Dissolved ozone decomposition in presence of activated carbon at low pH: how experimental parameters affect observed kinetics of the process.

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**Supplementary information**

Numbers in italics above following tables figures and paragraphs correspond with numbers of paragraphs in Main Document, in which a particular table/figure/paragraph is mentioned first time.

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| Table S1. Activated carbon characterization | | | |
| Carbon name | AS | F300 | F400 |
| Specific surface SBET [m2 g-1] | 1155 | 790 | 789 |
| Porosity [cm3 g-1] | 1.11 | 0.55 | 0.57 |
| Average pore diameter [nm] | 3.83 | 2.77 | 1.45 |
| pHpzc [-] | 7.13 | 7.51 | 10.05 |
| Acidity [mval g-1] | Not analyzed | 0.120 | 0.000 |
| Basicity [mval g-1] | Not analyzed | 0.621 | 0.621 |
| Elementary analysis [mass%] | 84.5 C, 2.4 H, 1.3 N, 0.31 S | 0.45 N, 89.38 C, 0.93 H, 0.69 S | 0.397 N; 88.09 C; 0.755 H; 0.685 S |
| Ash [mass%] | 0.07 | 5.8 | 7.1 |

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| Table S2: Activated carbon fractions. Geometric model based on following data is described with Fig. S19. | | | |
| Carbon fraction [mm] | Average carbon granule diameter [mm] | Geometric surface of a single spherical carbon grain [mm2] | Growth of geometric surface per mass unit of carbon (biggest grain = 100%) [%] |
| 0.063-0.125 | 0.0940 | 0.295 | 1330 |
| 0.125-0.250 | 0.1875 | 0.589 | 667 |
| 0.250-0.315 | 0.2825 | 0.887 | 442 |
| 0.315-0.400 | 0.3575 | 1.123 | 350 |
| 0.400-0.500 | 0.4500 | 1.414 | 278 |
| 0.500-1.000 | 0.7500 | 2.356 | 167 |
| 1.000-1.500 | 1.2500 | 4.909 | 100 |

*3.1*

Figure S1: Natural logarithm of dissolved ozone molar concentration against time, for three subsequent ozone decomposition experiments on the same portion of carbon. ○: 1st experiment, ∆: 2nd experiment, □: 3rd experiment. Conditions: active carbon amount 1g L-1, initial pH = 2.00, initial ozone concentration = 6.5±0.5mg L-1.

Figure S2: Square root of dissolved ozone molar concentration against time, for three subsequent ozone decomposition experiments on the same portion of carbon. ○: 1st experiment, ∆: 2nd experiment, □: 3rd experiment. Conditions: active carbon amount 1g L-1, initial pH = 2.00, initial ozone concentration = 6.5±0.5mg L-1.

*3.3*

According to (pseudo)first order kinetics; points not fitting the assumed curves are omitted. This procedure was found to be applicable only if carbon dose was equal to or higher than   
1g L-1 (for F400 carbon, in given conditions). For that reason, only these results are presented in Fig. S9. Data values are given in Tab. S3.

Figure S3: Natural logarithm of dissolved ozone molar concentration against time, for various active carbon amounts: ♦: 1g L-1, ■: 2g L-1,●: 5g L-1.Conditions: Initial pH = 2.00, initial ozone concentration = 6.5±0.5mg L-1. Points not fitting the assumed curves are omitted.

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| Table S3: Rate constants and linearity (R2 parameter) for ozone decomposition processes for highest activated carbon amounts. Values for (pseudo)first order kinetics (Fig. S9). Non-fitting data points discounted. Symbols are corresponding with symbols in Fig. S9. Corresponding values covering all data points are also given (*italics*). | | |
| Activated carbon dose [g L-1] | (Pseudo)first order rate constant [min-1] | R2 [%] |
| 1.00 (♦) | 0.0203 *(0.0212)* | 99.49 *(98.89)* |
| 2.00 (■) | 0.0574 *(0.0728)* | 99.43 *(92.29)* |
| 5.00 (●) | 0.1602 *(0.2508)* | 99.51 *(87.44)* |

Figure S4: Natural logarithm of dissolved ozone molar concentration against time, for various active carbon amounts (description of symbols in Table S4, right below). Conditions: Initial pH = 2.00, initial ozone concentration = 6.5±0.5mg L-1. Chart A) carbon dose range 0.0-0.2g L-1, chart B) carbon dose range 0.2-5.0g L-1.

