ELECTRONIC SUPPLEMENTARY INFORMATION

Emerging investigator series: Environmental safety assessment of 11 novel metal oxide/hydroxide nanocomposite adsorbents for advanced magnetic removal and recovery of phosphorus from wastewater

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Materials and Methods

<u>Supplementary S1</u> - Toxicity tests using naturally bioluminescent bacteria *Vibrio fischeri*

- **Kinetic bioluminescence inhibition test (modified 'Flash Assay') with bacteria *Vibrio fischeri* (ISO-21338:2010)**

The *Vibrio fischeri* acute kinetic bioluminescence inhibition assay was performed at 30-min exposure time and room temperature (~20°C, AC-controlled) in 96-well microplates (non-tissue culture treated, Greiner-Bio-One) according to the modified Flash-assay standard ISO protocol (ISO-21338:2010, 2010) described in (Mortimer et al., 2008). The lyophilized *Vibrio fischeri* bacteria (Aboatox, Turku, Finland) were reconstituted in a solution containing 20 g/L NaCl, 2.035 g/L $MgCl_2 \cdot 6H_2O$ and 0.3 g/L KCl. All nanocomposite suspensions and their serial dilutions were prepared in 2%NaCl. Each microplate well received 100 µL nanocomposite test suspension in 2%NaCl and was then supplemented with 100 µL bacterial suspension in 2%NaCl in a Microplate luminometer Orion-II with auto-controlled dispenser unit, operated with Simplicity-software 4.2 (Berthold-Detection-Systems, Pforzheim, Germany). Bacterial luminescence was recorded continuously in the first 30 s after dispensing (without sample mixing) and then the luminescence was recorded again after 30-min incubation. All experiments were performed at least in 3 replicates (n=3) and each measurement series included both negative (2%NaCl) and positive ($ZnSO_4 \cdot 7H_2O$) controls. The inhibition of bacterial luminescence (INH%) by the toxicants was calculated as follows:

$$INH\% = 100 - \frac{IT_{30}}{KF \times IT_0} \times 100 \quad (1)$$

$$KF = \frac{IC_{30}}{IC_0} \quad (2)$$

where KF is a correction factor accounting for the natural loss of luminescence in the control sample (bacteria in 2%NaCl). The maximum luminescence values in the first 5 s after dispensing test bacteria into the control and test samples, are indicated with IC_0 and IT_0, respectively. And IC_{30} and IT_{30} are the respective luminescence values of control and test sample after 30 min. The nominal concentration of a compound reducing the bacterial bioluminescence by 50% is defined as the half maximal effective concentration (EC_{50}). The nanocomposite-specific 30-min EC_{50} values were calculated as described in section 2.4.

The precursor metal salts were also tested for toxicity due to dissolution of directly bioavailable metal ions. Expectedly, $ZnCl_2$ was "harmful" (30-min EC_{50} = 17.5 mg-Zn^{2+}/L), comparable with

positive control $ZnSO_4 \cdot 7H_2O$ (30-min EC_{50} = 7.8 mg-Zn^{2+}/L). As foreseen, $CaCl_2 \cdot 2H_2O$ and $MgCl_2 \cdot 6H_2O$ were non-toxic to *V.fischeri*. The precursor salts $FeCl_3 \cdot 6H_2O$ and $ZrOCl_2 \cdot 8H_2O$ had in-test pH 3-5.5, below the recommended *V. fischeri* range (pH 6−8.5), but adjusting pH with NaOH formed precipitates which discredits the results for these two salts.

- **Viability assay ('Spot Test')**

Vibrio fischeri viability assay ('Spot test') was performed following essentially the methodology described by Suppi et al. (Suppi et al., 2015) with a small modification using 2% NaCl as the incubation medium (isotonic medium for marine bacteria *V. fischeri*) instead of distilled water which is commonly used for other bacterial strains.

The 'Spot test' assay evaluates the ability of the toxicant-exposed bacteria to form colonies on a toxicant-free nutrient agar after 2-h and 24-h exposure to the tested nanocomposites (toxicants). Briefly, at the end of the 'Flash Assay', the 96-well microplates with *V. fischeri* and the toxicants were incubated at room temperature (~20°C) in the dark for 2 h and 24 h without shaking. After 2-h and 24-h exposure to the toxicants (in 2% NaCl), 3 µL of the cell suspension from each microplate well was pipetted as a 'spot' onto an agarized Beneckea-Harvey (BH) growth medium containing: yeast extract 3 g/L, tryptone 5 g/L, glycerol (99%) 2 mL/L, NaCl 30 g/L $Na_2HPO_4 \cdot 12H_2O$ 9.45 g/L, KH_2PO_4 1 g/L, $(NH_4)_2HPO_4$ 0.5 g/L, $MgSO_4 \cdot 7H_2O$ 0.3 g/L, agar 15 g/L. The inoculated agar plates were incubated at room temperature in the dark for two days (48 h) until the bacterial growth was visible. The colonies were visually analyzed in the dark when bacteria started to emit light and photographs were taken at 48 h. The MBC values (minimum bactericidal concentration) of the investigated nanocomposites were determined visually and defined as the lowest tested nominal concentration which inhibited completely the ability of *Vibrio fischeri* to form visible colonies after plating ("spotting") onto toxicant-free agar plates. The tested nominal concentrations included exponential (3-fold) dilution series of the nanocomposite suspensions in the range of 1-1000 mg/L (as total dry mass) and of the soluble precursor metal salts in the range of 0.1-1000 mg metal/L (depending on the toxicity of the compound). All tests were repeated 3 times.

