ORGANIC COMPOSITIONS FOR ECOLOGICAL PROTECTION OF ARCHITECTURAL HERITAGE

Elena Hera[1], Carmen Mincea[1], Alexandra Pasareanu[1], Mariana Popescu[2], Elena Dobre[2], Sanda Velea[2], C. Lazureanu[1], F. Oancea[1]*

[1] Research - Development Institute for Plant Protection, Bucharest
[2] National Research - Development Institute for Chemistry and Petrochemistry, ICECHIM- Bucharest

[1*] correspondence address:
Research-Development Institute for Plant Protection
Bd. Ion Ionescu de la Brad nr. 8, CP 013813, S 1,
Bucharest, ROMANIA
Tel.: 004-021-2693231 (32, 34)
Fax.: 004-021-2693239
e-mail: lilihera@yahoo.com

Abstract:
This paper presents the results regarding assessment of biological action of 13 samples prepared in ICECHIM laboratories on mosses and lichens. The samples with the best efficacy were used in order to develop original compositions with potential biocide action for control the bodies responsible for architectural heritage biodegradation. The selected samples for further studies were the following: DL4 (glutaraldehyde, methyl hexadeciltrimetilammonium, diethylene), DL6 (2-ethylhexanoate acid), DL1 (benzalkonium chloride, didecildimetilammonium chloride, glutaraldehyde and sodium bicarbonate), DL3 (benzalkonium chloride, didecildimetilammonium chloride, imbentinU/070 and citric acid), DI (irgasan), and DPN (horseradish extracts). These samples have proved an increased percentage of inhibition of the mosses on stone substrate and of lichens grown on brick tiles.

KEY WORDS: ecological control, biocides, arhitectural heritage, biodegradation

INTRODUCTION

Biodegradation of art objects, monuments and buildings heritage is a peculiar occurence of biologic degradation, because the prevention and treatment methods are mostly different from those used in different industries, taking into account that processed objects belong to the artistic and cultural heritage of humanity. These objects, are formed of ordinary materials, but each of them depicts a special case, for which are asked peculiar research and treatment solutions.

One of the first authors who taped this subject was Schulze, who, in 1938 (Hawks, 2001), written about the materials' biology. (Hueck, 2001), defined the biodegradation as being the undesirable alterations of the materials' properties affected by the vital functions of the organisms. (Urzi and Krumbein 1994), considered the biodegradation as an irremovable loss of an artifact's value and/or infrormation due to the attack of the living organisms.

The climatical environment agents act also sinergically with the biodegradation agents (Papsida et al., 2000), rarely being a protection agent as like the case of some churches from Galicia, placed on the seaside, where the lichens protect the wall against the salt air (Carballal et al., 2001).

The microorganisms can produce the degradation of stone from which are build some buildings, and also some concrete structures, and parietal paintings (Gonzales et al., 1999), being demonstrated the effect of these microorganisms on the building materials.

The development of lichens, algae, and *Briophyta (mosses*), is strictly entailed by the local environmental conditions.

The biomass accumulation by this ecologic class of organisms, can be substrate and support for other organisms that have biodegradation activity (Caneva & Salvadori, 1989). The organisms' association can be an indicator of the chemical-physical parameters of environment-substrate (Caneva et al.,1991; Seaward, 1997).

Those described above were the reason for the project– BIOGREEN- accomplished by ICECHIM Bucharest as coordinator, in partnership with other four research institutes, that proposed achievement of new biocides products and new ecologic technologies for their administration, for the integrate preservation of the architectural cultural heritage from Sibiu area, the European Cultural Capital in the year 2007.

The results carried out in this paper refer to the assesment of biologic action on mosses and lichens for some samples accomplished in ICECHIM laboratories.

Aim

The accomplished experiments carried out the selection and development of some original compositions, grounded on biologic active natural extracts and/or chemical compunds with a high biocide action, designed for the control of responsible organisms for biodegradation of immovable cultural heritage.

MATERIAL AND METHOD

Materials – Samples with different content of active ingredient, and 2 standard products: BENAC 50 and MICOBOR, professional biocides, having a broad-spectrum action on mosses and lichens. The samples subjected to the biologic screening are shown in Table 1.

In order to accomplish the biologic screening of studied samples concerning the quantification of the their biologic action against mosses and lichens, it was performed 3 experiments.