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| Table S4. Rate constants of ozone decomposition processes in presence of various activated carbon amounts. Values for (pseudo)first (Fig. S4) order kinetics. Symbols are corresponding with symbols in Fig. S4. | |
| Carbon amount  [g L-1] | (Pseudo)first order rate constant [min-1] |
| 0 (◊) | 0.0042 |
| 0.01 (□) | 0.0046 |
| 0.05 (+) | 0.0056 |
| 0.1 (⁎) | 0.0063 |
| 0.2 (×) | 0.0088 |
| 0.35 (○) | 0.0127 |
| 0.5 (▲) | 0.0161 |
| 1 (♦) | 0.0212 |
| 2 (■) | 0.0728 |
| 5 (●) | 0.2508 |

Figure S5: Reciprocal of dissolved ozone molar concentration against time, for various active carbon amounts (◊: 1g L-1, □: 2g L-1, ○: 5g L-1). Conditions: Initial pH = 2.00, initial ozone concentration = 6.5±0.5mg L-1

Figure S6: Reciprocal of dissolved ozone molar concentration against time, for various active carbon amounts (◊: 1g L-1, ○: 0.5g L-1,□: 0.35g L-1, ∆: 0.2 g L-1 ). Conditions: Initial pH = 2.00, initial ozone concentration = 6.5±0.5mg L-1.

Figure S7: Reciprocal of dissolved ozone molar concentration against time, for various active carbon amounts (∆: 0.2g L-1, ○: 0.1g L-1, □: 0.05g L-1, ◊: 0.01g L-1, +: 0g L-1). Conditions:   
Initial pH = 2.00, initial ozone concentration = 6.5±0.5mg L-1.

Figure S8: Dissolved ozone molar concentration against time, for two active carbon amounts (□: 2g L-1 ○: 5g L-1). Conditions: Initial pH = 2.00, initial ozone concentration =   
6.5±0.5mg L-1.

Figure S9: Square root of dissolved ozone molar concentration against time, for two active carbon amounts (□: 2g L-1 ○: 5g L-1). Conditions: Initial pH = 2.00, initial ozone concentration = 6.5±0.5mg L-1.

Figure S10: Natural logarithm of dissolved ozone molar concentration against time, for two active carbon amounts (□: 2g L-1 ○: 5g L-1). Conditions: Initial pH = 2.00, initial ozone concentration = 6.5±0.5mg L-1.

Figure S11: Square root of reciprocal of dissolved ozone molar concentration against time, for two active carbon amounts (□: 2g L-1 ○: 5g L-1). Conditions: Initial pH = 2.00, initial ozone concentration = 6.5±0.5mg L-1.

Figure S12: Reciprocal of dissolved ozone molar concentration against time, for two active carbon amounts (□: 2g L-1 ○: 5g L-1). Conditions: Initial pH = 2.00, initial ozone concentration = 6.5±0.5mg L-1.

Figure S13: Square root of dissolved ozone molar concentration against time, for various active carbon amounts (symbols explained in Tab. S5, right below). Conditions: Initial pH = 2.00, initial ozone concentration = 6.5±0.5mg L-1. Chart A) carbon dose range 0.0-0.2g L-1, chart B) carbon dose range 0.2-5.0g L-1.

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| Table S5. Rate constants of ozone decomposition processes in presence of various activated carbon amounts. Values for half order (Fig. S13) kinetics. Symbols are corresponding with symbols in Fig. S13 | |
| Carbon amount  [g L-1] | Half order rate constant  [(√(mol L-1)) min-1] |
| 0 (◊) | 0.454×10-4 |
| 0.01 (□) | 0.527×10-4 |
| 0.05 (+) | 0.583×10-4 |
| 0.1 (⁎) | 0.698×10-4 |
| 0.2 (×) | 0.936×10-4 |
| 0.35 (○) | 1.314×10-4 |
| 0.5 (▲) | 1.594×10-4 |
| 1 (♦) | 2.033×10-4 |
| 2 (■) | 4.743×10-4 |
| 5 (●) | 14.292×10-4 |

*3.5*

Figures S14 and S15 are divided into two charts (A and B) to avoid overlapping the plotted curves each other. This division is particularly important in this case, because this figure illustrates that for lower initial ozone concentrations (chart A) the trend is different than for higher initial ozone concentrations (chart B). One should notice that initial ozone concentration at which the trend changes is slightly higher (about 7mgO3 L-1) than for half order kinetics (for which it is about 6mgO3 L-1). Growth of homogenous process (pseudo)first order rate constant along with initial ozone concentration increase was found to be negligible.