Supplementary S2 – Composition of the OECD TG 201 algal growth medium

Composition of OECD-TG-201 test medium

Component	OECD	
	mg/L	mM
$NaHCO_3$	50.0	0.595
$NaNO_3$		
NH_4Cl	15.0	0.280
$MgCl_2 \cdot 6(H_2O)$	12.0	0.0590
$CaCl_2 \cdot 2(H_2O)$	18.0	0.122
$MgSO_4 \cdot 7(H_2O)$	15.0	0.0609
K_2HPO_4		
KH_2PO_4	1.60	0.00919
$FeCl_3 \cdot 6(H_2O)$	0.0640	0.000237
$Na_2EDTA \cdot 2(H_2O)$	0.100	0.000269*
H_3BO_3	0.185	0.00299
$MnCl_2 \cdot 4(H_2O)$	0.415	0.00210
$ZnCl_2$	0.00300	0.0000220
$CoCl_2 \cdot 6(H_2O)$	0.00150	0.00000630
$Na_2MoO_4 \cdot 2(H_2O)$	0.00700	0.0000289
$CuCl_2.2(H_2O)$	0.00001	0.00000006
pH	8.1	

Element composition of test media

Element	OECD
	mg/L
C	7.148
N	3.927
P	0.285
K	0.459
Na	13.704
Ca	4.905
Mg	2.913
Fe	0.017
Mn	0.115

Table S1: Composition of the OECD TG 201 algal growth medium for the bioassay OECD-201 and viability assay ('Spot Test') with green freshwater microalgae *Raphidocelis subcapitata*.

<u>Supplementary S3</u> – Phosphate adsorption tests for P pre-loading and saturation of nanocomposites ZnFeZr−6:1:1, ZnFeZr−6:1:1@MPs, CaFeZr−6:1:1 and MgFeZr−6:1:1

The goal of the phosphate adsorption tests was to preload selected representative adsorbents with phosphate - 2 with Zn (ZnFeZr−6:1:1 and ZnFeZr−6:1:1@MPs) and 2 without Zn (CaFeZr−6:1:1 and MgFeZr−6:1:1) - until saturation capacity is reached, i.e. until they are exhausted and can not uptake phosphate anymore. This step was undertaken to prevent undesired spontaneous adsorption of phosphate from the OECD-201 medium by the nanocomposites as phosphorus is a critical nutrient which is essential for algal growth.

For this purpose, the procedure described in the following diagram was implemented.

Ortho-phosphate (PO_4-P) was measured spectrophotometrically using a Spectroquant® test kit from Merck KGaA, Darmstadt, Germany with two measuring ranges 0.05-5.00 mg/L PO_4-P and 0.2-15.3 mg/L PO_4-P. Samples with higher concentrations were diluted accordingly.

The Spectroquant® Cell Tests come with prefilled 16 mm round cells and all the required reagents to perform the analysis according to the instruction leaflet provided. The method is analogous to EPA 365.2+3, APHA 4500-P E, and DIN EN ISO 6878.

After preloading the four selected adsorbents with phosphate, they were resuspended in deionized (milli-Q) water and in OECD-201 algae growth medium and their new stock concentrations were re-measured again before starting the toxicity tests, following the procedure described in the diagram below.

