

SUPPLEMENTARY FILE

Impact of Different Soil Solutions on the Stability and Photocatalytic Activity of Commercial Zinc Oxide Nanoparticles

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2. Materials and methods

2.2. Soil sampling and analysis

Soil sampling involved collecting 10 Regosol, 10 Chernozem, and 10 Solonetz topsoil samples from three different locations. The Regosol samples were taken from a forest near Tallya, Hungary, the Chernozems from an agricultural land near Szeged, Hungary, and the Solonetz samples from a meadow near Szatymaz, Hungary (Figure S1). The sampling was done in September 2021 and January 2022, from 0–20 cm depths. The topsoil samples from the 0–10 cm and 10–20 cm layers were mixed. After air drying for 10 days, the soil samples were sieved using a 2 mm diameter pore-sized sieve. The soil parameters, such as pH, electrical conductivity (E_c), total salt content, texture, and organic matter content, were determined following the Hungarian Standards (MSZ).

The pH values of the soil samples were measured using a digital pH meter (Inolab pH 720) after mixing them with deionized water in a ratio of 1:2.5¹. Soil textures were evaluated based on the plasticity index values according to Arany (Arany plasticity index). The index is calculated from the amount (cm³) of deionized water added to an air-dry soil sample (100 g) until reaching the upper limit of its plasticity, which is the moisture content at which a fine-grained soil can no longer be remolded without cracking. Ec values and total salt contents were analyzed with an Orion 3-Star conductivity meter (Thermo Electron Corporation) for water-saturated soil samples ($\pm 10 \mu\text{S}\cdot\text{cm}^{-1}$).¹⁻³

OM contents were determined using a UV–vis spectrophotometer (Spectronic Helios- γ , Thermo Fisher Scientific) after oxidation of the organic matter with 0.33 M K₂Cr₂O₇ in the presence of 95% H₂SO₄ overnight. As a result, the organic carbon content of the soil sample was oxidized, while Cr⁶⁺ ions were reduced to Cr³⁺ ions. The concentration of Cr³⁺ ions was measured at a wavelength of 590 nm, which is directly proportional to the organic carbon content.⁴

To determine the concentration of different major and trace elements (Na, K, Ca, Mg, Al, Fe, Mn, Zn, Cu, Ni, Co, As), we weighed 0.5 g of samples into a perfluoroalkoxy vessel, followed by the addition of 7 mL of aqua regia (HNO₃/HCl = 1:3). Soil samples were digested in a microwave oven (Anton Paar Multiwave 3000). Element concentrations in the digested samples were determined by ICP-OES (Optima 7000 DV, PerkinElmer) with a standard deviation of $\pm 10\%$.^{2, 3, 5, 6}

