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Research Article

The investigation of biotoxity of the anticorrosion agents

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ABSTRACT
The purpose of the present work is to assess to toxicity level of the bioactive commercial compounds. The results of a comparative toxicological study of the anticorrosion compounds' impact on the lower living organisms using biotest methodologies are presented in the article. The review of various groups of bioactive substances is given. The commercial additives used as disinfectants for livestock and veterinary arestudied, as well as fungicides for the different surfaces treatment. The qualitative and quantative analysis methods are used. The results obtained indicate the evident toxicological effect of biocides on various representatives of flora and fauna.
Key words: corrosion, anticorrosion additives, bioagents, biocides, toxicity, phytotest.

INTRODUCTION

Modern urban territories represent the heterotrophic anthropogenic ecosystems, which differ from natural ecosystems in some significant characteristics:

- the disconnected nutrient cycle – that means that the predominant flow of organic material is not formed within the ecosystem, butt is brought into the urban ecosystem from the outside. Cities are unable to exist without a constant supply of resources and energy. So, the following trait is:

– instability, which means that it is impossible to achieve the naturel ecological balance;

– artificial regulation of climate, spatial and energy resources.

All these factors have a definite impact, which is expressed not only in the environmental impact, but also in the damage of buildings, facilities and structures as the major elements of urbanized territories. That's why the level of corrosion has increased significantly in recent years. The harmful corrosion impact has different origin, which depends on the type of active agent [1, 2].

Among all the types of corrosion the biocorrosion, caused by various

microorganisms' impact, is the least studied one (in terms of preventing or limiting the effect). Solid waste, in plenty produced by the city, formates nutrient medium for a number of bioagents' colonies and creates the favorable conditions for the mutation of microorganisms and the formation of new, more viable species. Currently, the microbial pests can not only consume organic matter. The range of species that use chemical compounds as a nutrient substrate has broadened. The major part of such species use iron, sulphates and carbonates, which are in the building materials' matrix. Colonising the surface of the material, biological agents secrete caustic acids that destroy the matrix and contribute to its elements'"washout", also the accumulation of the total biomass of the colonies leads to wedging, cracking and delamination of the material [3-6]. Thus, the bioagents' impact is characterized by the degradation of the material on all the structural levels. On the other hand, their negative influence on human health is evident. Most modern species of fungi,living on the inner walls of buildings, are pathogenic and cause allergic reactions, diseases of the respiratory tract and the gastrointestinal tract [7, 8].

Due to the number of reasons, the solution of this problem is an extremely complex and controversial task. One of the most common ways is the treatment of the contaminated surfaces using anti-corrosion agents – biocides, varying by the composition and the microbiological counteraction.

Despite the high efficiency, there are several problems,connected with the biocidal treatment. The main disadvantage of such method is a short biocidal effect, which can cause not only an increase in the economic cost of fungi and mold control, but also the adaptation of pests to biocides. The time interval between the initial and the subsequent application of the active substance givesapossibilityfor pests to develop protective mechanisms of biocide toxins neutralization [9,10]. However, these toxins, causing no harm to bioagents, are still dangerous for the environment. This is the next serious problem with biocidal treatment of the modern materials.

The active substance, which is in the composition of any biocide, has to neutralize the activity of spores of fungi and mold. However, due to the external factors, the outflow of the active substance into the environment is possible. That causes the negative consequences towards the living organisms of different origin. In this regard, when using anti-corrosion additives of the biocidal purpose, the ecotoxical effect has to be controlled carefully, which represents the purpose of the present work.

MATERIALS AND METHODS

During the complex studying of the biocidal component's toxicity, it is necessary to execute the biological testings on living organisms, which belong to various ecological groups, that's why the test-objects were chosen among the representatives of plants – grain oats, and animals – Daphnia Magna. The following indicators were chosen as the analyzed features: the growth rate and the viability.For the research, there were chosen following commercial biocides: Dinovis, MegaDez, Sikagard, Bioplast, Silver Nanoparticles – asthe most widely used in Russia. These additives represent the types of disinfectant, fungicidal and bactericidal means, used to counteractthe microorganisms of different classes.Dinovis is used as a mean for disinfection in the livestock and veterinary and for the infectious animal diseases prevention. It is an aqueous concentrate containing glyoxal, alkyldimethylbenzylammonium chloride (ketamin), 2-methylimidazole, functional components.