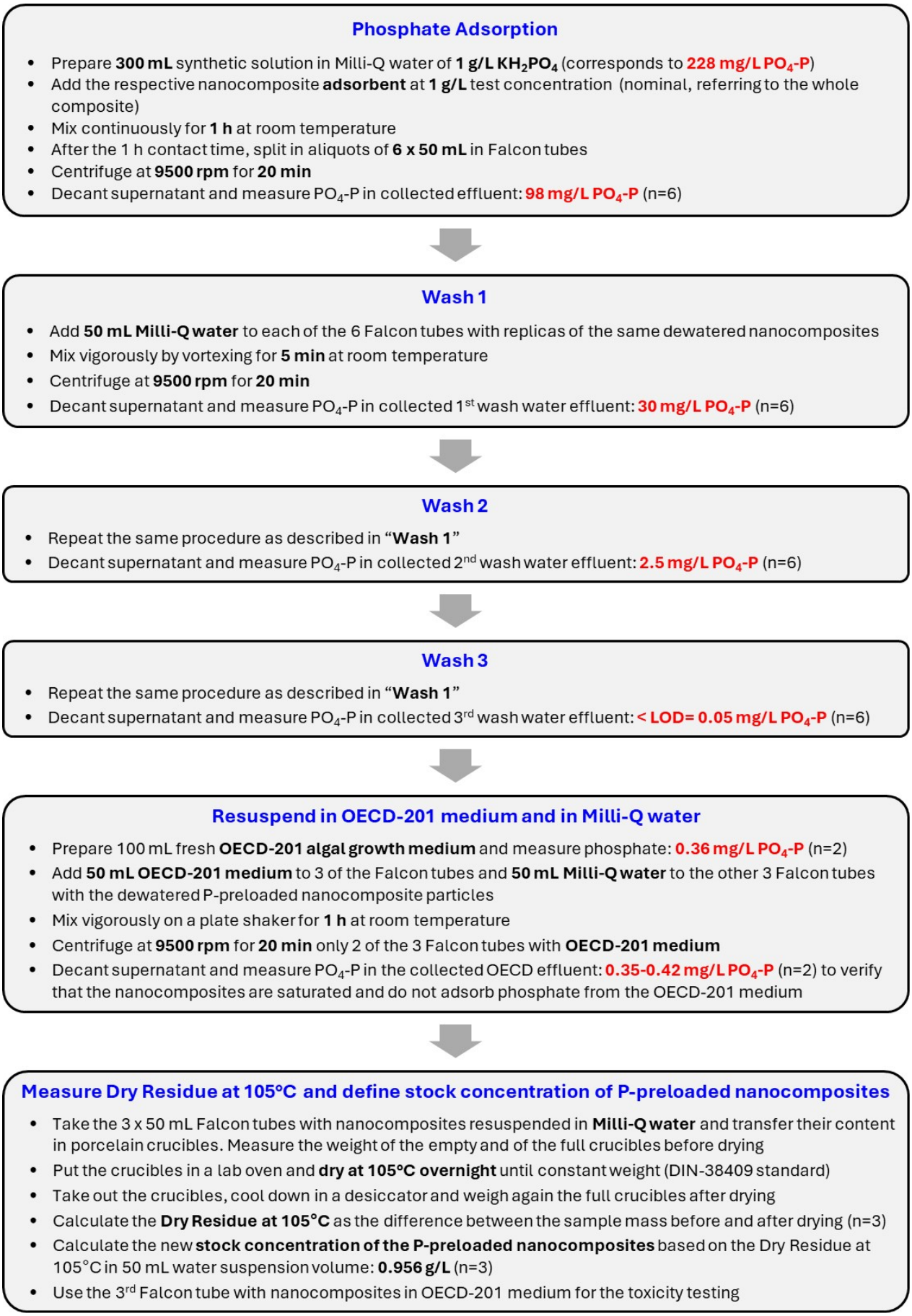

Fig. S1: Scheme for pre-loading with phosphate the adsorbents ZnFeZr−6:1:1, ZnFeZr−6:1:1@MPs, CaFeZr−6:1:1 and MgFeZr−6:1:1.

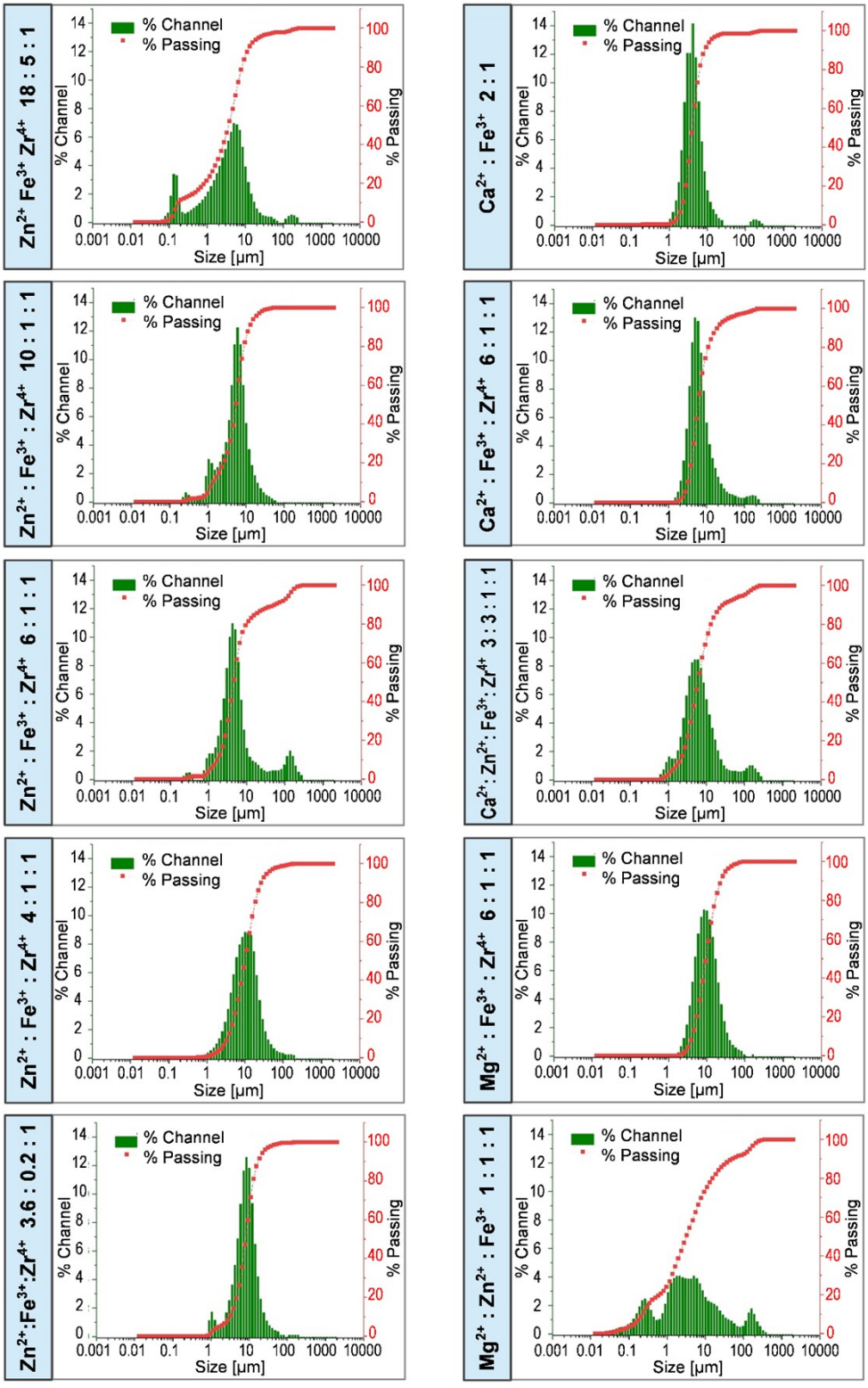

Fig. S2: Particle size distribution analysis (primary size) performed with laser diffraction, showing median diameter d_{50}=1-10 µm for all as-synthesized nanocomposites. Left panel: ZnFeZr-based materials; Right panel: Ca-/Mg-containing materials (Drenkova-Tuhtan et al., 2024).