Experiment I –on a brick wall populated with mosses,

Experiment II –on a stone wall,

Experienta III –laboratory study in order to control the lichens

The Experiments I and II, each comprised 29 variants, out of which 26 represent the testing concentrations of the samples, 2 have been treated with products used as standard and a chech test variant. Each variant contained 3 repetitions – 1 repetition = 0.25 sqm.

The biologic material consisted of mosses grown on walls from different building materials (brick, stone).

The Experiment III have been set up in 29 variants, out of which 26 represent thecentration of the studied samples, 2 with the standard products, and one the untreated check test used for comparison. The biologic material consisiting of scaled brown lichens, have been found on tiles from the roof of an old, demolished house.

The colonised tiles with lichens have been brought in the laboratory, cleaned by brushing, each tile featuring a repetition (0.08 sqm). A variants contains three repetitions.

The experimental samples have applied each in 2 concentrations, by atomizing, in watery solution, using the tap. The tratment have been performed manually with the pump of 1 l, using 200 ml solution/sqm.

The observation have been performed before and after treatment at 5, 10, and 20 days for mosses and after 10 and 25 days for lichens. In both cases it was rstablished the inhibition percent of the mosses and lichens development through a visual assessment, relatively to the check test variant.

RESULTS

The biologic action of the tested samples in the control of Bryophyta is emphasized in the Tables 2 and 3.

In the table 2 it is emphasized the inhibition percent of the mosses development on brick substrate after 5, 10, and 20 days after the treatment application.

Tha samples have been tested at concentrations between 1 and 15% of formulated product. Analising the date from the table it is observed the sample DL 4, that inhibited 100% the mosses development at a concentration of 15%, and at 10%, the inhibition percent was contained between 80 and 95%, in the range of observations' performance (5 – 20 zile). A similar behavior has been observed at the sample DL 6 too; at the concentration of 15% it has a 100% inhibitory action against the mosses development after 10 and 20 days from the treatment. At the same sample, at a concentration of 10%, the values of the inhibition percent were contained between 70 and 100%, in the observation interval.

The mosses control registered at the variants treated with the samples DL 4 and DL 6, is placed at the level of those registered in the case of the standard products Benac 50 and Micobor (inhibition %=100).

Good results also have been obtained at the variants treated with the samples DL1 and DL3 at the concentration of 15%, where the mosses development inhibition percent were comprised between 80% and 100%, in the range of the observations' performance.

The Detergent samples with Irgasan (DI 2), and Detergent with natural product (DPN) at a concentration of 15% also shown a good mosses development inhibition action, the inhibition % being of 85% , after 20 days from the treatment. In the case of the other samples subjected to the biologic screening, the inhibition percent had values bellow those registered at the treated variants with the standard products.

These results have been obtained in the conditions where at the check test variant it was observed a normal development of the mosses.

For the same retrievable fraction it has been assessed the biologic action on the mosses grown on stone substrate, the results being emphasized in the Table 3.

Analising the data from the table 3, it is found that the same samples subjected to the biologic screening on a stone substrate, at the same concentrations registered very close values of the inhibition percent to those obtained on brick substrate, so the material nature didn't influence the action of the retrievable fractions.

It is foud out the best control of the Briophyta have been obtained at the variants treated with the samples: DL 4 and DL 6 at both concetrations, and with the samples DL1 and DL3 at the concetration of 15% (inhibition % = 100). Good results were observed also in the case of the sample DI 2 (inhibition % = 90). We make the notice that at both experiments didn't show up secondary noticeable effects on the substrate (brick and stone) subsequent the retrievable fractions applicationas like: colour alterations, spots, schimbări de culoare, pete, action of corrosion, etc.

The biocide action of the experimental samples in the control of lichens, it is emphasized in the Table 4.

The data from the table show the inhibition percent of the lichens 10 and 25 after the treatment. A good inhibition of 85 – 90 % 25 days after the treatment have been registered at the variants tretated with the samples: DI2- 90%, DPN- 85%, DL 1- 85%, DL 3 - 90%, DL 4- 90%, and DL 6- 90% at a concentration of 15%. These values are placed at the level of the inhibition percent obtained at the variants treated with the products Micobor (85%) and Benac 50 (90%), used as standard. Realtively to the check test, at these variants it noticed that the scale represented by the lichens cultures, they burst, peeled, were removed easely with a spatula, better of wood, with the aim to keep the substrate intact. The weak biocide action have been observed at the variants treated with the reamaining samples where at a concentration of 15%, the inhibition percent had values lower than 80%.

