Construction and Building Materials 142 (2017) 506–513

Contents lists available at ScienceDirect

Construction and Building Materials

journal homepage: www.elsevier.com/locate/conbuildmat

Development and modeling of the effective bioactive poultices for reducing the nitrate content in building materials

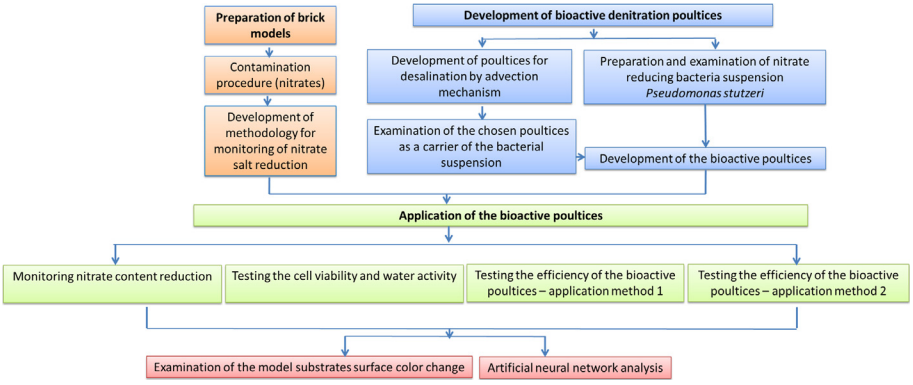
Snezana Vucetic [a,*], Jonjaua Ranogajec [a], Sinisa Markov [a], Ana Vidakovic [a], Helena Hirsenberger [b], Oskar Bera [a]

[a] University of Novi Sad, Faculty of Technology, Bul. Cara Lazara 1, 21000 Novi Sad, Serbia
[b] University of Novi Sad, Faculty of Technical Science, Trg Dositeja Obradovića 1, 21000 Novi Sad, Serbia

HIGHLIGHTS

- Reducing nitrate salt contents in the affected objects.
- Development and modeling of the effective bioactive poultices.
- Poultices provide a suitable microenvironment for the *P. stutzeri* metabolic activity.
- Used an ANN model in order to reduce the time of experiments and the cost.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 14 November 2016
Received in revised form 23 February 2017
Accepted 9 March 2017
Available online 21 March 2017

Keywords:
Nitrate content reduction
Bioactive systems
Building materials
ANN model

ABSTRACT

Two types of poultices, selected after the investigation of a number of raw materials, whose combination showed desired activities, were combined with a *Pseudomonas stutzeri* suspension to yield effective bioactive poultices for reducing the nitrate content in the model bricks. The efficiency was studied as a function of the application mode, porosity of the brick models, bacterial cells viability, and depth of the models. The outcome of the study is an ANN model with a high correlation coefficient, emphasizing that the depth of the bricks is the most influential (negative) factor considering the denitration efficiency.

1. Introduction

Building materials are prone to undergo complex deterioration processes of chemical, physical, and biological transformations caused by atmospheric factors [1]. A primary result of these processes is the formation of soluble salts, which is most pronounced in the case of porous building materials in both contemporary and historical structures [2,3].

Salt-induced deterioration is a natural process, and therefore it cannot be fully prevented but only slowed down by reducing the salt content in the affected objects. Attempts to control the environmental conditions could be a good solution to reduce the incidence of crystallization/dissolution cycles of soluble salts by minimizing their destructive effects on the built-in materials. However, to achieve and maintain appropriate climatic conditions

* Corresponding author.
E-mail address: snezanap@uns.ac.rs (S. Vucetic).

http://dx.doi.org/10.1016/j.conbuildmat.2017.03.075
0950-0618/

for preservation is an almost impossible task, so that some direct intervention methods are needed. Currently, the uses of water-based poultices, plasters, electro-kinetic desalination, and biocleaning have been aimed to reduce the content of soluble salts [4–6]. Literature searches show that electro-kinetic desalination and biocleaning are not so commonly used for this purpose. Although the poultices and plasters are widely used to reduce salt content in conservation procedures, the obtained results are often variable and unpredictable because of the difficulties related to exact specification of pore-size distribution [4,7].

Although microorganisms have been considered as common causative agents of biological deterioration of building materials, they can also take a positive role in the removal of nitrate deposits (biocleaning process), which are otherwise difficult to remove by traditional techniques. There are different ways of using bacteria for this purpose: (i) immersion of a carrier into a bacterial solution and (ii, iii) direct application of bacteria onto a carrier or substrates. Materials as cotton, Hydrobiogel-97, Carbogel, and agar have been used as carriers for this purpose [6,8]. Publications dealing with the usage of conventional water-based poultices as supports for bacteria cultures are rather scarce. Namely, only about 30 articles related to biocleaning of building materials (www.sciencedirect.com) can be found, the fact which leaves room for further investigation.

The strategic hint of adding bacteria into/onto water-based poultices is to increase the cleaning capacity of these materials. The poultice playing the role of a carrier ensures the transport of soluble salts from the interior of the built-in material to the surface of the object which is subjected to cleaning. For this purpose, poultices must possess a wide pore size distribution, incorporating large pores that can act as reservoirs for wetting, and small pores to ensure advection from the substrate to the poultice [4].

In recent years, modeling techniques such as artificial neural networks (ANN), have been widely used in numerous investigations of building materials [9,10]. However, in the field of cultural heritage (concerning all possible aspects), one can find only a small number of publications. Reports on modeling in the field of biocleaning are also scarce. The usage of ANN models has several advantages, non-linearity, adaptively (i.e., learning from inputs parameters), generalization, and model independence (there is no need for *a priori* models) [10]. All these features are of special importance, especially in the field of cultural heritage.