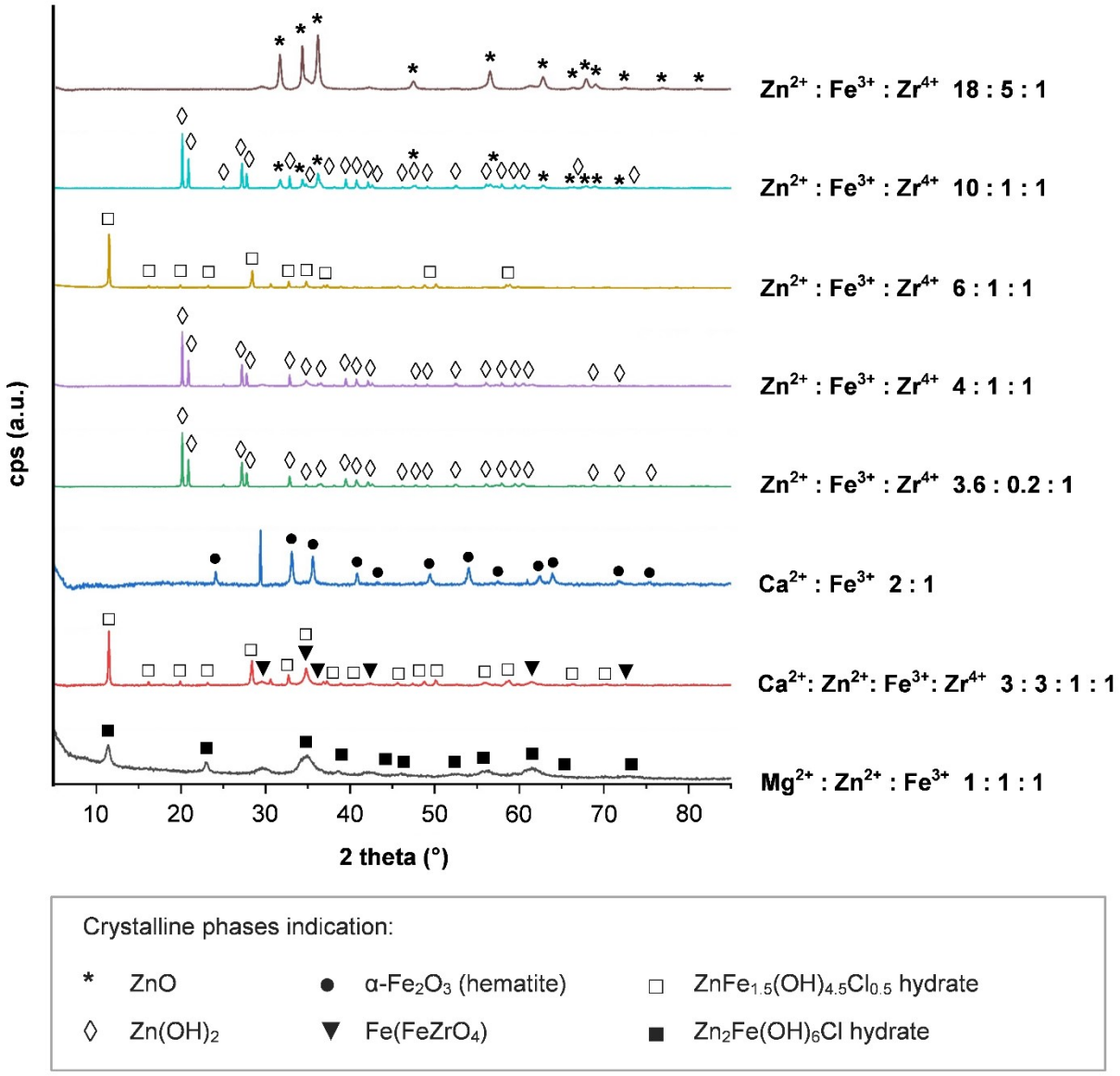

Fig. S3: Samples crystallinity analysis with X-ray diffraction (XRD) of all ZnFeZr-based (top five diffractograms) and three Ca-/Mg-containing (bottom three diffractograms) nanocomposites (Drenkova-Tuhtan et al., 2024).

