Biocidal Properties of Gypsum Stone Modified with *Reynoutria sachalinensis* Raw Materials

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The current stage of the construction industry development implies increased requirements for building materials to maintain and improve global environmental processes. The understanding by ecologists globally of the danger of anthropogenic impact on the global environment has been reflected in the formulation of Sustainable Development Goals (SDGs). Thus, scientists and engineers are turning to safe plant-based raw materials as innovative building materials. Of particular interest for practice is the use of *Reynoutria sachalinensis*, which may exhibit biocidal properties. The purpose of this study was to obtain a gypsum stone modified with an extract from the green mass of *R. sachalinensis*, as resistant coating to fouling by microscopic fungi. The results indicated 10% decrease in the required water addition to gypsum paste when using plant extract, a slowdown of the initial and final setting time of the modified gypsum paste samples compared to the control samples by 6 and 7 min, respectively, and a slight decrease in bending and compressive strengths of the samples of 12.5% and 6%. The 100% resistance of the modified samples to fouling by microscopic mould fungi was also revealed.

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INTRODUCTION

The current stage of development of building materials' science involves the designing of new multifunctional materials that would demonstrate a set of unique characteristics and at the same time would be friendly and safe for humans and the environment. In addition, within the framework of Sustainable Development Goals (SDGs), researchers are increasingly turning to safe plant-based raw materials, which can be effectively used for various purposes, in particular, to design innovative building materials (Boros and Tőzsér 2023).

The durability of building materials can be regarded as one of their most important characteristics. Nevertheless, all building materials in operation are subject to destruction for a number of reasons: under the influence of aggressive external medium, for example, the air atmosphere in large cities is saturated with exhaust gases, volatile organic compounds (VOCs), nitrogen and sulfur oxides, or wastewater from large industrial enterprises, salts dissolved in water, *etc.* (Mydin *et al.* 2012).

An important factor in the processes of building material deterioration can be considered the destruction of its structure under the influence of microorganisms – various bacteria, microscopic fungi, and lichens (Abdelghany *et al.* 2019). Colonizing the surface of the cement stone, microorganisms gradually penetrate the structure of the material, changing its external appearance, peeling, delaminating the surface layer, and decreasing mechanical parameters (Elchishcheva *et al.* 2023). In addition, the activity of some types of mould fungi, for example, *Aspergillus niger*, can negatively affect human health, causing allergic reactions, respiratory diseases, and a general decrease in immunity, leading to the emergence of the so-called "sick building syndrome" (Sarvtin 2023; Loukou *et al.* 2024).

Currently, gypsum-based materials with high technological, operational, and aesthetic characteristics are widely used in construction: plasticity of gypsum paste, rapid strength gain, excellent adhesion to various surfaces, fire resistance, air and vapor permeability, which contribute to maintaining a favorable microclimate in living area. Gypsum stone, however, has reduced moisture resistance, which, combined with the porosity of the material, makes it an excellent substrate for colonization by microscopic mold fungi (Grishina and Korolev 2019; Krejsová and Doleželová 2019).

Various biocidal additives are presented in large amounts on the market; however many of them may be toxic for nature and humans and also quite expensive. In addition, microorganisms develop resistance to existing biocidal compositions sooner or later, which is an incentive to expand the range of biocidal additives (Strokova *et al.* 2021; Issayeva *et al.* 2024). Thus, a promising direction in the search and creation of new biocidal additives for building materials that would be effective, environmentally friendly, and affordable agents are required.

As mentioned above, of particular interest for practice is the introduction of plants to create "green" eco-friendly building materials with improved characteristics. As such a plant component, we can consider a plant of the Polygonaceae family *Reynoutria sachalinensis (R. sachalinensis)*, which previously grew mainly on the territory of Japan, Sakhalin, and the Kuril Islands and now actively spreading over vast territories.

It is known that flavonoids are an extensive class of plant polyphenols having pronounced antioxidant, tannic, and antibacterial effects (Selim *et al.* 2024; Almehayawi *et al.* 2024). They are found in large quantities in several plants of the Polygonaceae, Lamiaceae, Rosales, and Fabaceae families and in particular in *R. sachalinensis*. According to Alrikabi *et al.* (2021), the herbal part of *R. sachalinensis* contain anthraquinones, resveratrol, flavonoids rutin, hyperoside, isoquercitin, gallic, chlorogenic, and trans-cinnamic acids. The total content of flavonoids in the green mass according to the article is 432.82 ± 10.82 mg/kg.

Previous studies (Chen *et al.* 2022; Kharlamova 2022; Qun *et al.* 2023; Nguyen *et al.* 2023; Zhang *et al.* 2023) indicate that anthraquinone, quercitin, gallic and chlorogenic acids demonstrate exceptional value.

The cited literature allowed the authors to formulate the purpose of the work, which was to obtain an improved gypsum stone that is resistant to fungi modified with an extract from *R. sachalinensis*. To achieve this goal, the objectives of the study were defined: to obtain an extract from the herbal part of *R. sachalinensis*, to introduce it into the gypsum binder, and to study the ability of the obtained samples of building material to resist fouling with microscopic mould fungi, as well as to investigate the construction, technical and mechanical properties of gypsum stone.