MegaDez is a highly effective disinfectant system based on alkyldimethylbenzylammonium chloride (QAS) and the aldehydes (glutaraldehyde and glyoxal) in concentrationsproviding maximum efficacy and the low toxicity of working solutions.Sikagard 715 W is a water-repellent impregnation on a silicate basis. Increases the contamination resistance and reduces the growth of fungi and microorganisms.Bioplast is the bactericidal additive used in the field of mining, storage and transportation of oil and products, which are exposed to pathogens. It is characterized by the presence of

polyhexamethyleneguanidine hydrochloride and Quaternary ammonium salts (alkylbenzyldimethylammonium chloride) in its composition.Silver Nanoparticles as a water colloidal solution, stabilized by PVP (Ag/PVP/W 500). It is used as a biocidal additive for the creation and production of a variety of materials and products for sanitary purposes with a biocidal (including antibacterial, antiviral, antifungal) properties.The water solutions of additives were used as the raw materials. The concentrationswere determined according to the manufacturers' recommendations (table. 1).

Table I. Additive's concentrations in the water solutions.

Additive's name	Concentration in the water solution,%
Dinovis	0,5
MegaDez	0,5
Sikagard	2
Bioplast	0,25
Silver nanoparticles	0,02

For the toxicity analysis towards living organisms the technique of short-term biotest was used [11]. The average number of test-objects who survived in the experimental solutions of the additives over a period of 96 h, comparing to control, was used for the assessment of the results as the survival rate.

Synchronized Daphnia culture's exposure into the vessels was carried out in a following order: using the glass tube young (newborn) Daphnia were caughtand placed into the vessel with the experimantal liquid. Specimens in an amount of 10 were exposed for 96 hours.

The estimation of the survived Daphnia specimenswascarried out after 1, 24, 48, 72, and 96 h. The test-objects were supervised every hour during the initial period of the experiment (4 h), the next day 1-2 times a day. During the supervisionthe survived and dead organisms were counted, as well as the percentage of survived individuals. The crustaceans' death time was determined as the onset of immobility (Daphnia lies on the bottom of the glass, swimming movements are absent and doesn't renew with the slight shaking of the flask). Daphnia were not fed during the experiment.

Daphnia mortality in the experimental liquids comparing to control was calculated, using the formula:

$$A = \frac{X_к - X_m}{X_к}, \qquad (1)$$

where$X_к$ – the average number of Daphnia survived in control; X_m – average number of Daphnia that survived the test-medium.

The toxicity assessment of the proposed biocides was carried out through their hazard class according to the method [12]. The method is based on measuring the intensity of germination of test-culture seeds (cereal products) placed in solutions of the experimental liquids.

Oat was selected as the test culture due to the more stable and reproducible data comparing with other cereal cultures. The test culture was grown in Petri dish, while the distilled water was chosen as a control medium. At the bottom of each dish, coveredwith filter paper 25 oat seeds were placed. The solutions of test substances (5 ml) were also poured into the dish, with solution distribution all over the dish bottom. After that, the samples were placed in a thermostat for 7 days.

At the end of theexposure time the control measurement of the root length was carried out both on the test-culture in control and experimental solutions. The object of measurement for each seed was the longest root. Visual assessment of samples didn't depend on the calculation method, since the calculation method takes into account only the root length of the most active oat seedling, which does not provide a complete vision of phytotoxicity of the studied biocide.

Determination of the phytotoxic effect is carried out by comparing the results of control and experimental seeds of test-culture. As a quantitative assessment of phytoeffectthe estimated value $E_т$ (braking effect) acts, determined by the formula:

$$E_т = \frac{L_к - L_{оп}}{L_к} \cdot 100\ \%, \qquad (2)$$

whereL_k is an average root length of test cultures in the control solution (mm)

L_{on} – the average root length of test cultures in the experimental (working) solution (mm).

The solutions of additives, obtained by diluting the initial solution of the additive with a given concentration by the distilled water, were used for the study. Depending on the method of testing the degree of dilution was different. For phytotest the original solutions were diluted 10, 100 and 1000 times. In the case of biotesting due to the ultrahigh sensitivity of the test-objects the original solutions were diluted to achieve concentrations of active substance in the system 10^{-6} and 10^{-9}.

RESULTS AND DISCUSSION.

Data analysis for biotestingof the additives shows their negative impact on the habitats of living organisms: most of the extracts significantly increased mortality comparing with the control (aerated tap water) (table 2).

Data analysis of the biological testing of additives.Three experimental samples of five reach 100% mortality after 14 hours. This may indicate the presence in the solutions, and consequently, in the composition of the test substances, components that have acute toxic effect on living organisms. As the degree of harmful effect (toxicity)on Daphnia, as biological indicators of water purity, sensitive to its composition changes, increases, the studied biocides can be placed in the following order: Dinovis → Sikagard → MegaDez → Silver Nanoparticles → Bioplast.

Table II. Daphnia mortality (%) time depending on the solution

Medium	Exposition time,h			
	1	*24*	*48*	*96*
Pure water	0	0	20	20
In the concentration 10^{-6}				
Dinovis	0	90	100	100
MegaDez	0	100	100	100
Bioplast	0	100	100	100
Silver Nanoparticles	0	100	100	100
Sikagard	0	10	100	100
In the concentration 10^{-9}				
Dinovis	0	0	100	100
MegaDez	0	90	100	100
Bioplast	0	100	100	100
Silver Nanoparticles	0	100	100	100
Sikagard	0	100	100	100

It should be mentioned that the ranking is relative because of the complete mortality of test objects. The only difference is in the speed of extinction processes.