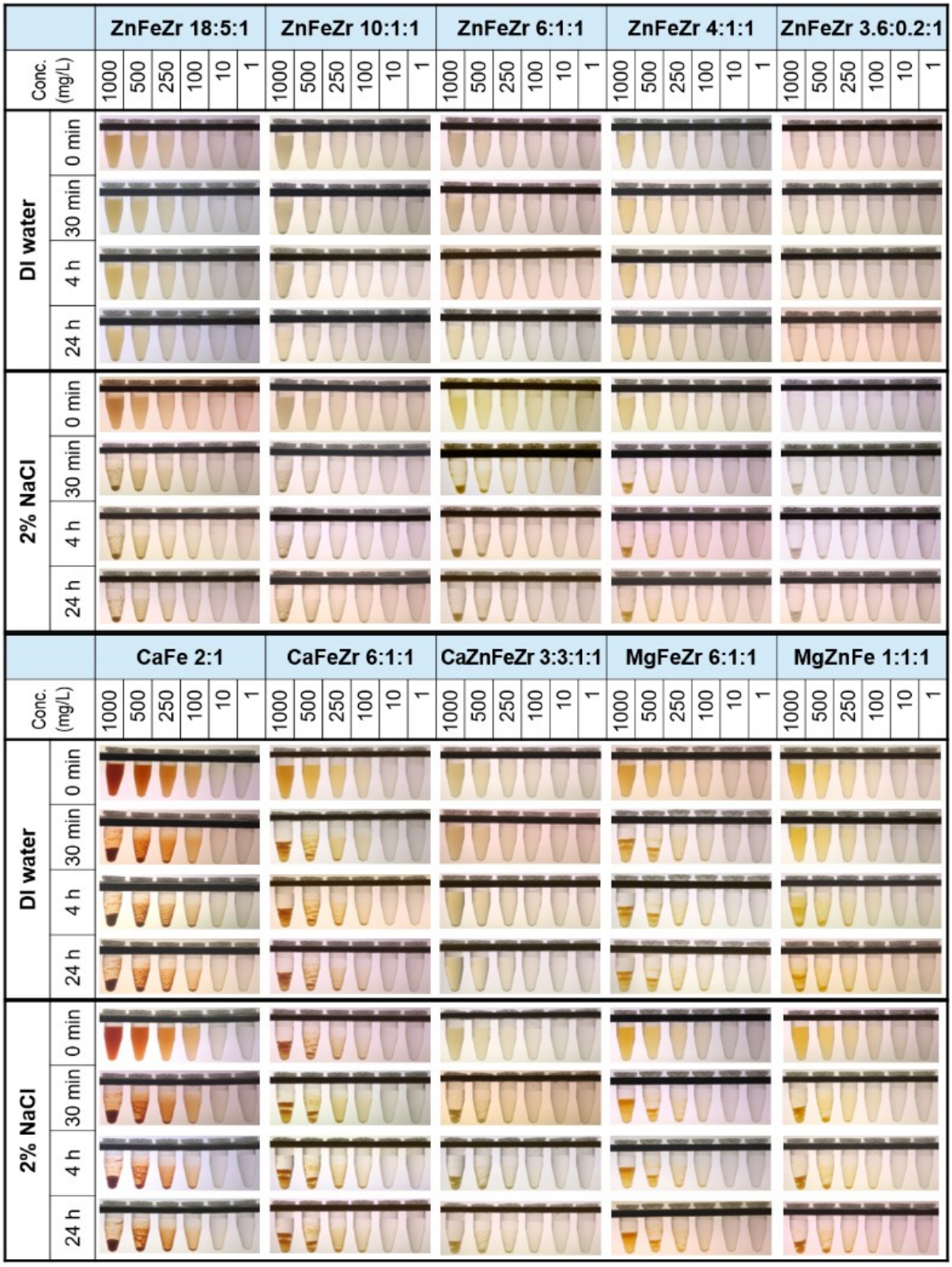

Fig. S4: Settling of the studied materials' particle suspensions: visualization of their stability in DI water (upper panel) and 2% NaCl (lower panel) at 0 min, 30 min, 2 h and 24 h (Drenkova-Tuhtan et al., 2024).

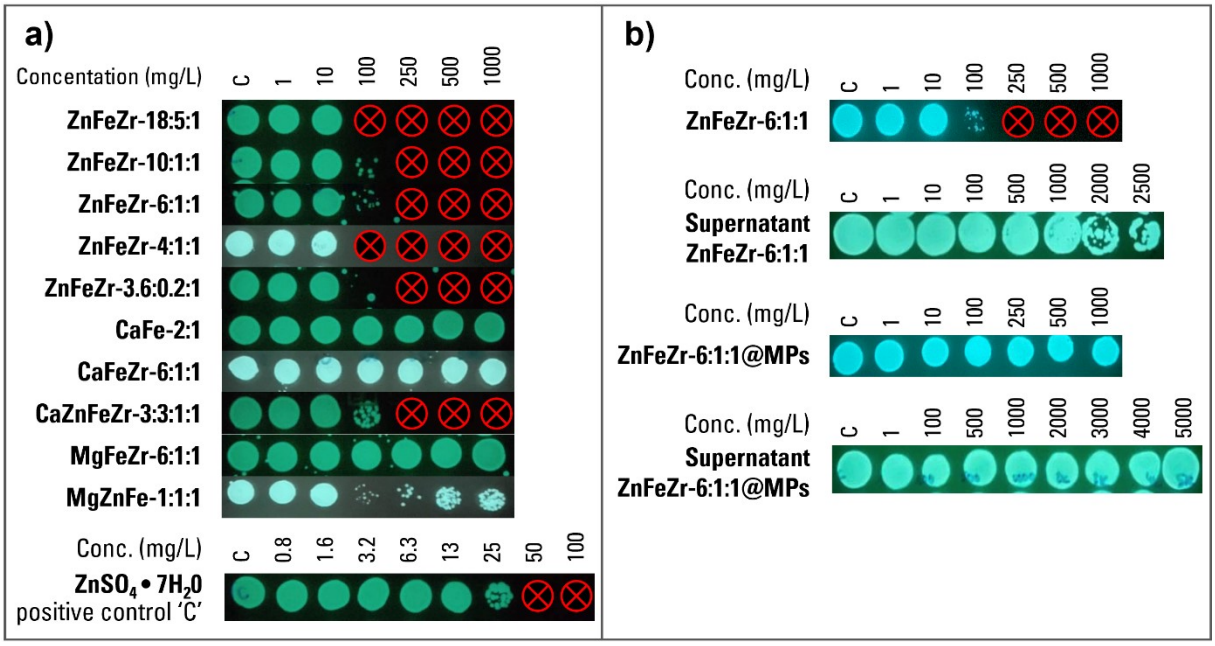

Fig. S5: Viability of bacteria *Vibrio fischeri* and minimum bactericidal concentration (MBC) after 24-h exposure to: **a)** all as-synthesized composites and **b)** the pilot-scale tested composite ZnFeZr 6:1:1, its magnetic version ZnFeZr 6:1:1@MPs and their respective filtered particle-free supernatants.

Remarks: All *V. fischeri* results are adopted from (Drenkova-Tuhtan et al., 2024).

Viability was determined based on colony-forming ability of the bacteria exposed to the tested compounds in 2%NaCl for 24 h at ~20°C. After exposure, 3 µL bacterial suspension was transferred to a toxicant-free agarized nutrient medium and plates were incubated for 48 h at room temperature. Blue-green spots are bioluminescent bacterial colonies photographed in the dark after 48-h incubation. MBC is the lowest tested concentration which inhibited completely the bacterial growth (no visible colonies detected): All concentrations are nominal and refer to "mg-compound/L", except for Zn-salts: "mg-Zn/L".