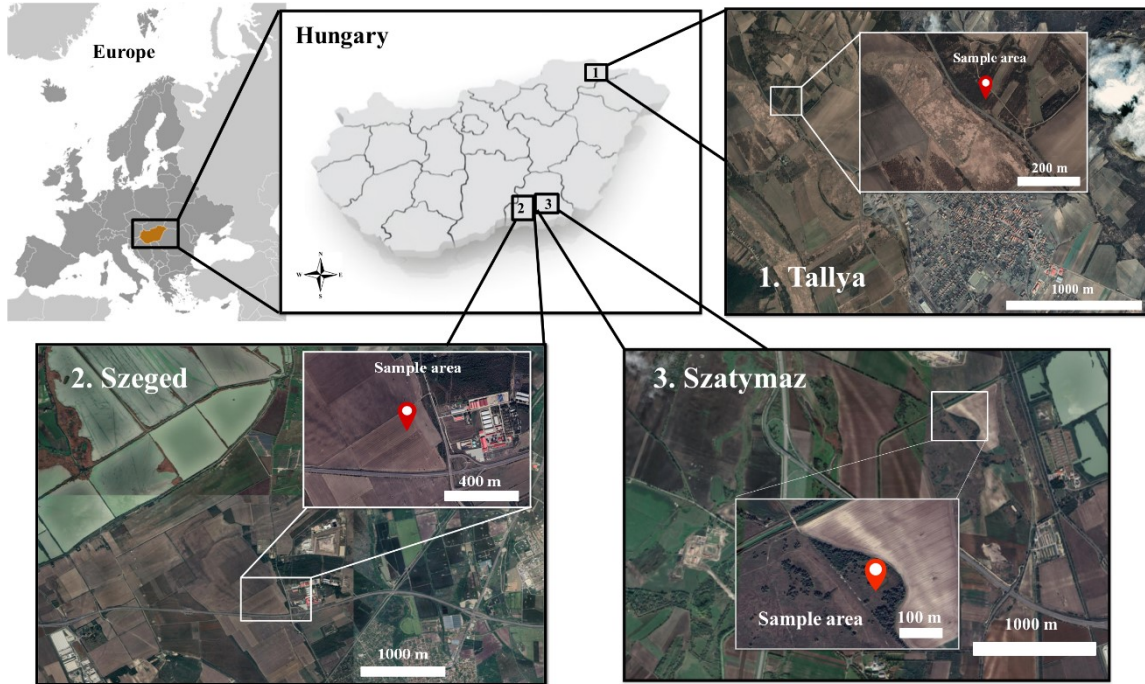


Figure S1. Location of the sample areas

2.3. Soil solution preparation and analysis

Determination of COD. Determination of COD. The exact concentration of a 0.002 M potassium permanganate solution was determined. To prepare the oxalic acid solution, 0.6303 g of $(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$ was weighed out and slightly diluted with H_2SO_4 (1:15). The resulting solution was then quantitatively washed into a volumetric flask and made up to the mark. The concentration of the prepared solution was approximately 0.05 M, and the exact concentration was calculated from the actual measured mass. The 0.005 M oxalic acid measuring solution for titration was obtained from this solution through a tenfold dilution. In the Erlenmeyer flask, 20 cm³ of the 0.005 M oxalic acid solution was measured from a burette and 5 cm³ of a 1:2 dilution of H_2SO_4 was added. The solution was heated to 80-90 °C and titrated while hot with 0.002 M KMnO_4 until the solution turned pale pink. The exact concentration of the potassium permanganate solution consumed during the titration was calculated based on the volume of oxalic acid measuring solution used. The chemical oxygen demand for the water sample was determined. A 500 cm³ volumetric flask was used, and an unknown quantity of the user-prepared 0.05 M oxalic acid solution was added, making up to the mark. 100 cm³ of the resulting solution was transferred into a 300 cm³ Erlenmeyer flask, and then 5 cm³ of a 1:2 dilution of sulphuric acid and a few pieces of pumice were added. The solution was brought to a boil, and while boiling, 20 cm³ of the 0.002 M potassium permanganate measuring solution was added. The solution was boiled for exactly 10 minutes (strictly observing the boiling time was crucial). Finally, the boiling process was stopped. In the determination, the substances in the water were reacted with known amounts of potassium permanganate. The excess oxidizing agent was then oxidized with a known amount of potassium hydroxide, and oxalic acid was added to the remaining oxidizing agent. The excess oxalic acid was then titrated back with the KMnO_4 solution. Thus, the determination of the total oxidizing agent (KMnO_4) was calculated from the 20 cm³ consumed in the back titration. Meanwhile, the total reducing agent ($(\text{COOH})_2$) represents the oxidizable organic matter content of the sample + 20 cm³. The average of the consumptions obtained by titration of the water sample must be subtracted from the consumption obtained for the blank test to calculate the COD ^{7, 86, 76, 76, 76, 75, 64, 5}(260-16, 1967b)⁸⁷⁷⁷⁷⁶⁵.

3. Results and discussion

3.1. Properties of soil solutions and their possible effects on ZnO NPs

Table S1.

