Supplementary Materials: Article Title

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2.2. Effect of MWCNT on Methane Production by Anaerobic Sludge

For acetate and butyrate, since their degradation was slower, these measurements were continued, at larger time intervals, until the recorded values of methane production reached more than 50% of the theoretical (calculated based on the stoichiometry of the reactions presented in Table S1)..

Table S1. Reactions involved in ethanol and butyrate oxidation, and their corresponding standard Gibbs free energy changes

Reaction no.	Equation	$\Delta G^{0'}$ (kJ reaction^{-1})[1]
1	*Ethanol oxidation* $C_2H_5OH + H_2O \rightarrow C_2H_3O_2^- + H^+ + 2\ H_2$	+9.6
2	*Butyrate oxidation* $C_4H_7O_2^- + 2\ H_2O \rightarrow 2\ C_2H_3O_2^- + H^+ + 2\ H_2$	+48.3
3	*Acetoclastic methanogenesis* $C_2H_3O_2^- + H_2O \rightarrow CH_4 + HCO_3^-$	-31.0
4	*Hydrogenotrophic methanogenesis* $4\ H_2 + HCO_3^- + H^+ \rightarrow CH_4 + 3\ H_2O$	-135.6
5	*Syntrophic ethanol oxidation to methane* $C_2H_5OH + 0.5\ H_2O \rightarrow 1.5\ CH_4 + 0.5\ HCO_3^- + 0.5\ H^+$	-89.2
6	*Syntrophic butyrate oxidation to methane* $C_4H_7O_2^- + 2.5\ H_2O \rightarrow 2.5\ CH_4 + 1.5\ HCO_3^- + 0.5\ H^+$	-81.5

2.3. Effect of MWCNT on Methane Production by the Indigenous Microorganisms in River Sediment

Sediment samples were collected in Ribeira da Granja, close to the Granja beach (Vila Nova de Gaia, Portugal) (Figure S1)

Figure S1. Sediment sampling in Ribeira da Granja, Vila Nova de Gaia, Portugal

3.1. Effect of MWCNT on Methane Production by Anaerobic Sludge

SMPR from acetate correlated highly with MWCNT concentration, as shown by the calculated correlation coefficient of 0.998 (Figure S2)

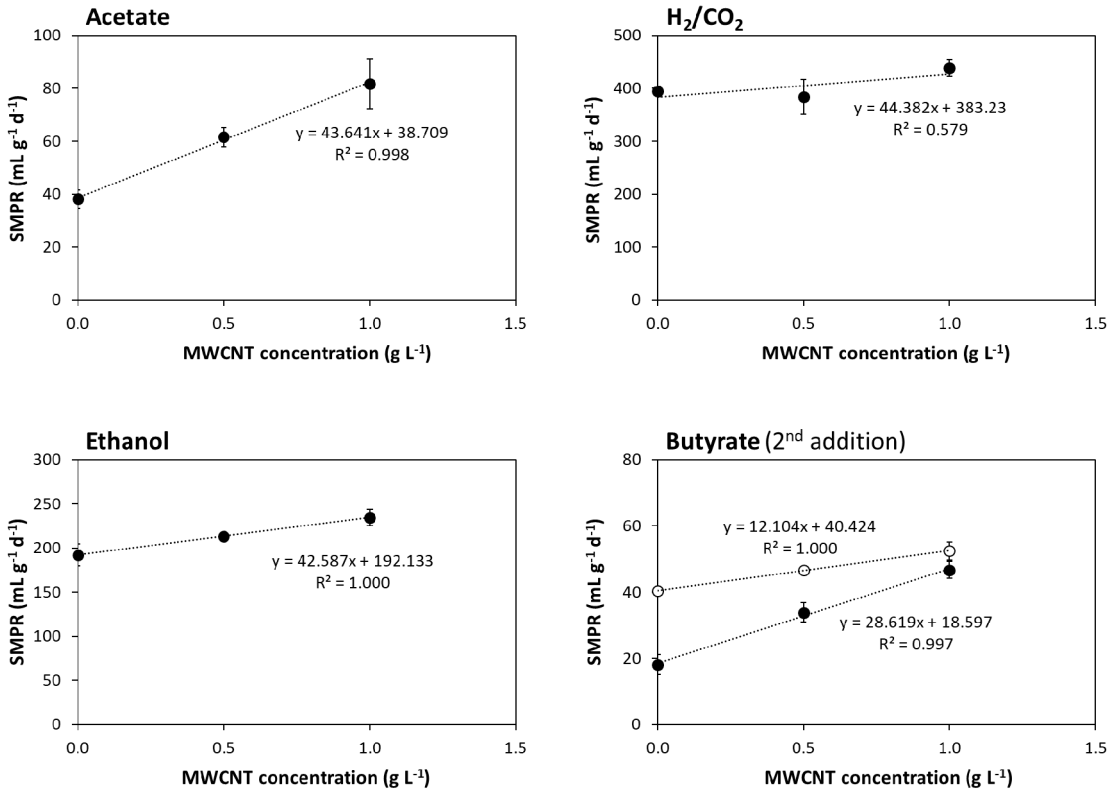

Figure S2. Linear correlation between MWCNT concentration and the specific methane production rate (SMPR) for acetate (a), H2/CO2 (b), ethanol (c) and butyrate (2nd addition, t = 0-20 h and t > 20 h) (d). Each point is the average of three experimental replicates.