(Pseudo)first order kinetics

Figure S14: Natural logarithm of dissolved ozone molar concentration against time, for various initial ozone concentrations (symbols explained in Tab. S6, right below). Conditions: Initial pH = 2.00, dose of activated carbon = 1g L-1.

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| Table S6: Rate constants and linearity (R2 parameter) for ozone decomposition processes for various initial ozone concentrations. Values for (pseudo)first order kinetics (Fig. S14). Symbols are corresponding with symbols in Fig. S14. | | |
| Initial ozone concentration  [mg L-1] | (Pseudo)first order rate constant [min-1] | R2  [%] |
| 1.32 (+) | 0.1158 | 96.85 |
| 1.93 (×) | 0.0737 | 82.10 |
| 3.64 (◊) | 0.0351 | 97.63 |
| 4.62 (⁎) | 0.0263 | 98.99 |
| 7.13 (○) | 0.0212 | 98.89 |
| 7.87 (Δ) | 0.0243 | 99.26 |
| 10.31 (□) | 0.0269 | 99.82 |

Half order kinetics

Figure S15: Square root of dissolved ozone molar concentration against time, for various initial ozone concentrations (symbols explained in Tab. S7, right below). Conditions: Initial pH = 2.00, activated carbon concentration = 1g L-1 Chart A) initial ozone concentration range 1.32-4.62mg L-1, chart B) initial ozone concentration range 4.62-10.31mg L-1.

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| Table S7: Rate constants and linearity (R2 parameter) for ozone decomposition processes for various initial ozone concentration. Values for half order kinetics (Fig. 15). Symbols are corresponding with symbols in Fig.S15. | | |
| Initial ozone concentration [mg L-1] | Half order rate constant  [(√(mol L-1)) min-1] | R2  [%] |
| 1.32 (+) | 3.87×10-4 | 97.2 |
| 1.93 (×) | 2.62×10-4 | 96.5 |
| 3.64 (◊) | 2.07×10-4 | 98.5 |
| 4.62 (⁎) | 1.92×10-4 | 98.7 |
| 7.13 (○) | 2.03×10-4 | 99.3 |
| 7.87 (Δ) | 2.38×10-4 | 96.9 |
| 10.31 (□) | 2.94×10-4 | 98.1 |

*3.6*

Figure S16.: Relation between natural logarithm of ozone concentration and reaction time for various agitation speeds (●: 200rpm, ■: 400rpm, ♦: 600rpm, ▲: 800rpm, **—**: 900rpm,   
○: homogenous process 900rpm). All possible points shown. Initial pH = 2.00, amount of activated carbon (if used) = 1g L-1, initial ozone concentration = 6.5±0.5mg L-1.Figure S17: Relation between square root of ozone concentration and reaction time for various agitation speeds (●: 200rpm, ■: 400rpm, ♦: 600rpm, ▲: 800rpm, **—**: 900rpm,   
○: homogenous process 900rpm). All possible points shown. Initial pH = 2.00, amount of activated carbon (if used) = 1g L-1, initial ozone concentration = 6.5±0.5mg L-1.

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| Table S8. Comparison between regression linearity of half (0.5) and (pseudo)first (1.) order kinetics describing the same ozone decomposition experiments | | | | | |
| Experiment: | 200 rpm | 400 rpm | 600 rpm | 800 rpm | 900 rpm |
| R2 (0.5) [%] | 98.9 | 96.5 | 95.7 | 97.3 | 98.7 |
| R2 (1.) [%] | 98.9 | 90.0 | 93.1 | 96.3 | 96.2 |

Figure S18: Relation between natural logarithm of ozone concentration and reaction time for various agitation speeds (●: 200rpm, ■: 400rpm, ♦: 600rpm, ▲: 800rpm, **—**: 900rpm,   
○: homogenous process 900rpm). Points not fitting to linear curves (number of points chosen arbitrary) were discounted. Initial pH = 2.00, amount of activated carbon (if used) = 1g L-1, initial ozone concentration = 6.5±0.5mg L-1.