Basic parameters of the soil samples

Sample	pH (H₂O)	OM (%)	Ec (μS·cm⁻¹)	Texture
REG1	4.79	4.92	289	Loamy
REG2	4.53	7.32	285	Loamy
REG3	4.87	7.76	251.7	Clay Loamy
REG4	4.68	5.04	238.3	Sandy Loam
REG5	4.61	7.1	180.1	Clay Loamy
REG6	4.56	3.56	250.7	Loamy
REG7	4.42	8.6	246	Clay Loamy
REG8	4.62	5.72	270	Clay Loamy
REG9	4.87	4.52	250	Loamy
REG10	4.73	6	296.7	Clay Loamy
CH1	7.86	1.94	538	Sandy Loam
CH2	7.82	2.42	471	Sandy Loam
CH3	7.82	3.16	665	Sandy Loam
CH4	7.81	3.1	670	Sandy Loam
CH5	7.84	2.84	591	Sandy Loam
CH6	7.9	3.22	482	Sandy Loam
CH7	7.78	2.42	621	Loam
CH8	7.81	2.72	542	Sandy Loam
CH9	7.77	2.58	717	Loam
CH10	7.74	2.7	715	Sandy Loam
SOL1	9,75	1,46	1182	Sand
SOL2	10,07	0,84	1310	Sand
SOL3	10,04	1	1872	Sand

SOL4	9,88	0,36	1601	Sand
SOL5	9,89	1	2124	Sand
SOL6	10,2	1,2	3054	Sand
SOL7	9,89	0,74	2021	Coarse Sand
SOL8	9,9	0,82	1732	Coarse Sand
SOL9	9,64	1	1692	Sand
SOL10	9,89	0,9	2633	Sandy Loam

Table S2

Physicochemical properties of the soil solutions

Samples	pH	IS (mmol·L⁻¹)	COD (mg·L⁻¹)
CH1	7.76 ± 0.1	3.38 ± 0.1	20.5 ± 0.3
CH2	7.72 ± 0.3	3.39 ± 0.1	21.3 ± 0.5
CH3	7.71 ± 0.1	4.12 ± 0.1	20.6 ± 0.2
CH4	7.79 ± 0.4	4.59 ± 0.1	21.2 ± 0.5
CH5	7.69 ± 0.1	3.86 ± 0.1	20.6 ± 0.4
CH6	7.72 ± 0.1	3.19 ± 0.08	20.4 ± 0.3
CH7	7.75 ± 0.2	4.15 ± 0.1	21.0 ± 0.4
CH8	7.74 ± 0.2	3.42 ± 0.05	20.7 ± 0.3
CH9	7.81 ± 0.5	4.62 ± 0.09	21.1 ± 0.4
CH10	7.73 ± 0.2	4.84 ± 0.1	20.8 ± 0.3
CHALL*	7.74 ± 0.2	3.96 ± 0.2	20.9 ± 0.4
REG1	4.85 ± 0.08	1.89 ± 0.08	163.8 ± 3.4

REG2	5.05 ± 0.12	2.09 ± 0.12	166.1 ± 2.9
REG3	4.87 ± 0.06	2.04 ± 0.09	159.3 ± 3.6
REG4	5.10 ± 0.15	1.93 ± 0.08	168.4 ± 3.2
REG5	5.02 ± 0.1	2.01 ± 0.1	160.6 ± 2.8
REG6	4.94 ± 0.08	2.11 ± 0.15	167.2 ± 3.9
REG7	4.98 ± 0.13	1.91 ± 0.06	161.9 ± 2.3
REG8	4.92 ± 0.11	2.02 ± 0.13	164.7 ± 3.7
REG9	5.00 ± 0.09	1.94 ± 0.07	165.3 ± 4.1
REG10	4.90 ± 0.07	1.96 ± 0.11	162.5 ± 2.6
REGALL*	4.95 ± 0.1	1.99 ± 0.1	165 ± 1.2
SOL1	9.1 ± 0.3	12.36 ± 0.26	201 ± 0.6
SOL2	9.5 ± 0.25	12.33 ± 0.28	219.9 ± 1.1
SOL3	9.2 ± 0.22	11.73 ± 0.25	187.1 ± 3.5
SOL4	9.7 ± 0.18	11.9 ± 0.27	196.4
SOL5	9.3 ± 0.21	12.12 ± 0.29	214.5 ± 0.9
SOL6	9.6 ± 0.23	11.74 ± 0.24	193.6 ± 5.1
SOL7	9.0 ± 0.28	12.40 ± 0.23	208.3 ± 1.3
SOL8	9.4 ± 0.19	11.98 ± 0.27	220.1 ± 5.6
SOL9	9.1 ± 0.27	12.27 ± 0.25	218.7 ± 3.7