Phytotest results confirm the previously obtained data on the toxic effect of additives' solutions on the functioning of the test objects (table. 3).

Table III. Performance of braking effect depending on the type of additive.

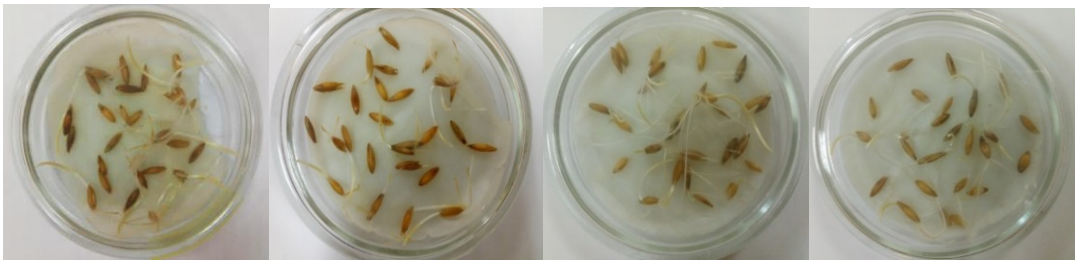
Additive	Braking effect, %	
	Without dilution	*1:1000*
Dinovis	100	83,8
MegaDez	100	82,1
Bioplast	14	21,4
Silver Nanoparticles	100	83
Sikagard	100	72

The introduction of additives' solution into extracts for plant growth leads to a significant inhibition of their growth. Thus, the use of initial solutions eliminates the germination of the oats roots. Dilution of the experimental system reduces the braking effect. However, regardless of the type of additive, values for the braking effect substantially exceed the thresholds of toxicity.In order to analyze the phytotoxic effect of biocidal components visual assessment of oat grain was carried out.(Fig. 1-5).First of all, it

should be mentioned that in the test medium the test-culture gave good germination (Fig. 1): There is good development of the root system and the greater length of grain sprouts. There is no tarnish, no sign of decay on the surface of grains.

Fig.1. The nature of the oat growth in distilled water (control medium)

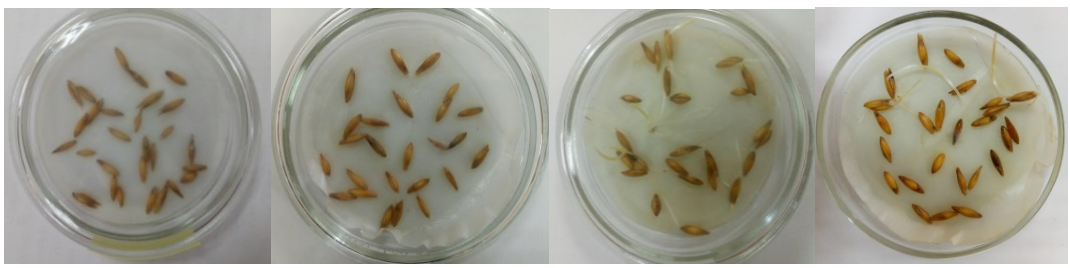
In case of experimental compounds visible differences are primarily in degree of purity of the grains of test-culture and germination.In the dish with the initial solution of Bioplast there is a lack of elements of the root system and germs in 40 % of the grains (Fig. 2, a). However, all sprouted grains have such well-developed germs and roots that it is impossible to make an absolute conclusion about the presence of an acute toxic effect in the original dilution. Dilution of the initial solution in the ratio of 1/10 the percentage of non-germinated grains increases and reaches 50 %, and only 24 % of the remaining grain sprouts also have weak rudiments of the root system (Fig. 2, b). When diluted in the ratio of 1/100 the growth of both roots and sprouts of the test culture is observed with a total percentage of non-germinated grains 28 % (Fig. 2, c). A 1/1000 dilution leads to a reduction of the toxic effect of a biocide, resulting in the reduction in the percentage of non-germinated grains up to 24 % of the total number of test-objects. It is important to mention the fact that the Bioplast in any of the dilutions did not cause rotting of the beans culture. Overall, there is a clear relationship between the concentration of the biocide and the degree of seed germination in solutions. The increase in the toxic effect of dilution 1/10 in comparison with the original can be explained primarily by the presence in the sample of the so-called “dead seeds”, originally unable to sprout. In any case, this effect requires further studying.



a *b* *c* *d*

Fig. 2. The nature of the oat growth in solution on the basis of Bioplast, depending on the degree of dilution:a – initial solution; b – 1/10; c – 1/100; d – 1/1000.