Fig. S6: Settling of composite CaFe-2:1 (100 mg/L test concentration) during the *Daphnia magna* acute immobilization test (Left image: beginning of the test; Right image: end of the test after 48 h).

Table S2: Total metal concentrations (mg-Me/L) in 100 mg/L homogenized suspensions in DI water (left panel) of the tested materials measured with ICP-OES, and in 100 mg/L exposure concentration in OECD-202 medium/"Standard Freshwater" (right panel) of homogenized tested materials measured with TXRF (n=3) prior to the start / in the beginning of the *Daphnia magna* tests.

Composite name	Nominal exposure concentration	Measured precursor metal concentrations in 100 mg/L homogenized suspensions of the oxide/hydroxide precipitates										Zn-fraction by molar mass
		Measured Me-concentrations (DI water) **ICP-OES analysis**					Measured Me-concentrations (OECD-202 medium) **TXRF analysis**					
		Zn^{2+}	Fe^{3+}	Zr^{4+}	Ca^{2+}	Mg^{2+}	Zn^{2+}	Fe^{3+}	Zr^{4+}	Ca^{2+}	Mg^{2+}	
	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(wt%)
ZnFeZr-18:5:1	100	52.7	13.0	3.7	n.a.	n.a.	45.4 ± 7.9	10.2 ± 1.5	n.d.	n.a.	n.a.	36.6
ZnFeZr-10:1:1	100	55.0	5.1	7.2	n.a.	n.a.	46.6 ± 8.9	3.2 ± 1.5	n.d.	n.a.	n.a.	37.0
ZnFeZr-6:1:1	100	43.7	6.8	9.5	n.a.	n.a.	37.1 ± 4.5	5.5 ± 0.6	n.d.	n.a.	n.a.	26.2
ZnFeZr-4:1:1	100	38.9	9.5	13.6	n.a.	n.a.	32.3 ± 6.8	7.5 ± 1.8	n.d.	n.a.	n.a.	24.1
ZnFeZr-3.6:0.2:1	100	41.6	2.4	16.9	n.a.	n.a.	36.4 ± 21.1	1.6 ± 1.2	n.d.	n.a.	n.a.	25.4
CaFe-2:1	100	n.a.	56.2	n.a.	1.9	n.a.	n.a.	49.7 ± 2.3	n.a.	60.9 ± 2.0	n.a.	n.a.
CaFeZr-6:1:1	100	n.a.	21.7	31.2	1.7	n.a.	n.a.	14.7 ± 0.04	n.d.	40.6 ± 12.8	n.a.	n.a.
CaZnFeZr-3:3:1:1	100	31.3	11.2	16.0	0.0	n.a.	27.8 ± 3.5	9.1 ± 0.8	n.d.	50.9 ± 2.6	n.a.	18.3
MgFeZr-6:1:1	100	n.a.	20.6	29.3	n.a.	1.8	n.a.	14.7 ± 0.08	n.d.	n.a.	< LOD	n.a.
MgZnFe-1:1:1	100	28.8	25.9	n.a.	n.a.	3.5	26.2 ± 0.04	21.5 ± 1.2	n.a.	n.a.	< LOD	16.7
ZnFeZr-6:1:1@MPs	100	8.7	> 50.0	1.9	n.a.	n.a.	12.6± 0.1	22 ± 0.7	n.d.	n.a.	n.a.	5.2

Table S3: Total metal concentrations (mg-Me/L) in water samples collected from the water column at 100 mg/L exposure concentration at the end of the *Daphnia magna* tests after 48 h (n=3). Samples were analyzed with TXRF. The Zr^{4+} and Mg^{2+} values were below the limit of detection (<LOD) for all samples.

Composite name (100 mg/L nominal exposure concentration)	Total metal concentrations in the water column after 48 h exposure (n=3) (mg-Me/L)				
	Zn^{2+}	Fe^{3+}	Zr^{4+}	Ca^{2+}	Mg^{2+}
ZnFeZr-18:5:1	2.63 ± 1.18	0.19 ± 0.12	< LOD	56.8 ± 5.3	< LOD
ZnFeZr-10:1:1	1.34 ± 0.11	0.18 ± 0.07	< LOD	72.5 ± 11.7	< LOD
ZnFeZr-6:1:1	1.91 ± 0.38	0.13 ± 0.08	< LOD	51.2 ± 10.7	< LOD
ZnFeZr-4:1:1	1.34 ± 0.24	0.14 ± 0.07	< LOD	47.9 ± 9.5	< LOD
ZnFeZr-3.6:0.2:1	1.14 ± 0.19	0.13 ± 0.08	< LOD	59.2 ± 10.6	< LOD
CaFe-2:1	0.04 ± 0.01	0.08 ± 0.04	< LOD	37.5 ± 6.1	< LOD
CaFeZr-6:1:1	0.03 ± 0.01	0.25 ± 0.41	< LOD	42.4 ± 23.6	< LOD
CaZnFeZr-3:3:1:1	1.92 ± 0.82	0.10 ± 0.10	< LOD	47.3 ± 9.97	< LOD
MgFeZr-6:1:1	0.07 ± 0.03	0.06 ± 0.00	< LOD	40.2 ± 17.2	< LOD
MgZnFe-1:1:1	0.97 ± 0.15	0.16 ± 0.10	< LOD	55.4 ± 11.5	< LOD
ZnFeZr-6:1:1@MPs	0.59 ± 0.20	0.23 ± 0.21	< LOD	63.0 ± 9.2	< LOD

Table S4: Total metal concentrations (mg-Me/L) in the water column for all nominal exposure concentrations at the end of the *Daphnia magna* tests after 48 h (n=3). Samples were analyzed with TXRF. The Zr^{4+} and Mg^{2+} values were below the limit of detection (<LOD) for all samples.

