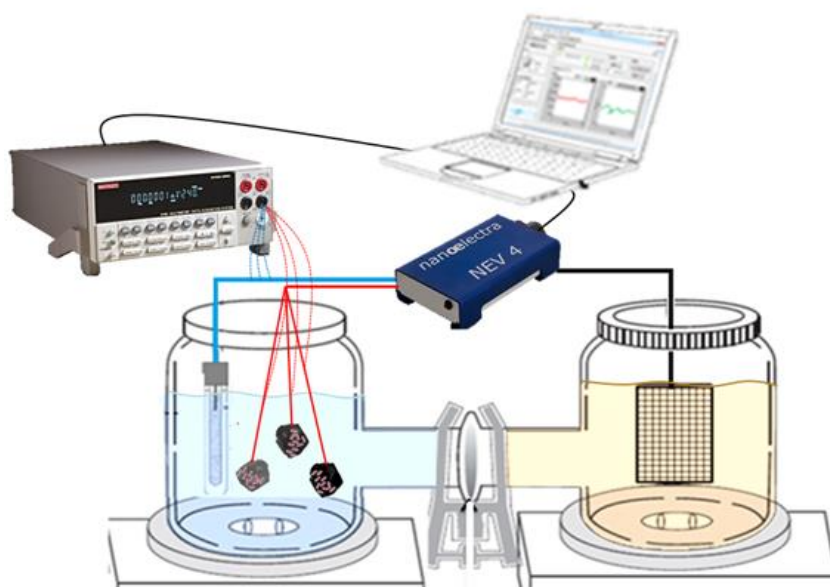

Fig. S1. Scheme of the used H-type cell and experimental set-up to carry out the voltammetric characterization of single granules of the different conductive materials and the potentiostatic treatment to promote biofilm growth.
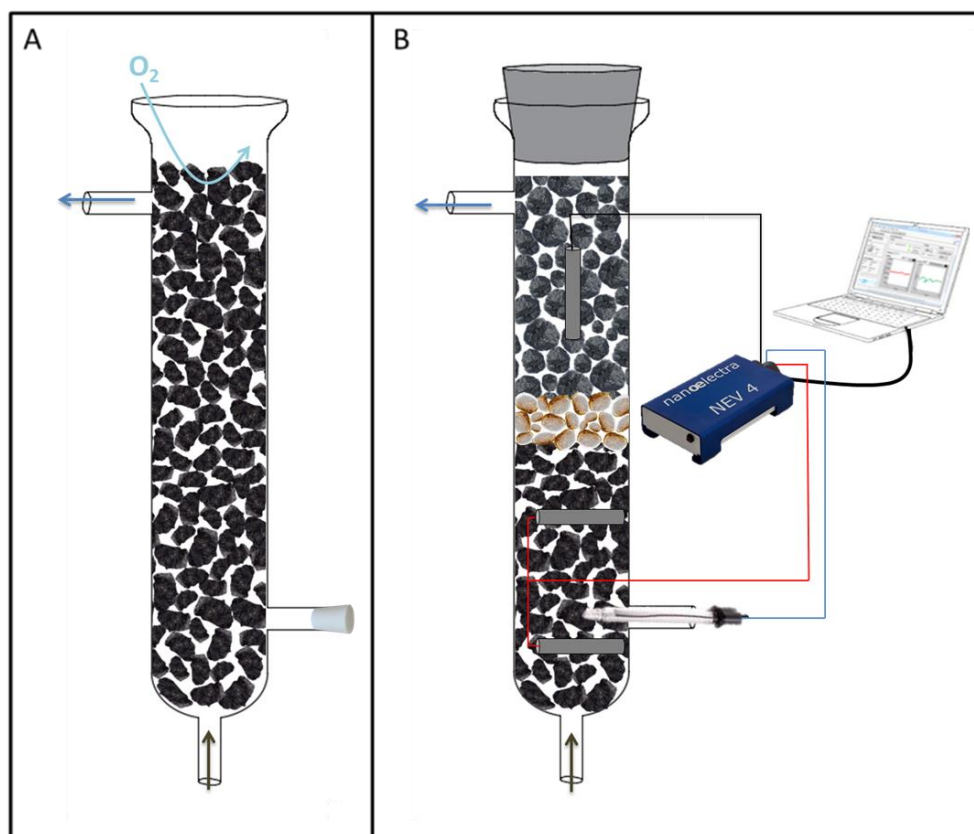
Fig. S2. Scheme of the used laboratory-scale upflow electroconductive biofilters: A. single-electrode (snorkel) configuration; B. three-electrode configuration, with the anode (down), the counter-electrode (up), and the reference electrode (buried in the anode).
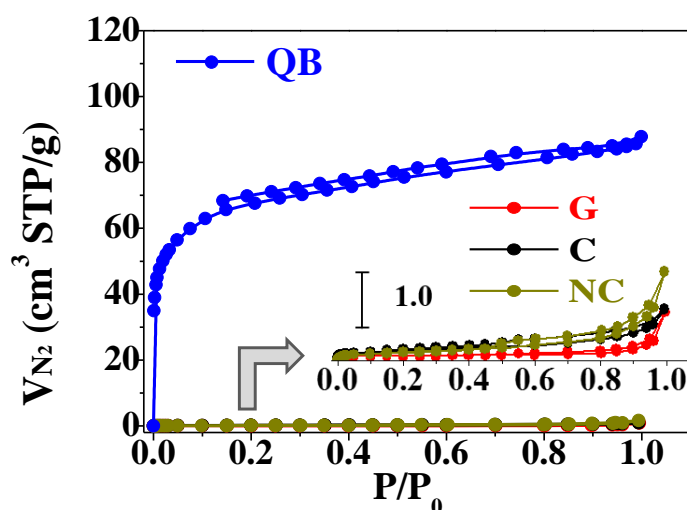