Table 1

Samples with potential biocide action

Nr.crt.	Code	Active ingredient	% a.i.
1.	DI 2	Irgasan	2
2.	DPN	Horseradish natural extract	5
3.	DL 1	Benzalkonium chloride 50%, didecildimetilamonium chloride 50%, glutaraldehyde 50%, sodium bicarbonate	15
4.	DL 2	Benzalkonium chloride 50%, glutaraldehyde 50%, sodium tetraborate	15
5.	DL 3	Benzalkonium chloride 50%, didecildimetilamonium chloride 50%, IMBENTIN U/070, citric acid	15
6.	DL 4	Glutaraldehyde 50%, hexadeciltrimetilamonium bromide, diethylene glycol	15
7.	PMH 01	Boric acid, borax, glycerol	18
8.	PMH 02	Esters of the C2-C8 acids with 8-hidroxichinolin	15
9.	PMH 03	Ammonium quaternary salts of the alkyl-phosphoric acids	16
10.	DL 5	Glycerol	65
11.	DL 6	2-etlhyhexanoic acid	50
12.	DL 7	**Acid 2-etylhexanoic, tetraethylamina salt**	20
13.	DL 8	**PAP**	0.2

Table 2

Biologic action in control of mosses developed on brick substrate

No.	SAMPLE	Experimental concentration (%)		% inhibition after days:		
		c.p.	a.i.	5	10	20
1.	DI 2 (2% a.i.)	10	0.2	30	55	70
		15	0.3	65	80	85
2.	DPN (5% a.i.)	10	0.5	25	50	65
		15	0.75	55	70	85
3.	DL 1 (15% a.i.)	10	1.5	15	65	75
		15	2.25	80	85	100
4.	DL 2 (15% a.i.)	10	1.5	10	30	45
		15	2.25	25	50	70
5.	DL 3 (15% a.i.)	10	1.5	40	45	55
		15	2.25	80	90	100
6.	DL 4 (15% a.i.)	10	1.5	80	85	95
		15	2.25	100	100	100
7.	PMH 01 (18%a.i.)	5	0.9	20	35	50
		10	1.8	50	60	70
8.	PMH 02 (15% a.i.)	1	0.15	15	30	45
		5	0.75	45	60	70
9.	PMH 03 (16% a.i.)	1	0.16	0	15	25
		5	0.8	20	30	35
10.	DL 5 (65% a.i.)	10	6.5	0	0	0
		15	9.75	0	0	0
11.	DL 6 (50% a.i.)	10	5.0	70	90	100
		15	7.5	85	100	100
12.	DL 7 (20% a.i.)	10	2.0	0	10	30
		15	3.0	15	75	80
13.	DL 8 (0.2% a.i.)	10	0.02	25	50	50
		15	0.03	50	80	80
14.	BENAC 50 (standard) (50%a.i.)	10	5.0	95	100	100
15.	MICOBOR (standard) (67% a.i.)	20	13.4	75	95	100
16.	Check test	-	-	0	0	0

Table 3

Biologic action in mosses control developed on stone substrate

No.	SAMPLE	Tested concentration (% c.p.)	Tested concentration (% a.i.)	% inhibition after days:		
				5	10	20
1.	DI 2 (2% a.i.)	10	0.2	40	60	70
		15	0.3	60	75	90
2.	DPN (5% a.i.)	10	0.5	30	45	65
		15	0.75	50	65	85
3.	DL 1 (15% a.i.)	10	1.5	20	65	80
		15	2.25	70	80	100
4.	DL 2 (15% a.i.)	10	1.5	15	25	30
		15	2.25	25	45	70
5.	DL 3 (15% a.i.)	10	1.5	45	60	70
		15	2.25	80	85	100
6.	DL 4 (15% a.i.)	10	1.5	70	80	95
		15	2.25	100	100	100
7.	PMH 01 (18%a.i.)	5	0.9	15	40	55
		10	1.8	50	65	70
8.	PMH 02 (15% a.i.)	1	0.15	15	25	30
		5	0.75	40	55	60
9.	PMH 03 (16% a.i.)	1	0.16	5	10	25
		5	0.8	20	25	30
10.	DL 5 (65% a.i.)	10	6.5	0	0	0
		15	9.75	0	0	0
11.	DL 6 (50% a.i.)	10	5.0	70	90	100
		15	7.5	90	100	100
12.	DL 7 (20% a.i.)	10	2.0	5	15	30
		15	3.0	20	65	80
13.	DL 8 (0.2% a.i.)	10	0.02	30	45	55
		15	0.03	50	75	80
14.	BENAC 50 (standard) (50% a.i.)	10	5.0	100	100	100
15.	MICOBOR (standard) (67% a.i.)	20	13.4	70	90	95
16.	Check test	-	-	0	0	0