Considering the above, the aim of this study was to investigate the possibility of the coupling good properties of the selected poultices and of the *Pseudomonas stutzeri* cells, due to their proven efficiency "in biocleaning of nitrate alterations on the wall paintings" [8], to form effective bioactive denitration poultices. Based on our studies of different poultice materials, two combinations were selected, which, to our knowledge, had not been used before. The experiments were carried out on laboratory-prepared brick models with characteristics similar to those of the medieval Bac Fortress (Serbia) brick structures, in which a high level of nitrate salts was identified, to slow down their deterioration. After studying the efficiency of the developed systems as a function of the porosity of poultice and of the contaminated models, way of the poultices application, bacterial cells viability, and brick model depths, an ANN model was constructed for predicting the dependence of the denitration process based on the above specified factors.

2. Materials and methods

The experimental procedure for the development of the bioactive denitration systems is shown in Fig. 1, which includes five main subgroups of experiments: (I) preparation and contamination of brick model; (II) preparation, selection and application of the water poultices; preparation and examination of the bacterial suspension; (III) development and efficiency analysis of the bioactive poultices; (IV) monitoring of the developed systems, and (V) mathematical processing of the experimental data.

2.1. Preparation and contamination of the brick models

Based on the characteristics of the brick samples taken from the historical site of the Bac Fortress, the brick models were prepared in the form of cubes of $4 \times 4 \times 4$ cm. Their mineralogical composition and textural properties were close to those of the original bricks. The models were made by molding a manually prepared mixture consisting of the old brick powder and clay taken from a pit near the Bac Fortress with deionized water in a mass ratio (brick powder:clay:water) of 8:72:20. The model bricks were fired in a laboratory kiln (2 h at T max of 980 °C) [11].

The brick models were contaminated with potassium nitrate at a level of 50 mg/g. This level of contamination was chosen based on the fact that the maximum concentration of nitrate measured in the historical bricks was approximately 50 mg/g [12]. The samples were completely immersed in a saturated solution of potassium nitrate for 2 h, dried in an oven at 105 °C for 6 h, and then kept at room temperature. A uniform distribution of nitrate was achieved (see below), as its concentration was the same at the depths of 2, 10 and 20 mm of the brick model after a stay of 7 days at ambient conditions. Moreover, a visual inspection showed no nitrate salt efflorescence on the surface of the brick models, even after two weeks at room temperature.

2.2. Selection of the components, design, and examination of the poultices

The poultice components and their contents were selected to suit the individual properties of the contaminated models, which is essential for the advection mechanism of denitration [13]. The poultices (11 combinations) were prepared using the following materials: kaolin, cellulose, sand, talc, lightweight aggregate, and water, Table 1. All these components are easily accessible. The exception is the lightweight aggregate, produced within the European project EUREKA E!4696 [14]. The purpose of this material was to ensure most favorable porosity of the designed poultices in order to retain the water necessary for a normal bacterial activity. The usage of talc as a component of poultices is a novelty. Despite its hydrophobic nature, the presence of talc was beneficial due to its surface adsorption capacity [15]. Kaolin was used for its shrinking properties [13]. In all cases the components were firstly mixed in dry state and then water was added until appropriate consistency was reached (relative density of the freshly prepared poultices is given in Table 1). Considering the covering adhesion, workability, application to vertical surfaces, textural properties and shrinkage, only two of the eleven preliminarily prepared poultices were selected for the detailed study and formation of bioactive poultices. The visual appearance of the prepared poultices was monitored after 24 h, 5 days and 2 weeks stay at room temperature. Their physical properties were studied according to the recommendations summarized by R.P.J. van Hees et al. [13].

The denitration process was monitored only through one face of the brick models, the other five were covered with silicon, to ensure unidirectional diffusion. The freshly prepared poultice was vertically applied as a 1-cm thick layer on the contaminated brick models surface. The duration time of the poultices on the surface of brick models was: 1 h, 2 h, 3 h; 1, 2, 3 days and 2×3 days and 3×3 days. A fresh layer was additionally applied 2 times/3 times per 3 days in the case of the latter two cases, respectively. The poultice was then removed from the surface of the brick model and the nitrate content was determined in the powder sampled by drilling the models to the depth of 2, 10 and 20 mm (five different positions on the surface were selected for drilling). The depth of the drilling was controlled based on the drilling resistance measurement system (DRMS Cordless, Sint Technology, Italy). The nitrate content was measured on an Evaluation 600 UV–VIS spectrophotometer, after extracting 1 g of the powder with 100 ml of deionized water [16,17]. The denitration efficiency was calculated as follows: $Eff = (c_o - c_h)/c_o$, where c_o was the initial concentration of nitrate, and c_h was the nitrate concentration after the defined period of the poultice application.

Total porosity and pore size distribution of dry poultices and the contaminated models were determined by mercury intrusion porosimetry (Hg Porosimeter Carlo Erba 2000 WS, Italia), while the BET surface area was determined by low-temperature nitrogen adsorption-desorption measurements at 77 K (Micromeritics ASAP 2010).

2.3. Preparation of the bacterial suspension

Based on the previous results [6], the strain ATCC 17588 of *Pseudomonas stutzeri* was used for potassium nitrate removal from the contaminated brick models. The strain was grown in Nitrate Broth (Difco™, Becton, Dickinson and Company, Le Pont-de-Claix, France) medium and incubated at 37 °C for 24 h. After centrifugation (3×4200 rpm for 10 min), the obtained pellet was washed twice and suspended in sterile distilled water. The final cell concentration was adjusted to approx. 10^8 CFU ml^{-1}.