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Evaluation of the Toxicity of Nanostructural Aluminium Oxyhydroxide with the Help of Hydrobionts

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Abstract

The toxicity of the aqueous extracts from the sorption material containing the particles of nanostructured aluminium oxyhydroxide, modified with colloidal silver and non-modified ones, with respect to Daphnia and luminescent bacteria was studied. It was established that the toxicity of aqueous extracts is due to the presence of Al^{3+} ions migrating into water with low salt content, and oligodynamic action of silver.

Key words: nanostructured aluminium oxyhydroxide, toxicity, biotesting, *Daphnia Magna Straus*, *Vibrio fischeri*, colloidal silver, aluminium ions

INTRODUCTION

Investigation of the possible negative effect of nanoparticles and nanoparticle-based materials on human organism is becoming urgent during the recent years. On the one hand, unique properties of nanomaterials allow achieving qualitatively new results in medicine for directed delivery of medical preparations, for the development of biosensors, wound bandaging materials with wound healing, bactericidal, hemostatic properties. On the other hand, there is a potential risk of the application of nanoparticles, which is connected with their high penetrating power and chemical activity. At present, the toxicity of nanoparticles and nanomaterials is determined with the help of tests involving microorganisms, cell cultures and hydrocoles [1–8].

For the application of sorption material containing nanostructured aluminium oxyhydroxide to water purification or as wound bandaging material [9, 10], important problems are those connected with the possibility of nanoparticle migration from the sorbent into the environment and the potential danger of nanoparticles for the organism.

The goal of the present work was to study the ability of nanoparticles to migrate from the material into aqueous media and to evaluate the toxicity of water extracts, due to the presence of separate nanoplates, their agglomerates and the dissolved components of sorption material, to hydrocoles.

EXPERIMENTAL

Two types of material obtained according to the procedure described in [10] were used in the studies. The material containing no silver was nonwoven fabric composed of acetylated cellulose fibres (AC) 1–3 μm in diameter; aluminium oxyhydroxide nanoplates 100–200 nm in size and 2–5 nm thick, agglomerated into coral-like structures 0.5–5.0 μm in size were immobilized on the surface and in the interfibrillar space of the fabric. The material with

silver contained also the particles of colloid silver (0.02 %) 15–20 nm in size, adsorbed on aluminium oxyhydroxide.

Number-average and mass-average particle size distributions were determined with the help of a disc centrifuge CPS DC 24000. Turbidity of water extracts was determined according to the procedure described in [11], aluminium concentration was measured as described in [12].

Water extracts were prepared as follows. Material samples, 60 g in mass each, were placed in glass beakers with 1200 mL of distilled or dechlorinated aerated tap water, the beakers were capped with glass to decrease water evaporation, and left at a temperature of 24 °C and natural illumination for 5 days. The contents of the glasses were mixed once a day by shaking. After exposure for 5 days, 1000 mL of water from each beaker were decanted and filtered through a White Ribbon paper filter washed preliminarily with hot distilled water to remove aggregated aluminium oxyhydroxide particles and microfibers of the polymer matrix. The reference sample was distilled water or dechlorinated and aerated tap water kept under the same conditions (24 °C, 5 days). Extracts based on distilled water were conditioned by adding NaCl to the total salt content of 100 mg/L before biotesting.

In order to obtain reliable results, biotesting was carried out with two test objects: the simplest Crustacea *Daphnia Magna Straus* and luminescent bacteria *Vibrio fischeri* NRRL-B-11177.

The toxicity of water extracts for *Daphnia Magna* was tested according to the procedure FR.1.39.2001.00283.

Tests with *Vibrio fischeri* were carried out according to the ISO 11348±2, 2007 standard. Luminescence was measured with the help of LUMIStox luminometer at (15±2) °C. Water extracts were diluted with a 2 % NaCl solution; the acidity of the solutions was brought to pH 7.0 with the help of 0.1 M NaOH or 0.1 M HCl solutions. The concentration of dissolved oxygen in the samples under study was 8–9 mg/dm^3. The reference for comparison was a 7.5 % solution of NaCl.