Fig. S3. N_2 adsorption-desorption isotherms at -196 ° C of the bed materials before being used as electrogenic biofilters: G = graphite; C = coke; QB = Quercus biochar; NC = gravel.
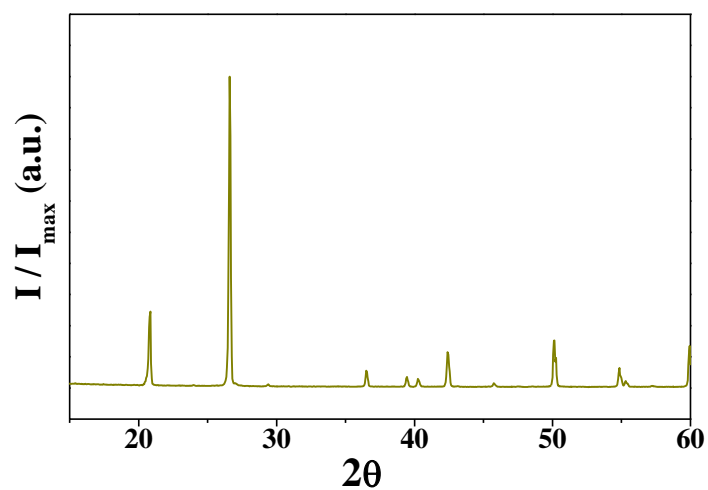
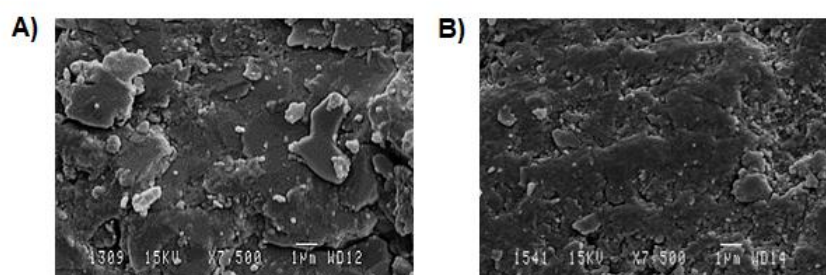**Fig. S4.** X-ray diffractogram of the gravel (NC).