Table 4

Biologic action on lichens control

No.	SAMPLE	Tested concentration (% c.p.)	Tested concentration (% a.i.)	% inhibition after days:	
				10	25
1.	DI 2 (2% a.i.)	10	0.2	50	75
		15	0.3	70	90
2.	DPN (5% a.i.)	10	0.5	45	60
		15	0.75	65	85
3.	DL 1 (15% a.i.)	10	1.5	40	60
		15	2.25	50	85
4.	DL 2 (15% a.i.)	10	1.5	35	40
		15	2.25	45	55
5.	DL 3 (15% a.i.)	10	1.5	60	70
		15	2.25	75	90
6.	DL 4 (15% a.i.)	10	1.5	50	80
		15	2.25	85	90
7.	PMH 01 (18%a.i.)	5	0.9	10	40
		10	1.8	30	80
8.	PMH 02 (15% a.i.)	1	0.15	30	30
		5	0.75	60	70
9.	PMH 03 (16% a.i.)	1	0.16	20	35
		5	0.8	40	50
10.	DL 5 (65% a.i.)	10	6.5	0	0
		15	9.75	0	0
11.	DL 6 (50% a.i.)	10	5.0	60	75
		15	7.5	85	90
12.	DL 7 (20% a.i.)	10	2.0	20	30
		15	3.0	35	60
13.	DL 8 (0.2% a.i.)	10	0.02	15	30
		15	0.03	30	60
14.	BENAC 50 (standard) (50% a.i.)	10	5.0	90	90
15.	MICOBOR (standard) (67% a.i.)	20	13.4	75	85
16.	Check test	-	-	0	0

CONCLUSIONS

The samples DL 4 and DL 6 inhibited 100% the development of mosses on brick substrate, at a concentration of 15%, and at 10% the inhibition percent was between 95-100%, 20 days after the treatment, ranging at the level of those registered at the standard products, Benac 50 (inhibition % = 100) and Micobor (inhibition % = 95) in the same observation range.

- A good biocide action also emphasized the samples DL1 and DL3 at the concetration of 15%, where the inhibition percent of the mosses development was ranged between 80% and 100% in the interval of observations performance.

- The Detergent sample with Irgasan, at a centration of 15% also registeres a good percent of mosses inhibition development on brick substrate, this one being of 85%, 20 days after the treatment. In the case of the other samples subjected to the biologic screening, the inhibition percent had values bellow those registered at the variants treated with standard products.

- A very good control of mosses on stone substrate has been obtained at the variants treated with the samples DL1, DL3, DL 4, and DL 6, where the inhibition percent was of 100 % and the Detergent with Irgasan fraction, with an inhibition percent of 90%.

- A good inhibition percent of lichens 25 days after the treatment have been registered at the variants treated with the samples: DL 2 - 90%, DL 1 – 85%, DL 3 – 90%, DL 4 – 90%, and DL 6- 90%, at a concentration of 15%, these values placing at the inhibition level obtained at the variants treated with the products Micobor and Benac 50, used as standard.

REFERENCES

Caneva C., Salvadori O., (1989) . *Biodeterioration of stone Studies and Documents on the Cultural Heritage, no.16, UNESCO*, 182-234.

Carballal R., Paz-Bermudez G., Sanchez-Beisma M.D., Prieto B., (2001) *Lichen Colonization of Coastal Churches in Galicia, biodeterioration implications, Intl. Biodegr.* 47, 157-163.

Gonzales et. al., (1999). *Bacteria Isolated from Rock Art Paintings, the case of Altamira Shelter (South Spain) Journal of Microbiological Methods. Editor Elsevier* 123-127.

Hawks, C., (2001). *Historical survey of the source of contamination of Ethnographic materials in museum collections, Collection Forum*, 16, 1-2, 2-11.

Hueck H.J.,(2001). *The biodeterioration of materials-an appraisal, Intl. Biodet & Biodegr*.,48, 5-11.

PAPSIDA S.,et al., (2000). *Enhancement of physical weathering of buildings by microbial populations, Intl. Biodet & Biodegr.* 46, 305-317.

Urzic., Krumbein W.E., (1994). *Microbial Impacts on Cultural heritage Durability and Change The Science, Responsibility and Costs of Sustaining Cultural Heritage ed. Krumbein W.ED., etc. EDS Willey and Son*, 107-135.