SOL10	9.5 ± 0.24	12.01 ± 0.28	198.8 ± 0.4
SOLALL*	9.4 ± 0.2	12.03 ± 0.3	227.2 ± 1.6

CHALL* - a homogeneous sample that was formed by combining the 10 Chernozem soil solution samples

REGALL* - a homogeneous sample that was formed by combining the 10 Regosol soil solution samples

SOLALL* - a homogeneous sample that was formed by combining the 10 Solonetz soil solution samples

3.2. Crystal structure, morphology and optical properties of ZnO NPs

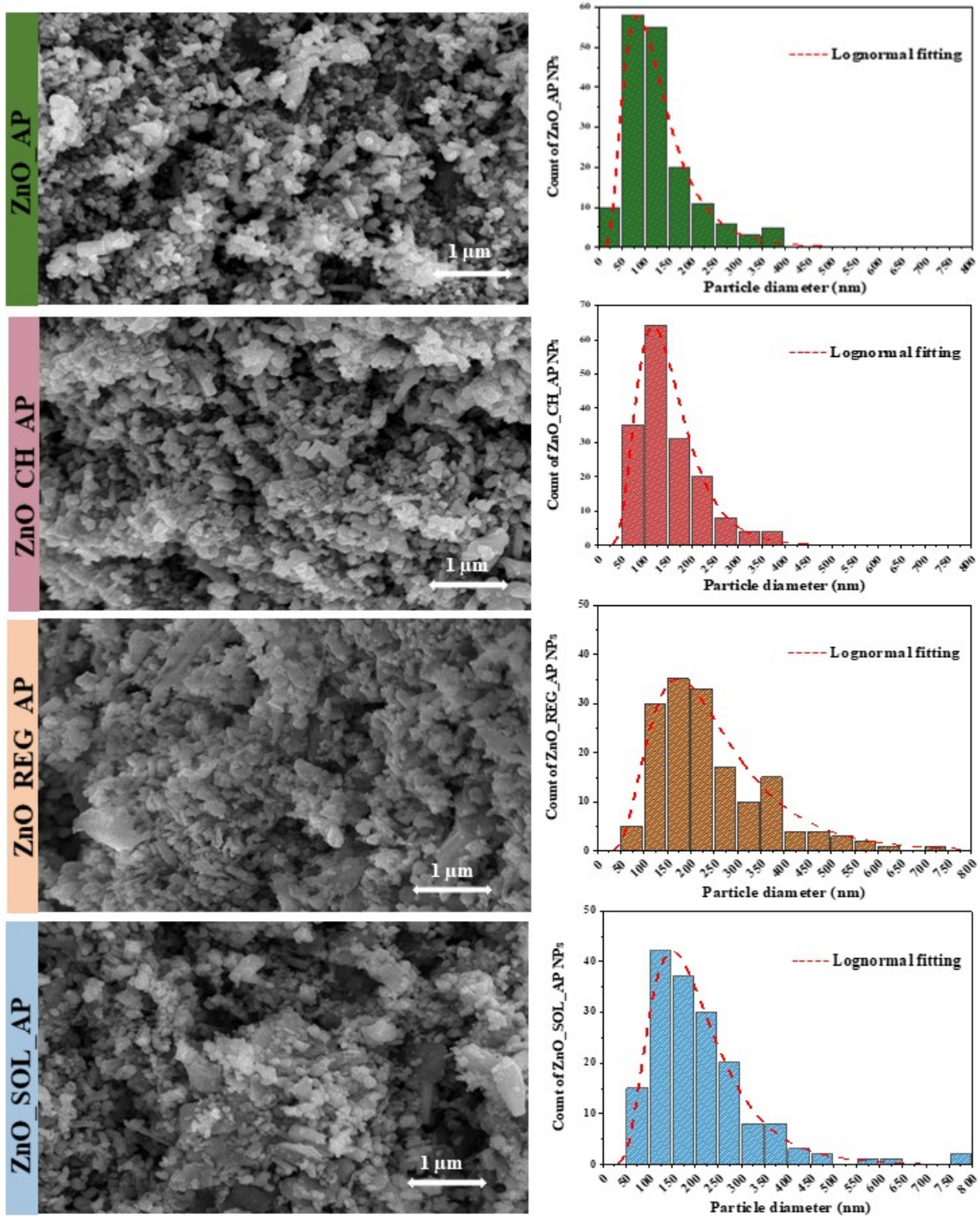