The concentration of dissolved oxygen in the samples under investigation exceeded 6 mg/dm^3 during all the experiments, pH was 6.5–8.0.

RESULTS AND DISCUSSION

First of all, the concentration and particle size in eater extracts migrating from the bandaging material were determined. It was established that almost the same amounts of particles migrate into distilled and tap water; the size of nearly 70 % of the particles is 100–200 nm (Fig. 1, *a*).

This value corresponds to the size of a separate nanosheet of aluminium oxyhydroxide. The conventional particle concentration calculated according to CPS data is equal to 2–4 mg/L. The mass concentration of separate nanosheets is less than 1 % (see Fig. 1, *b*), while the rest is coral-shaped agglomerates of aluminium oxyhydroxide nanosheets 1.0–5.0 μm in size [13].

It was established that the concentration Al^{3+} in the extract based on distilled water increases sharply after exposure for 3 days: during the first day it is equal to 0.22, the second day – 0.28, the third – 0.30, the fourth – 2.92, the fifth – 2.90 mg/L. Quite contrary, in tap water it remains constant and does not exceed 0.05 mg/L. For the extract of AC and reference samples, aluminium concentration is less than 0.05 mg/L. An increase in aluminium concen-

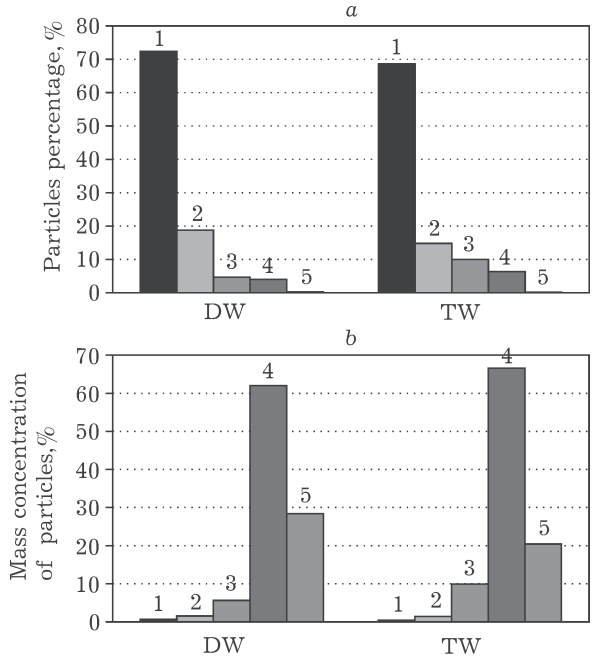

Fig. 1. Numerical average (*a*) and mass-average (*b*) size distribution of the particles of aluminium oxyhydroxide in water extract based on distilled water (DW) and tap water (TW). Particle size (μm): 0.1–0.2 (1), 0.2–0.5 (2), 0.5–1.0 (3), 1.0–3.0 (4), 3.0–5.0 (5).

TABLE 1

Toxicity of water extracts from AC and silver-free material with respect to daphnids, mortality %

Samples	Duration of observation, h									
	0.5	1	2	3	4	24	48	72	96	144
					Extracts based on distilled water					
Material	20	70	10							
AC	0	10	0	10	0	10	20	10	20	20
Reference	0	0	10	20	10	20	10	10	10	10
					Extracts based on tap water					
Material	0	0	0	0	0	0	0	10	20	20
AC	0	0	0	0	0	0	0	10	10	30
Reference	0	0	0	0	0	10	10	10	10	30

tration occurs at the background of decrease in turbidity (7.3 FTU after 1 day, 2.0 FTU during the second day and then less than 0.01 FTU); an increase in turbidity was observed directly after the samples of the material were placed in water. For the samples of extracts from AC and reference samples turbidity was also less than 0.01 FTU. Therefore, an increase in aluminium concentration is connected with the migration of Al^{3+} ion into water.