Composite	Nominal exposure conc. (mg/L)	Zn^{2+} (mg/L)	Fe^{3+} (mg/L)	Zr^{4+} (mg/L)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)
ZnFeZr-18:5:1	3.125	0.97 ± 0.15	0.14 ± 0.17	<LOD	56.32 ± 11.00	<LOD
	6.25	1.80 ± 0.23	0.11 ± 0.12	<LOD	49.53 ± 10.98	<LOD
	12.5	2.35 ± 0.14	0.14 ± 0.05	<LOD	53.55 ± 19.37	<LOD
	25	2.12 ± 0.64	0.19 ± 0.10	<LOD	51.13 ± 14.61	<LOD
	50	2.23 ± 0.67	0.17 ± 0.13	<LOD	50.04 ± 8.59	<LOD
	100	2.63 ± 1.18	0.19 ± 0.12	<LOD	56.77 ± 5.25	<LOD
ZnFeZr-10:1:1	3.125	1.41 ± 0.04	0.15 ± 0.08	<LOD	58.26 ± 17.60	<LOD
	6.25	1.99 ± 0.44	0.11 ± 0.07	<LOD	53.96 ± 1.21	<LOD
	12.5	2.02 ± 0.56	0.13 ± 0.07	<LOD	63.79 ± 4.62	<LOD
	25	2.25 ± 0.39	0.15 ± 0.09	<LOD	69.47 ± 8.56	<LOD
	50	1.76 ± 0.07	0.15 ± 0.09	<LOD	74.97 ± 5.11	<LOD
	100	1.34 ± 0.11	0.18 ± 0.07	<LOD	72.46 ± 11.74	<LOD
ZnFeZr-6:1:1	3.125	1.06 ± 0.03	0.14 ± 0.08	<LOD	57.31 ± 5.49	<LOD
	6.25	1.82 ± 0.08	0.12 ± 0.12	<LOD	52.90 ± 9.92	<LOD
	12.5	1.67± 0.56	0.14 ± 0.10	<LOD	55.18 ± 8.46	<LOD
	25	2.21 ± 0.54	0.14 ± 0.06	<LOD	52.04 ± 6.75	<LOD
	50	1.85 ± 0.70	0.15 ± 0.11	<LOD	51.53 ± 2.82	<LOD
	100	1.91 ± 0.38	0.13 ± 0.08	<LOD	51.22 ± 10.74	<LOD
ZnFeZr-4:1:1	3.125	0.70 ± 0.11	0.09 ± 0.10	<LOD	47.66 ± 4.64	<LOD
	6.25	1.22 ± 0.11	0.12 ± 0.09	<LOD	49.03 ± 8.23	<LOD
	12.5	2.01 ± 0.10	0.28 ± 0.23	<LOD	54.90 ± 6.60	<LOD
	25	2.12 ± 0.26	0.11 ± 0.09	<LOD	48.24 ± 6.25	<LOD
	50	1.77 ± 0.30	0.12 ± 0.10	<LOD	50.21 ± 6.29	<LOD
	100	1.34 ± 0.24	0.14 ± 0.07	<LOD	47.86 ± 9.54	<LOD
ZnFeZr-3.6:0.2:1	3.125	1.0 ± 0.01	0.11 ± 0.09	<LOD	65.50 ± 5.44	<LOD
	6.25	1.81 ± 0.01	0.10 ± 0.07	<LOD	60.73 ± 6.10	<LOD
	12.5	2.31 ± 0.13	0.11 ± 0.10	<LOD	55.99 ± 11.91	<LOD
	25	1.89 ± 0.17	0.11 ± 0.11	<LOD	54.76 ± 12.52	<LOD
	50	1.60 ± 0.43	0.13 ± 0.08	<LOD	53.0± 13.13	<LOD
	100	1.14 ± 0.19	0.13 ± 0.08	<LOD	59.17 ± 10.59	<LOD
CaFe-2:1	50	0.05 ± 0.02	0.08 ± 0.02	<LOD	39.59 ± 6.37	<LOD
	100	0.04 ± 0.01	0.08 ± 0.04	<LOD	37.51 ± 6.14	<LOD
CaFeZr-6:1:1	50	0.10± 0.11	0.07 ± 0.0	<LOD	43.26 ± 15.43	<LOD
	100	0.03 ± 0.01	0.25 ± 0.41	<LOD	42.43 ± 23.59	<LOD
CaZnFeZr-3:3:1:1	3.125	0.53 ± 0.04	0.10 ± 0.09	<LOD	55.56 ± 4.50	<LOD
	6.25	0.96 ± 0.11	0.11 ± 0.09	<LOD	56.15 ± 7.55	<LOD
	12.5	1.73 ± 0.19	0.13 ± 0.08	<LOD	54.91 v 13.64	<LOD
	25	1.77 ± 0.85	0.11 ± 0.07	<LOD	54.48 ± 3.44	<LOD
	50	2.17 ± 0.28	0.09 ± 0.09	<LOD	52.23 ± 10.03	<LOD
	100	1.92 ± 0.82	0.10 ± 0.10	<LOD	47.27 ± 9.97	<LOD
MgFeZr-6:1:1	50	0.07 ± 0.02	0.09 ± 0.03	<LOD	41.48 ± 15.48	<LOD
	100	0.07 ± 0.03	0.06 ± 0.0	<LOD	40.16 ± 17.20	<LOD
MgZnFe-1:1:1	3.125	0.53 ± 0.22	0.24 ± 0.05	<LOD	56.28 ± 4.66	<LOD
	6.25	0.41 ± 0.12	0.11 ± 0.07	<LOD	52.69 ± 6.74	<LOD
	12.5	0.47 ± 0.14	0.17 ± 0.10	<LOD	52.89 ± 5.33	<LOD
	25	0.70 ± 0.02	0.20 ± 0.12	<LOD	56.80 ± 3.72	<LOD
	50	0.88 ± 0.05	0.18 ± 0.10	<LOD	51.90 ± 15.06	<LOD
	100	0.97 ± 0.15	0.16 ± 0.10	<LOD	55.40 ± 11.45	<LOD
ZnFeZr-6:1:1@MPs	50	0.41 ± 0.09	0.08 ± 0.01	<LOD	62.78 ± 0.46	<LOD
	100	0.59 ± 0.20	0.23 ± 0.21	<LOD	63.01 ± 9.20	<LOD