Fig. S5. SEM micrographs of gravel before (A) and after (B) be used as material for biofilter operation.

Table S1. Characteristics of influent real urban wastewater after the Inhoff tank (average ± SD)		
Parameter	Value	Units
pH	7.2 ± 0.4	---
Conductivity	1335 ± 307	µS/cm
Dissolved oxygen	1.0 ± 0.6	mg/L
Redox potential (ORP)	-175 ± 55	mV
Total suspended solids (TSS)	166 ± 111	mg/L
Volatile suspended solids (VSS)	117 ± 58	mg/L
BOD_5	238 ± 134	mg/L
COD	805 ± 98	mg/L
Total nitrogen (TN)	51.7 ± 13.4	mg N/L
Ammonium nitrogen (NH_4N)	41.4 ± 15.5	mg N/L
Nitrate nitrogen (NO_3N)	2.0 ± 4.8	mg N/L
Total phosphorous (TP)	7.1 ± 3.0	mg P/L

Table S2. Width (FWHM) and position as well as the calculated interlayer spacing and crystallite dimensions for the characteristic diffraction peaks of the graphite crystalline structure for graphite (G), coke (C) and biochar (QB) materials.

Sample	h k l [a]	FWHM[b] °2θ	Peak pos.[c] °2θ	d-spacing[d] (c/a) Å	Crystallite size[e] (Lc/La) Å
G	0 0 2	0.180	26.577	3.35343	628
C	0 0 2	3.768	25.404	3.50554	22
QB	0 0 2	8.392	23.520	3.78191	10
G	1 0 0	0.309	42.404	2.13130	653
C	1 0 0	3.846	43.207	2.09353	43
QB	1 0 0	8.050	43.810	2.06611	20

a Crystallographic planes (Miller indices) of graphite.
b Full Width at Half Maximum.
c Position of the peaks corrected from the position of the standard Si.
d Distance between the planes of the crystalline lattice calculated from the angle of Bragg by the law of Bragg
e Vertical (Lc) or horizontal (LA) microcrystal size calculated from the width of the peaks (002) or (10), respectively, by the Scherrer equation.

Table S3. Spectral parameters from the most important Raman bands of graphite (G), coke (C) and biochar (QB) materials.

Sample	D		G			2D	
	v_D cm^{-1}	Δv_D cm^{-1}	v_G cm^{-1}	Δv_G cm^{-1}	I_D/I_D+I_G %	v_{2D} cm^{-1}	Δv_{2D} cm^{-1}
G	1350.2	41.1	1579.5	21.3	5.0	2705.6	57.7
C	1359.0	127.3	1598.7	57.5	42.7	2695.5	130.0
QB	1343.5	182.0	1587.4	77.2	44.4	2694.5	283.0

Table S4. Surface chemical composition according to XPS analysis for graphite (G), coke (C) and biochar (QB), before and after being used as polarized electrogenic biofilter bed at 0.6 V.

Sample	Mass surface composition (%)						ΔO	ΔN	ΔFe
	C	O	P	S	N	Fe			
G	98.3	1.7	0.0	0.0	0.0	0.0			
G0.6	87.6	7.5	2.3	0.6	0.8	1.2	5.8	0.8	1.2
C	88.1	10.0	0.0	1.1	0.8	0.0			
C0.6	85.4	11.3	0.0	1.5	1.1	0.7	1.3	0.3	0.7
QB	81.0	16.7	0.9	0.4	0.9	0.0			
QB0.6	77.6	15.5	1.9	1.0	1.7	2.4	---	1.2	2.4