

# Silica xerogel–hydrogen peroxide composites: Their morphology, stability, and antimicrobial activity

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## Abstract

Hydrogen peroxide was incorporated into silica xerogel matrix over the concentration range from 3.8 to 68.0 wt% via the sol–gel route. The obtained composites were characterized by scanning electron microscopy (SEM) and differential scanning calorimetry (DSC). The release rates of H<sub>2</sub>O<sub>2</sub> from the composites into the aqueous phase were examined. In most cases, a 90% release was attained after ca. 10 min, and it was only slightly dependent on H<sub>2</sub>O<sub>2</sub> concentration and particle size. The antimicrobial activity of the composite containing 3.59% H<sub>2</sub>O<sub>2</sub> was evaluated against *Escherichia coli* and *Micrococcus luteus*. A comparative assay was carried out for aqueous solution of H<sub>2</sub>O<sub>2</sub> of the same concentration. The results demonstrated a potent microbicidal efficacy of the composite. Furthermore, diffusion range of the hydrogen peroxide from the solid composite into an agar medium matched that of the H<sub>2</sub>O<sub>2</sub> in aqueous solution. The stability tests with the xerogels containing 3.8, 26.4, and 68.0% of H<sub>2</sub>O<sub>2</sub> showed that after 63 days respective losses of the H<sub>2</sub>O<sub>2</sub> at 3 °C were 8.8, 9.7, and 6.2%. Both the DSC results and the stability tests have shown that the molecular water present in the pores stabilizes the composite, probably through improving the binding of the H<sub>2</sub>O<sub>2</sub> molecules onto the silica surface.

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## 1. Introduction

In today's highly industrialized environment, pollution control is a crucial factor taken into consideration when new technologies are designed. Simple transfer of contaminants from one medium to another becomes no longer acceptable. For this reason, there is an urgent need to promote environmentally friendly chemicals. Hydrogen peroxide is such a "green" powerful and versatile oxidant whose degradation products are oxygen and water [1]. Unfortunately, hydrogen peroxide poses certain risks owing to its instability in the presence of catalytic amounts of heavy metals, alkalies, and even air-borne particulates. For this reason, efforts have been continued to design forms of the compound with improved safety during storage and han-

dling. Three stable, solid peroxohydrates have been developed and marketed, namely sodium percarbonate (2Na<sub>2</sub>CO<sub>3</sub>·3H<sub>2</sub>O<sub>2</sub>), sodium perborate (NaBO<sub>3</sub>·xH<sub>2</sub>O<sub>2</sub>; x = 1 or 4), used mainly as bleaching agents in washing powders [2], and an urea–hydrogen peroxide (1:1) adduct, used in hair bleaching, skin disinfection, teeth whitening, and as an efficient oxidant in organic synthesis [3,4]. Relatively stable monooleic cubic phases containing hydrogen peroxide have been reported as a gel for wounded skin disinfection [5].

A sol–gel technology that was developed during the last two decades offers new possibilities for incorporating active agents within silica matrix [6–9]. The most essential features of the technique are:

- (i) ultrahomogeneity—incorporated molecules can be separated at a nano-scale level;
- (ii) low processing temperature—also temperature-sensitive molecules can be processed;

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- (iii) non-toxicity of silica gel matrix—final composites can be implemented as sustained-release drug delivery systems or biocompatible implantable materials.

Recently, a composite has been developed in our laboratory by using the sol–gel technique, which contains hydrogen peroxide embedded in silica gel. Upon drying, the resulting xerogel contains up to 70% of  $H_2O_2$ . Because the  $H_2O_2$  molecule is the smallest one showing internal rotation about the O–O bond, interactions between hydrogen peroxide and silica gel seem to be of fundamental importance for understanding adsorption phenomena. In our recent work, we highlighted some of the structural and energetic features of the system by means of Fourier transform infrared (FTIR) spectroscopy and quantum-chemical calculations [10].

The title composites are a new solid form of hydrogen peroxide. We expect that the  $H_2O_2$  incorporated in the inert and non-toxic silica xerogel, will be an interesting alternative for teeth whitening systems based on the urea–hydrogen peroxide adduct. Besides, silica xerogel seems to be a better carrier of  $H_2O_2$  in wounded skin disinfection taking into account that urea may be irritant to sensitive skin in topical applications [11]. We also expect that the composite with the low  $H_2O_2$  concentration (up to 4%) could be applicable in a sticking plaster disinfectant. The silica xerogel with high load of the  $H_2O_2$  could act as an active sorbent for the neutralization of locally contaminated areas. The other potential application of the xerogel could be for small portable drinking water disinfectant systems used under field conditions. In that case, there should be a need for removing of the excessive peroxide from the treated solution. This is, however, a prospect for another research.