While using the solution of Dinovis as the growth medium in the dish with the initial dilution and in the bowl with a 1/10 dilution the seed germination is missing completely, the some grains are moldy and have putrid spots, which indicates the toxicity of the disinfectant (Fig. 3, a, b).



a *b* *c* *d*

Fig. 3. The nature of the oat growth in solution on the basis of Dinovis

depending on the degree of dilution: a – the initial solution; b – 1/10; c – 1/100;d – 1/1000.

When diluted 1/100 some growth is noticed, however, the percentage of non-germinated grains is still high – 50 %, in addition, on the surface 28% of grains show some traits of decay (Fig. 3, c). However,

the further dilution of the liquids on the surface leads to the decrease of rotting grains amount is slightly reduced. The number of sprouts of grain increases (Fig. 3, d).

The results obtained using a solution of MegaDez as the working environment, are similar to the previous data. In the dish with the initial solution, there was no germination of any of the grains (Fig. 4, a). In addition, the toxic effect was clearly evident as there was the decay and darkening of more than 50 % of the sample test-objects.

a *b* *c* *d*

Fig. 4. The nature of the growth of oat in solution on the basis of MegaDez depending on the degree of dilution:a – the initial solution; b – 1/10; c – 1/100; d – 1/1000.

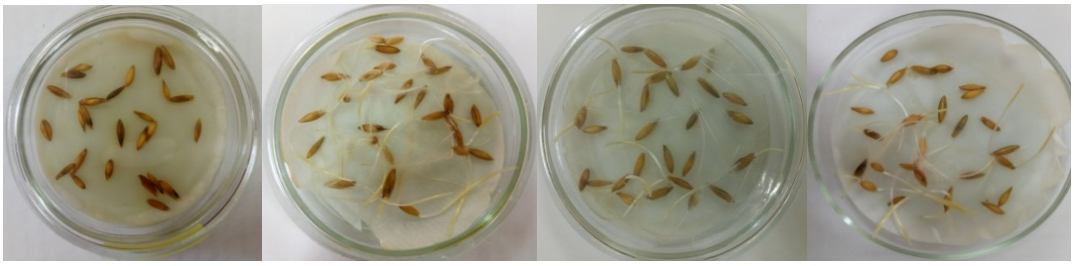
It is noteworthy that none of the following dilutions – 1/10, 1/100, 1/1000 gave positive germination indicators of the grains (Fig. 4, b–d). It is important to note that the decrease of the concentration of MegaDez in the experimental solutions improves the quality of the test-culture. However, basing on visual analysis, it can be concluded about the high toxicity of this compound towards the living organisms. The presence of additives has a negative impact on the integrity of the cell tissues of the studied culture, as well as the viability of the whole grain. In the case of oat grain germination in the initial solution with silver nanoparticles, no growth was observed, the test objects have neither the root system nor sprouts (Fig. 5, a).

However, the dilution of the initial solution in a ratio of 1/10 there is a jump in the growth of the root system and the test culture sprouts (Fig. 5, b). The state of the test-objects is good, with no signs of rot and darkening. While increasing the dilution degree, the number of sprouted grainsgrows: 8 % and 28% at dilution at 1/100 and 1/1000 (Fig. 5 c, d). The nature of the growth of the test culture in these dishes clearly demonstrates the processes of decay within the grain. In the bowl of a 1/1000 dilutionthere are about 50 % of the sprouted grains have surfacemould spots.

a *b* *c* *d*

Fig. 5. The nature of the growth of oat in solution on the basis of Silver Nanoparticles depending on the degree of dilution: a – the initial solution; b – 1/10; c – 1/100; d – 1/1000.

In the initial solution of the Sikagard additive there is no growth of roots and sprouts of investigated test-culture (Fig. 6, a).



a *b* *c* *d*

Fig. 6. The nature of the growth of oat in solution on the basis of Sikagard depending on the degree of dilution: a – the initial solution; b – 1/10; c – 1/100; d – 1/1000.

At a dilution of 1/10, the number of non-germinated grains in a percentage of the total number of grains in the dish is 20 %, signs of rotting, mold and darkening are not observed (Fig. 6, b). More than 80% of grains in addition to growing plants have a root system. At a dilution of 1/100 and 1/1000 the percentage of non-germinated grains is about 40% of the total (Fig. 6, c, d),also the decreasing of active substance concentration causes the number of rotten (moldy) grains increase.

CONCLUSION

According to the data obtained, the biocidal compounds studied in the work are toxical not only towards biological agents but also in relation to cells of living organisms. The results of the experiment confirm the potential hazard of the biocidal treatment of building materials for humans. Thus, at the moment the major value should be given to searching for the ways to reduce the Ecotoxicity of active components which will provide the optimum balance in the system “Man – Material – habitat”.

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