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Photoinitiator and anesthetic incorporation into mesoporous silica

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ABSTRACT

The sol–gel methodology affords mesoporous silica with controlled pore size. The resulting materials can be used to incorporate, immobilize, or encapsulate several molecules for further application as drug delivery systems, antibacterials, and photonic devices, just to mention a few examples. Dental resins employed in tooth repair consist of an organic matrix, a charged inorganic component, and union agents; a photoinitiator triggers resin polymerization. In this work, we incorporated the photoinitiator camphorquinone or the anesthetic ethyl 4-aminobenzoate into mesoporous silica. Characterization of the materials by infrared and electronic spectroscopy, thermal analysis, X-ray diffraction, and specific surface area confirmed the presence of the photoinitiator or the anesthetic in the silica matrix. Kinetic and equilibrium assays as well as absorption studies showed that the mesoporous silica obtained here can be applied as a drug delivery system.

1. Introduction

Over the last 30 years, the physical, mechanical, and esthetic properties of composite resins have led to their wide application in routine dental restoration [1,2]. Composite resins are a classic example of hybrid materials composed of an organic matrix and inorganic particles [3,4]. The combination of organic and inorganic components produces new properties: the inorganic particles provide the hybrid with rigidity and thermal stability, whereas the organic polymer yields a flexible composite resin that can be easily processed. Camphorquinone is used as a visible-light photoinitiator for medical applications; it can convert a monomer into polymer networks [5,6]. Dentists commonly use camphorquinone during dental restoration [7]. The local anesthetic ethyl 4-aminebenzoate, or benzocaine, a *para*-aminobenzoic acid ethyl ester, was the first synthetic agent to be used in clinical practice [8].

The discovery of molecular sieves by Mobil Corporation has prompted extensive investigation into hybrid materials [9,10]. The sol–gel methodology has been the preferred process to obtain mesoporous silica [11,12]. Surfactants have served as molding agents, to afford silica materials with different pore sizes [13–15]. Indeed, mesoporous silica prepared by the sol–gel methodology in the presence of a surfactant as pore template presents an organized structure that promotes new physical and chemical properties. These materials can interact with ions and/or molecules incorporated into the silica pores or immobilized onto the silica surface, which paves the way for their application in different areas, such as catalysis and sensor devices [10,16].

Silica nanoparticles are another important matrix into which several kinds of molecules, like antifungals [3], La(III) compounds, and chitosan [17,18], can be incorporated. Other matrixes, including alumina particles [19], oxide nanoparticles [20], and halloysite nanotubes [21], have also been employed to synthesize composite materials.

The literature contains many papers on the incorporation of pharmaceuticals and medications into mesoporous silica for controlled release studies. The silica matrix MCM-41 SBA-15 is the most often investigated for incorporation of the anesthetic and anti-inflammatory agent ibuprofen [22], levofloxacin [23], indometacin, [24,25], and furosemide [26]. Numerous other studies have been conducted on release systems involving mesoporous silica [27–32] and on technological applications for this matrix [33–36], but none of the literature articles have used the systems proposed herein. Therefore, we aimed to explore the ability of mesoporous silica to act as a controlled released system for various compounds. To begin with, we used compounds that are commonly applied in dental composite resins and incorporated either the photoinitiator camphorquinone or the local anesthetic ethyl 4-aminobenzoate into them. To synthesize the silica, we used the surfactant cetyltrimethylammonium bromide, which gave pores with ideal

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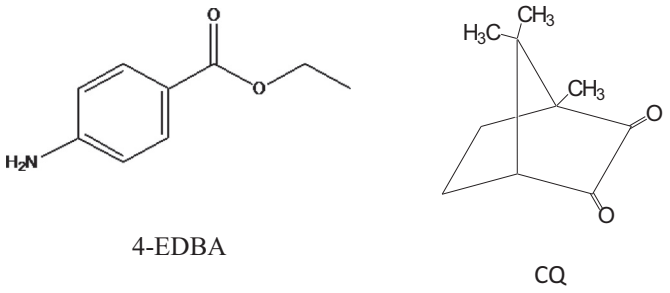

Fig. 1. Structure of 4-aminebenzoate (4-EDBA) and camphorquinone (CQ).

sizes to accommodate the target molecules. We characterized the samples by vibrational (infrared) and electron (UV–Vis) spectroscopy, thermal analysis, X-ray diffraction, and surface area.