Extracts from the sorption material based on distilled water turned out to be toxic for daphnids, unlike for extracts based on tap water (Table 1).

The concentration of nanoparticles is the same in both extracts, so the toxicity of the extract based on distilled water is likely due to increased concentration of aluminium ion.

It was demonstrated previously [14] that aluminium oxyhydroxide particles similar to those studied in the present work have a toxic effect on daphnids in the concentration 6–250 mg/L, while water-repelling coating decreases their toxicity. A decrease in the toxicity of nanoparticles with water-repelling coating may be connected with a decrease in their solubility due to the protective action of the coating.

In view of the fact that the extracts based on distilled water are toxic for hydrobionts, next we studied the extracts based on tap water. Test with daphnids was used to evaluate the changes in the toxicity of aluminium oxyhydroxide particles caused by modification with silver. It was established that water extracts containing aluminium oxyhydroxide particles modified with silver have a weak toxic effect on daphnids: after single dilution the extract was toxic for daphnids (100 % death within 24 and 96 h of experiment), after double dilution 50 % of daphnids died within 24 h, and 100 % died within 96 h. In the case of 4 times dilution, within 24 h, the extract turned out to be non-toxic for daphnids, while within 96 h their death was 20 %. Similarly to the first experiment, extracts from the material containing no silver turned out to be non-toxic.

Good convergence of results should be stressed for the tests of water extracts from both types of materials on daphnids using tap water kinds with different compositions. Investigations were carried out at the Sysin Research Institute of Human Ecology and Environmental Health (Moscow), State Environmental Committee of the Tomsk Region Administration and National Institute of Chemistry (Ljubljana, Slovenia).

TABLE 2

Toxicity of the water extract from silver-containing material with respect to luminescent bacteria *Vibrio fischeri* after contact for 30 min

Concentration of water extract, %	1.56	3.12	6.25	12.5	25	50	80	Reference	Standard
Average luminescence index	2.26	1.70	6.11	11.37	26.75	48.27	64.45	6.56	40

The second test object, namely luminescent bacterial, was used only to test water extracts of silver-containing material containing all components of interest and possessing weak toxic effect with respect to daphnids. The weak toxic action of the water extract from silver-containing material was expressed also with respect to luminescent bacterial (Table 2). It follows from the data shown in Table 2 that 50 % of the bacteria died after the 30 min contact with water extract diluted to 52.251 %. This corresponds to the results obtained during its tests with daphnids.

Investigations allow us to conclude that the use of distilled water, though it seems to be preferable medium for preparing water extracts because it does not contain foreign impurities, causes distortion of results on the evaluation of nanoparticle toxicity. In distilled water, we observe accumulation of aluminium ion which is toxic for hydrocoles, due to the dissolution of aluminium oxyhydroxide. In addition, even in the case of NaCl addition, the death of daphnids occurs substantially earlier than in tap water (see Table 1). This may be connected with the absence in distilled water of many dissolved salts that are essential for living organisms functioning, first of all calcium and magnesium salts. Therefore, the test based on distilled water creates the sum action of the toxicity of sample under study and unfavourable environment.

Thus, nanoparticles with the toxic action due to the migration of their components into the medium will exhibit much lower toxicity in the solutions with high salt content (native water, biological fluids) than in distilled water, or will be completely non-toxic.

CONCLUSIONS

1. Nanoplates of aluminium oxyhydroxide and their agglomerates 0.1–5.0 μm in size in the concentration 2–4 mg/L do not cause toxic action on hydrocoles – daphnids and luminescent bacteria.

2. Nanoparticles of aluminium oxyhydroxide in contact with distilled water slowly dissolve releasing Al^{3+} ions into water, and the extract becomes toxic for hydrocoles after long-term exposure (longer than 5 days).

3. Aluminium oxyhydroxide nanoparticles modified with silver are toxic with respect to daphnids and luminescent bacteria due to the oligodynamic action of silver.

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