*3.8*

Mathematic model concerning geometric external surface of carbon

Relation between external surface of sample of activated carbon and its granule diameter (assuming for this model that granules are spherical, homogenous and of the same size) is presented in Fig. S19. Data used to following calculations is given in Tab. S2.

Volume of a single granule (V) [mm3] (assumption: granule is a sphere of diameter d (and radius r) [mm]):

Mass of single granule (m) [mg] is:

Where ρ – density of model non-porous homogenous carbon granules, excluding vacancies between granules [mg mm-3]. Its value is not given by manufacturers (usually, only bulk density is available), but, assuming that this parameter does not change along with decreasing of granule size, it does not affect following calculations (). Therefore in this work relative geometric surface is usually used instead of unknown true external surface. However, this true value could be approximated by using bulk density and assuming a particular proportion between granules and vacancies (e.g. 74% is maximal possible value for spheres of the same diameter; this approximation was used to draw Fig. 11 in Main Document)

Geometric surface of single granule (s) [mm2] is , number of granules (n) in 1g of carbon is .

Geometric external surface of 1g of carbon (S) [m2 g-1] is therefore:

Figure S19: Relative (biggest granules = 100%) geometric surface of carbon granules against their average diameter.

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| Table S9: Characterization of F300 carbon fractions | | | | | |
| Fraction [mm] | 0.25-0.315 | 0.315-0.4 | 0.4-0.5 | 0.5-1.0 | 1.0-15 |
| Average granule diameter [mm] | 0.2825 | 0.3575 | 0.45 | 0.75 | 1.25 |
| Relative geometric surface [%] | 443 | 350 | 278 | 167 | 100 |
| Average pore diameter [nm] | 2.78 | 2.73 | 2.77 | 2.82 | 2.82 |
| Total pore volume [cm3g-1] | 0.49 | 0.46 | 0.46 | 0.44 | 0.47 |
| Micropores volume [cm3g-1] | 0.35 | 0.34 | 0.33 | 0.32 | 0.33 |
| SBET[m2 g-1] | 705 | 674 | 659 | 632 | 662 |
| Sint[m2 g-1] | 628 | 612 | 594 | 574 | 597 |
| Sext (SBET- Sint) [m2 g-1] | 77 | 62 | 66 | 58 | 65 |

Figure S20: (Pseudo)first order kinetics rate constant of ozone decomposition on carbon against average diameter of carbon granules (●, right y axis) and geometric external surface against average granules diameter (○, left y axis). Conditions: initial pH 2.00, initial ozone concentration = 6.5±0.5mg L-1, carbon dose = 1000mg L-1. Horizontal error bars indicate sieve range. Homogenous process rate constant was subtracted from all points.

Figure S21: (Pseudo)first order kinetics rate constant against relative geometric surface of activated carbon. Conditions: initial pH 2.00, initial ozone concentration = 6.5±0.5mg L-1, carbon dose = 1000mg L-1. Continuous regression line: fraction 0.25-0.315mm not included, dashed regression line: all fractions included. While for big granules relation appears to be linear, it is not linear for smaller carbon granules, explained in Main Document.

*3.10*

Figure S22: Square root of ozone concentration against time (0.5 order kinetics) for various carbon fractions (symbols explained in Tab. S10, right below). Only first 5 minutes shown. Conditions: initial pH 2.00, initial ozone concentration = 6.5±0.5mg L-1,   
carbon dose = 1000mg L-1.

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| Table S10: Values of (0.5 order kinetics) ozone decomposition rate constants for various carbon fractions, for first 5 minutes after 5 minutes of process | | |
| Activated carbon fraction [mm] | Rate constant 0-5 minutes [√(mol L-1) min-1] | Rate constant 5-60 minutes [√(mol L-1) min-1] |
| No carbon (○) | 0.492×10-4 | 0.493×10-4 |
| 1.0-1.5 (×) | 1.25×10-4 | 0.937×10-4 |
| 0.5-1.0 (\*) | 2.16×10-4 | 1.39×10-4 |
| 0.4-0.5 (+) | 3.56×10-4 | 1.86×10-4 |
| 0.315-0.4 (▲) | 4.97×10-4 | 2.14×10-4 |
| 0.25-0.315 (♦) | 8.89×10-4 | 2.61×10-4 |