EXPERIMENTAL

To obtain the samples of gypsum stone modified with plant-based components from *R. sachalinensis,* it was necessary at the first stage of the study to obtain an extract from the herbal part of the plant. The stems and leaves freshly collected in June were crushed to a mushy state, and water-ethanol extract was prepared as follows: the crushed herbal mass of 50 g was mixed with 500 mL of water-ethanol solution (ethanol to tap water ratio of 1:3) and stored at a temperature of 25 °C for 7 days, stirring periodically. Then, the mixture was filtered on a porcelain filter, the dry residue was discarded, the resulting transparent filtrate of light brown color was used to mix it with the gypsum mineral binder.

To make test samples, commercial gypsum plaster produced by Samarskiy Gipsoviy Kombinat CJSC (Samara, Russia) G-5 B II (β-hemihydrate) was used. The normal consistency of the gypsum pastes was determined by slump-flow test, measuring the spread of the gypsum paste flowing out of the cylinder when it was lifted, the slump flow value should be (180 ± 5) mm, the setting time was determined using the Vikat apparatus in accordance with EN 13279-2:2004 “Gypsum binders and gypsum plaster solutions. Part 2. Test methods” (“Gypsum binders and gypsum plasters — Part 2: Test methods”, NEQ). The normal consistency is characterized by the diameter of the gypsum spread flowing out of the cylinder when it is lifted. It is expressed as the water-to-gypsum ratio (%) required to obtain a gypsum mixture of standard consistency.

Next, control and modified gypsum stone samples were obtained. The amount of plant extract in the mixing liquid used was 50%. The mechanical characteristics of gypsum stone were evaluated *via* compressive strengths of the halves of the sample beams of size $40 \times 40 \times 160$ mm^3 at 2 h age in accordance with EN 13279-2:2004 using a laboratory hydraulic press (Controls 50-C8455, Italy).

To study the resistance to microscopic mould fungi, cubes of dimensions 3.0×3.0 cm^2 were prepared. Tests of gypsum stone samples modified with *R. Sachalinensis* extract for resistance test to mould fungi were carried out in accordance with Russian standard 9.048-89 (1989) “Unified system of corrosion and ageing protection. Technical items. Methods of laboratory tests for mould resistance”, which is similar to ASTM Standard C1894 − 22 “Microbially Induced Corrosion of Concrete Products” as follows: the surface of the samples was contaminated with a suspension of fungal spores *Aspergillus niger* van Tieghem, *Aspergillus terreus* Thom, *Aureobasidium pullulans* (de Bary) Arnaud, *Paecilomyces variotii* Bainier, *Penicillium funiculosum* Thom, *Penicillium ochro-chloron* Biourge, *Scopulariopsis brevicaulis* Bainier, *Trichoderma viride* Pers. Ex Fr. The concentration of fungal spores in the suspension was 1 to 2 million/cm^3. Samples contaminated with the suspension of fungi were placed in an open Petri dish in a desiccator and kept in conditions optimal for fungal growth: temperature 27 to 28 °C and 98% humidity for 28 days. At the end of the tests, the stage of fungi growth was evaluated in points on a 6-point scale.

“0” points – absolutely clean samples, absence of conidia and colony development (visually and under a microscope);

“1” point – visually clean samples, only small spots of mycelium in the form of individual stains are visible under the microscope, there is no sporulation;

“2” points – the external development of mycelium in the form of numerous spots, there is no sporulation;

“3” points – abundant mycelium overgrowth on the surface of the sample, the beginning of sporulation;

"4" points – on visual inspection, continuous mycelium growth and sporulation are clearly visible;

"5" points – deep mycelium damage to the entire sample area during intensive sporulation.

RESULTS AND DISCUSSION

At the first stage of the study, control and modified gypsum paste and stone samples were obtained and their properties were investigated (Table 1).

Table 1. Gypsum Paste and Stone Properties

Sample	Normal Consistency (%)	Setting Time (min)		Flexural Strength (MPa)	Compressive Strength (MPa)
		Initial	Final		
Gypsum binder + water (control)	60	14	20	2.7	5.2
Gypsum binder + *R. Sachalinensis* extract	54	18	25	2.4	4.9