The conversion of butyrate to methane took more than 10 days and no methane was produced during the first three days, showing the very low butyrate degrading activity of the community (Figure S3).

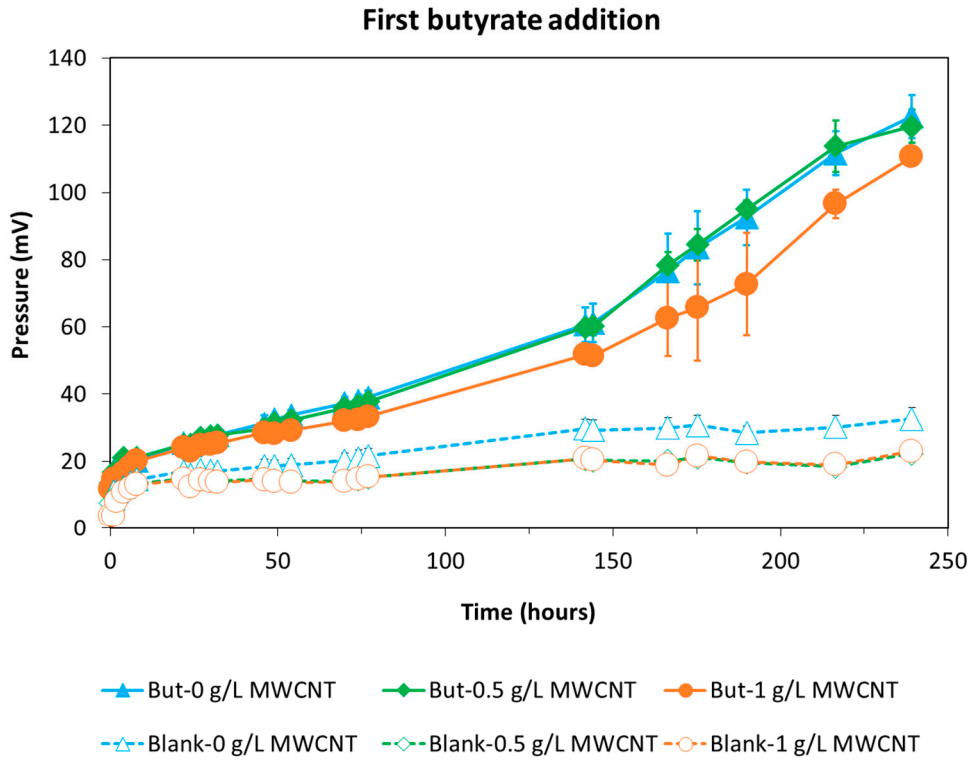

Figure S3. Pressure (mV) increase in the assays amended with butyrate (first addition), in the presence of different MWCNT concentrations: 0 g L-1 ( ), 0.5 g L-1 (•) and 1.0 g L-1 (•). Blank assays (no added substrate) are also shown (open symbols). The results presented are the averages and standard deviations for triplicate assays.

3.2. Effect of MWCNT on Methane Production by the Indigenous Microorganisms in River Sediment

ORP varied between −100 and −194 mV, and was higher (~45 to 50 mV difference) in the assays with MWCNT-Fe, relatively to the other conditions tested (Figure S4).

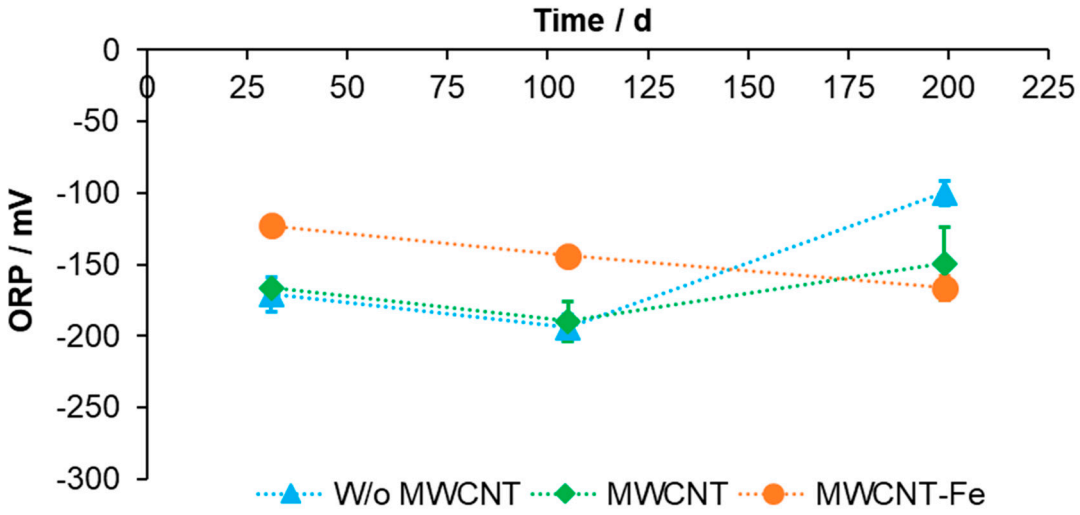

Figure S4. ORP values measured in the assays performed with river sediment in the absence of MWCNT (W/o MWCNT), and in the presence of MWCNT or MWCNT-Fe