Figure S2. SEM micrographs of ZnO NP samples after phenol degradation and after immersion in soil solution, and their corresponding size distribution histograms.

Table S3.

Bandgap values of the samples

Sample name	Bandgap (eV)
<i>ZnO_REF</i>	3.12
<i>ZnO_AP</i>	3.09
<i>ZnO_CH</i>	3.06
<i>ZnO_CH_AP</i>	3.17
<i>ZnO_REG</i>	3.09
<i>ZnO_REG_AP</i>	3.16
<i>ZnO_SOL</i>	3.04
<i>ZnO_SOL_AP</i>	3.04

3.3. Surface properties of ZnO NPs

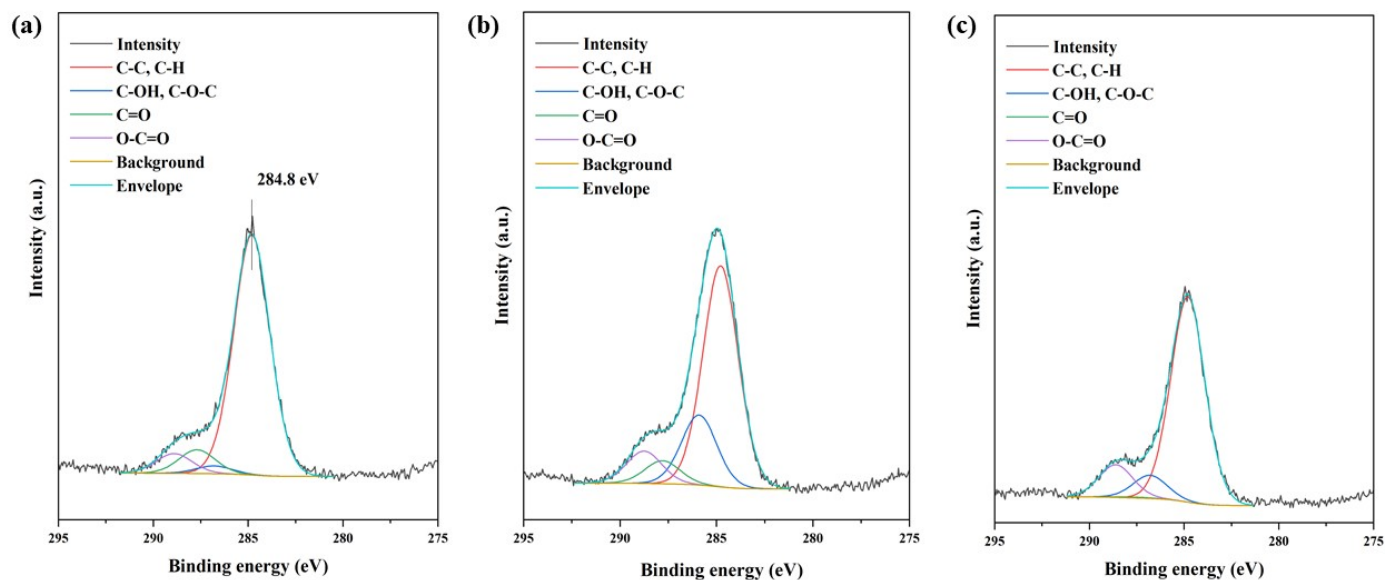


Figure S3. C 1S XPs spectra of the ZnO samples: **a)** ZnO_CH, **b)** ZnO_REG, **c)** ZnO_SOL.

References

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