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Abstract

Nanocomposite Metal Oxide/Hydroxide Adsorbents for Advanced Wastewater Treatment and Toxicological Risk Assessment for the Aquatic Environment †

Asya Drenkova-Tuhtan [1,*], Mariliis Sihtmäe [1], Irina Blinova [1], Kevin Uke [2], Heiki Vija [1] and Anne Kahru [1,3]

[1] National Institute of Chemical Physics and Biophysics, 12618 Tallinn, Estonia; mariliis.sihtmae@kbfi.ee (M.S.); irina.blinova@kbfi.ee (I.B.); heiki.vija@kbfi.ee (H.V.); anne.kahru@kbfi.ee (A.K.)
[2] Nordica | Nordic Aviation Group AS, 11101 Tallinn, Estonia; kevinuke95@gmail.com
[3] Estonian Academy of Sciences, 10130 Tallinn, Estonia
* Correspondence: asya.drenkova@kbfi.ee
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Phosphorus (P) is a key nutrient for agriculture [1], but is also an environmental pollutant that causes eutrophication and is commonly removed from wastewater [2]. Engineered nanostructured materials, predominantly metal oxides/hydroxides, are frequently reported as excellent adsorbents for phosphate [3], able to selectively remove P from wastewater to ultra-low concentrations [4], and facilitate P-recovery through reversible sorption [5]; however, their environmental safety is rarely addressed. This study assesses the ecotoxicological hazard of 10 highly efficient metal oxide/hydroxide nanocomposite P-adsorbents using toxicity tests involving two different food-web level test organisms: the naturally bioluminescent marine bacterium *Vibrio fischeri*, and the crustacean *Daphnia magna*. Nanocomposites were synthesized based on published procedures [6,7] via co-precipitation of 2-, 3- and 4-valent metal precursors (Zn^{2+}, Ca^{2+}, Mg^{2+}, Fe^{3+}, Zr^{4+}) at different molar ratios, and characterized with laser diffraction, ICP-OES, XRD and SEM. Among these, the pilot-scale tested ZnFeZr-6:1:1-oxyhydroxide [8] was modified by reducing the zinc fraction to minimize leaching of toxic Zn^{2+} ions. The composites' stability was investigated in deionized water and 2% NaCl (*V. fischeri* test medium), addressing agglomeration, settling and solubilization (the release of metal ions and/or potentially hazardous nanoparticles). All composites, their filtered supernatants and precursor metal salts were evaluated for their toxic potency (half-effective concentration, EC_{50} and minimum bactericidal concentration, MBC) using three different tests: a *Vibrio fischeri* 30 min bioluminescence inhibition assay (ISO-21338:2010) [9], a *V. fischeri* 24 h viability assay ('Spot test') and a *Daphnia magna* 48 h acute immobilization test (OECD-202) [10]. Only the Zn-containing composites showed inhibitory effects on both organisms. Those with the highest zinc fraction (ZnFeZr-18:5:1; ZnFeZr-10:1:1) were classified "harmful" to *V. fischeri* ($10 < EC_{50} \leq 100$ mg/L), and toxic to *D. magna* ($1 < EC_{50} \leq 10$ mg/L); therefore, they are environmentally unsafe for engineering applications. The ZnFeZr-6:1:1 (*V. fischeri* EC_{50} = 118 mg/L; *D. magna* EC_{50} = 7.7 mg/L) proved assumingly safe for both aquatic organisms once deposited on magnetic particles ZnFeZr-6:1:1@MPs (EC_{50} >> 100 mg/L, MBC > 1000 mg/L). All other composites without Zn were non-toxic, both to *V. fischeri*, and to the more sensitive *D. magna*.

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