Table S5: Acute toxicity of selected metals to *Daphnia magna*, *Vibrio fischeri*, *Raphidocelis subcapitata* and *Chironomus riparius* with their respective **L(E)C_{50} values (mg/L)** collected from literature.

Remark: The selected metals are representative of the precursor metal salts ($ZnCl_2$; $FeCl_3 \cdot 6H_2O$; $ZrOCl_2 \cdot 8H_2O$; $CaCl_2 \cdot 2H_2O$ and $MgCl_2 \cdot 6H_2O$) used for the synthesis of the studied nanocomposites.

	Metal				
Test organism	**Zn**	**Fe**	**Zr**	**Ca**	**Mg**
Daphnia magna	1.4 – 2.6 [a] ; 3.1 [b]	12.9 – 17.3 [c]	> 400 [d,f]	870 [d] – 2400 [e]	290 [d]
Vibrio fischeri	3.8 – 4.8 [g]	> 100 [h]	> 4.3 [k]	n/a*	n/a**
R. subcapitata	0.037 [i] – 0.1 [j]	> 1–10 [j]	1.3–2.5 [k] ; 4.6 [l]	n/a***	>100 [j]
Chironomus riparius	> 25 [m]	> 5.2 [n] ; > 49.8 [n]	n/a****	-	-

[a] (Blinova et al., 2010) : bulk ZnO or nano ZnO

[b] (Gonçalves et al., 2018) : nano ZnO

[c] (Blinova et al., 2018)

[d] (Okamoto et al., 2015) : $CaCl_2 \cdot 2H_2O$, $MgSO_4 \cdot 5H_2O$, $ZrCl_4$

[e] (ECHA Chemicals Database, 2025) : $CaCl_2 \cdot 2H_2O$

[f] (Załęska-Radziwiłł and Doskocz, 2016) : ZrO_2 EC_{50} > 400 mg/L

[g] (Mortimer et al., 2008) : Zn^{2+}, bulk ZnO or nano ZnO

[h] (ECHA Chemicals Database, 2025) : $FeCl_3 \cdot 6H_2O$ non-toxic all acute LC_{50} and EC_{50} > 100 mg/L & chronic NOEC > 1 mg/L

* $CaCl_2 \cdot 2H_2O$: no EC_{50} data available on ECHA chemicals database: https://chem.echa.europa.eu/

** $MgCl_2 \cdot 6H_2O$: no EC_{50} data available on ECHA chemicals database: https://chem.echa.europa.eu/

[i] (Aruoja et al., 2009) : bulk ZnO, nano ZnO or $ZnSO_4$ (mg-metal/L)

[j] (Aruoja et al., 2015) : nano ZnO (mg-compound/L); nano Fe_3O_4 and nano MgO (mg-compound/L)

[k] (Couture et al., 1989) : $ZrCl_4$ toxicity based on ATP energy stress on green micro-alga *S. capricornutum*

[l] (Simon et al., 2001) : Zr oxychloride, Zr nitrate, Zr ascorbate or Zr citrate: 50 µM Zr (4.561 mg/L) slightly inhibited the dry matter accumulation and insignificantly affected the growth rate of *Chlorella pyrenoidosa*.

*** $CaCl_2 \cdot 2H_2O$: no EC_{50} data available on ECHA chemicals database. Calcium has only been studied in terms of its detoxifying effect when applied with other, toxic, metals.

[m] (Béchard et al., 2008): $ZnCl_2$, mg metal/L, soft water (8 mg/L as $CaCO_3$ equivalents)

[n] (Canadian BC Ministry of Environment, 2008): $FeCl_3$; > 5.2 mg/L (50 mg/L as $CaCO_3$ equivalents), > 49.8 mg/L (250 mg/L as $CaCO_3$ equivalents)

[****] $ZrOCl_2 \cdot 8H_2O$: no L(E)C_{50} data available on ECHA chemicals database: https://chem.echa.europa.eu/

Table S6: Summary of all Zn-containing nanocomposites with their 48-h EC_{50} for *D. magna* and the corresponding Zn-normalized 48-h EC_{50} values, calculated based on the molar mass fraction of Zn (wt%) in the nanocomposites.

Composite name	Zn fraction by molar mass (wt%)	48-h EC_{50} whole composite (mg/L)	48-h EC_{50} Zn-normalized (mg/L)
ZnFeZr-18:5:1	36.6	4.4	1.6
ZnFeZr-10:1:1	37.0	6.5	2.4
ZnFeZr-6:1:1	26.2	7.7	2.0
ZnFeZr-4:1:1	24.1	9.0	2.2
ZnFeZr-3.6:0.2:1	25.4	5.7	1.4
CaZnFeZr-3:3:1:1	18.3	12.5	2.3
MgZnFe-1:1:1	16.7	> 100	n.d.
ZnFeZr-6:1:1 @ MP	5.2	>> 100	n.d.

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