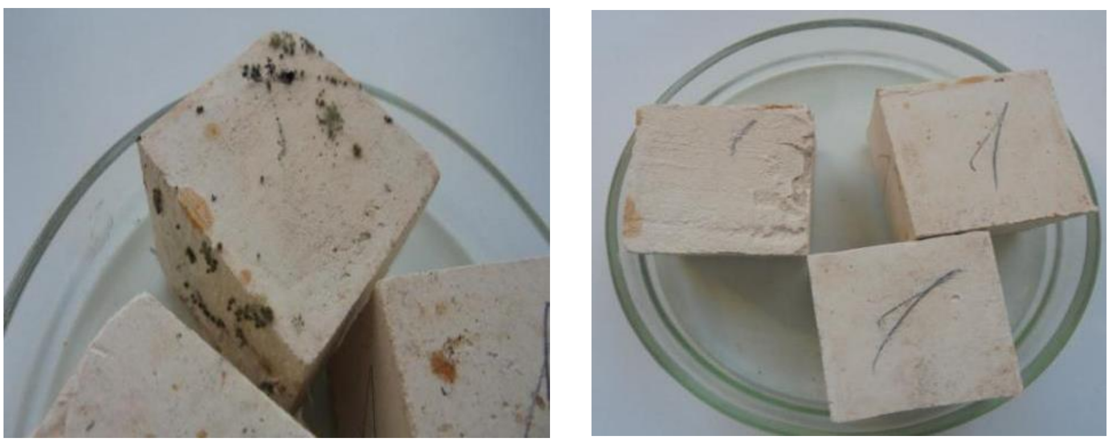
As shown in Table 1, the introduction of 50% *R. sachalinensis* extract into the mixing water led to a decrease in the normal consistency of gypsum paste by 10%, which is apparently due to the plasticizing effect of cellulose present in the plant extract: fibers can adsorb and wrap the particles of hydrating binder, slowing down the formation gypsum hydration products. Additionally, there was a slight slowdown of the initial and final setting time of the modified gypsum paste samples compared to the control samples: by 6 and 7 min, respectively, which is also probably due to the adsorption of cellulose macromolecules on binder particles. A similar situation was discussed by Vitola *et al.* (2020) and Marceau *et al.* (2022), where organic compounds were shown to retard the setting time of hydraulic binders (cement and hydraulic lime) and decrease their compressive strength.

The preparation of cement stone samples and the study of strength characteristics were carried out at a constant water-gypsum ratio, which was 57%: mineral binder powder was mixed with tap water (control) and with a liquid containing 50% of *R. sachalinensis* extract. As shown in Table 1, flexural and compressive strength decreased slightly at 2 h age; by 12.5% and 6%, respectively. Further, in the framework of this work, the resistance of gypsum stone to mould fungi deterioration was studied, the results of the study after 28 days of exposure in a thermostat are presented in the Table 2.

After 28 days of exposure in thermostat the gypsum stone surface was examined under a microscope. The color, shape and structure of the mycelium allowed the authors to determine mainly the presence of *Aspergillus niger*. From the presented data, it can be seen that all control samples had *Aspergillus niger* fungal fouling of 1 to 2 points, samples 1-1, 1-2, and 1-3 did not demonstrate fouling – "0" points, spore growth, conidia, and colony development were not detected under the microscope. The biostability of gypsum stone samples was assessed as follows: control samples K1, K-2, K3 80- 90%, gypsum stone samples modified with *R. sachalinensis* raw materials 1-1, 1-2, 1-3 – 100% (Fig. 1).

Table 2. Resistance of Gypsum Stone Samples Modified with *R. sachalinensis* Extract to mould Fungi after 28 days of Exposure in a Thermostat

Sample	Visual Shape of the Sample After the Test	Point	Biostability (%)
K-1	The surface development of mycelium in the form of numerous spots of *Aspergillus niger*, sporulation was absent.	2	80
K-2	The surface development of mycelium in the form of numerous spots of *Aspergillus niger*, sporulation was absent.	2	80
K-3	The surface development of mycelium in the form of numerous spots of *Aspergillus niger*, sporulation was absent.	1	90
1-1	There was no growth of spores, conidia, and colony development under the microscope.	0	100
1-2	There was no growth of spores, conidia, and colony development under the microscope.	0	100
1-3	There was no growth of spores, conidia, and colony development under the microscope.	0	100



(a) (b)

Fig. 1. Visual shape of the samples after the test: (a) - control sample, (b) - sample modified with *R. sachalinensis* extract

This test makes it possible to establish that the polyphenols and flavonoids, containing in the extract of *R. sachalinensis* inhibit the growth of microscopic mold fungi on the surface of gypsum stone.

CONCLUSIONS

1. The introduction of 50% of *R. sachalinensis* extract herbal part into the mixing water led to a decrease in the normal consistency of gypsum paste by 10% and a slowdown in the initial and final setting time, which is apparently due to the plasticizing effect of cellulose fibers present in the plant extract: they can adsorb on the surface of gypsum particles wrapping them and slowing the formation of gypsum hydration products.
2. There was a slight decrease in flexural and compressive strengths; by 12.5% and 6%, respectively, at 2 h age.

3. The 100% biostability of gypsum stone samples modified with *R. sachalinensis* extract to the mould fungi was revealed compared to the control sample containing only gypsum and water. On the surface of the control samples the growth of mucoromycetes spores of *Aspergillus niger* was visible.
4. The work demonstrates that it is reasonable to use *R. sachalinensis* extract to produce gypsum stone, which can be applied to create environmentally friendly gypsum building materials that are safe for humans and 100% resistant to mould fouling. Thus, the results of this research allow the authors to establish the possibility of modifying gypsum stone with *R. sachalinensis* extract to obtain environmentally friendly building materials safe for humans with increased resistance to fouling by microscopic mould fungi.

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