The purpose of the present study was to work out a method for preparation of silica xerogel–hydrogen peroxide composites over a broad spectrum of  $H_2O_2$  concentrations. The composites were characterized by means of scanning electron microscopy (SEM) and differential scanning calorimetry (DSC). An effort was undertaken to learn whether the co-adsorbed water molecules could stabilize the system (as it was shown in our theoretical calculations). In addition, release rates of  $H_2O_2$  from the composites into the aqueous phase were examined as well as the antimicrobial activity of the xerogels. The stability tests were performed at different temperatures,  $H_2O_2$  concentrations, and water-to-composite ratios.

## 2. Experimental

### 2.1. Materials

Sodium metasilicate solution (water glass); R-145,  $SiO_2/Na_2O$  mole ratio 2.5 (Enterprise WAMA, Lebork, Poland); hydrogen peroxide (30 wt%) (POCh, Gliwice, Poland); orthophosphoric acid (85 wt%) (POCh, Gliwice, Poland); Amberlite® IR 120 (Fluka AG, Germany). *Escherichia coli* ATCC 8739 strain was provided by Polish Collection of Microorganisms, Polish Academy of Sciences, Wrocław, Poland. *Micrococcus luteus* strain was provided by the Marine Chemistry and Biochemistry Department, IO PAS, Sopot,

Poland. Tests with *E. coli* were carried out in the Nutrient Agar medium [12], whereas with *M. luteus* the ZoBell medium was applied [13]. Microbicidal tests were performed using autoclaved deionized water from Milli-Q water purification system (Millipore Corp.).

### 2.2. Preparation of the silica xerogel–hydrogen peroxide composites

The cation-exchange method was used to prepare the silicic acid sol. Water glass, diluted 1:4 with distilled water was passed through a glass column packed with a swollen Amberlite, cation-exchange resin, to afford a solution of silicic acids (sol). The Si content of the sol, expressed as  $SiO_2$  was 5.0 wt%. Details of this procedure are described elsewhere [14]. The freshly prepared sol of silicic acids was mixed with 30%  $H_2O_2$  to give six solutions containing 0.5, 1, 2.5, 5, 10, and 20% of  $H_2O_2$ . To immobilize trace amounts of metal impurities which catalyze  $H_2O_2$  decomposition, the same amount of a stabilizer (0.03 wt% of orthophosphoric acid) was added to all the solutions. Fifty grams of each solution was then poured out onto the glass Petri dishes (90 mm in inner diameter and 15 mm in height). In the next step, the samples were dried at 70 °C up to 90% of a total mass loss to give xerogels containing from 3.8 to 68.0% of  $H_2O_2$ . In addition, for the system with 5% of initial  $H_2O_2$  concentration in the sol, composites were obtained of various mass losses. The hydrogen peroxide concentration in all the composites was determined by  $KMnO_4$  titration. To investigate the morphology of the samples, the intact xerogel monoliths were used. For the study of the release rate, both crushed monoliths (mean particle diameter of ca. 2 mm) and finely powdered xerogel samples (mean particle diameter of 13  $\mu m$ ) were used. For the differential scanning calorimetry measurements, antimicrobial assay and stability assessment, only powdered xerogel samples were taken. The particles size of powdered samples was determined by manual choosing of 150 particles from the optical microscope images (microscope—Motic B1-220A, Wetzlar, Germany, coupled with digital camera—Panasonic GP-KR 222E, Matsushita Communication Industrial, Japan) and measuring their area and diameter using UTHSCSA Image Tool software, Version 3.00.

### 2.3. Modelling approach

The geometry optimization of the H-bonded clusters of the water–four-fold siloxane ring and hydrogen peroxide–four-fold siloxane ring was performed using the Dgauss program [15] implemented within CAChe Software, Version 7.5.0.85. As the computational method, density functional theory (DFT) and exchange–correlation energy functional, B88-LYP, developed by Lee et al. [16] were applied, with a double zeta, DZVP basis set [17].

### 2.4. Morphology of the composites

For the scanning electron microscopy, a Tesla BS-300 instrument (Tesla Brno, Czech Republic) was employed. For the samples preparation, a piece of silica xerogel–hydrogen perox-

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