2. Material and methods

2.1. Materials

2.1.1. Mesoporous silica synthesis

The mesoporous silica was obtained by reacting tetraethylorthosilicate alkoxide (TEOS), water, and the surfactant cetyltrimethylammonium bromide (CTAB) at pH = 11; the pH was adjusted with ammonium hydroxide, and the mixture was stirred at room temperature for 24 h. The mesoporous silica was treated at 620 °C for 5 h, to eliminate the surfactant, and it was activated with 1.0 mol·L^{-1} hydrochloric acid for 1 h.

2.1.2. Preparation of camphorquinone (CQ) and ethyl 4-aminebenzoate (4-EDBA) solutions

The ethanolic CQ and 4-EDBA solutions were obtained by diluting 100 mg of CQ or 4-EDBA in 50 mL of ethanol, which gave standard CQ and 4-EDBA solutions with concentrations of 0.012 and 0.013 mol·L^{-1}, respectively. Fig. 1 illustrates the molecular structure of these compounds.

2.1.3. CQ or 4-EDBA incorporation into mesoporous silica

2.1.3.1. Kinetic study. Various systems were prepared for the kinetic studies. All the systems contained a fixed amount of adsorbent and adsorbate. The readings were accomplished at different reaction times.

In the case of CQ, an ethanolic CQ solution at 4000 ppm was mixed with 50.0 mg of mesoporous silica. The suspension was continuously stirred at room temperature and analyzed between 3 and 45 min. As for 4-EDBA, the kinetic study was conducted by mixing an ethanolic 4-EDBA solution at 2 ppm with 50.0 mg of mesoporous silica. The suspension was continuously stirred at room temperature and analyzed between 0.5 and 120 min.

Eq. (1) provided the amount of CQ or 4-EDBA molecules that adsorbed onto the mesoporous silica [37,38], to give SiO_2 + CQ or SiO_2 + 4-EDBA, respectively.

$$q_t = \frac{(C_i - C_t)\cdot V}{m} \quad (1)$$

where q_t (mg/g) is the amount of CQ or 4-EDBA adsorbed at time t (min), C_i (mg L^{-1}) is the initial CQ or 4-EDBA concentration in the solution, C_t (mg L^{-1}) is the CQ or 4-EDBA concentration in the solution at time t, V (L) is the solution volume, and m (g) is the mesoporous silica (adsorbent) mass.

2.1.3.2. Equilibrium study. For the equilibrium study, 50.0 mg of mesoporous silica and 5.0 mL of CQ solution at 3000, 3500, 4000, 4500, or 5000 ppm were used. In the case of 4-EDBA, 50.0 mg of mesoporous silica and 5.0 mL of 4-EDBA solution at 0.25, 0.50, 1.0, 1.5, or 2.0 ppm were employed. The suspensions were stirred for 2 h. The CQ and 4-EDBA concentrations were determined by UV–Vis spectroscopy. Eq. (2) helped to calculate the amount of adsorbed CQ or 4-EDBA molecules. Then, the isotherms were recorded [37,38].

$$q_e = \frac{(C_i - C_e)\cdot V}{m} \quad (2)$$

where q_e is the amount of adsorbed CQ or 4-EDBA (mg/g); C_i and C_e (mg L^{-1}) are the initial and equilibrium liquid-phase CQ and 4-EDBA concentrations, respectively; V is the solution volume (L); and m is the adsorbent mass (g).

2.2. Characterization

2.2.1. X-ray diffraction (XRD)

X-ray diffraction (XRD) was conducted at room temperature on a Rigaku Geigerflex D/max-c diffractometer equipped with monochromated CuKα radiation (λ = 1.54 Å). Diffractoframs were recorded in the 2θ range from 1.5 to 8° at a resolution of 0.05°.

2.2.2. Thermogravimetry (TGA/DTA)

The thermogravimetry analyses (TGA/DTA) were carried out on the analyzer Thermal Analyst 2100 from TA Instruments SDT 2960 with simultaneous DTA-TG. The experiments were accomplished in nitrogen atmosphere, at a heating rate of 20 °C min^{-1}, from 25 to 1000 °C.

2.2.3. Electronic spectroscopy (UV–vis)

The UV–Vis spectra were recorded from 200 to 800 nm on a Hewlett-Packard 8453 Diode Array spectrophotometer.

2.2.4. Infrared spectroscopy (FT-IR)

The infrared absorption spectra were acquired on a Frontier Perkin Elmer spectrometer operating in the ATR mode; the samples were scanned 16 times at a resolution of 4 cm^{-1}, from 4000 to 500 cm^{-1}.

2.2.5. Specific surface area

The specific surface area values were determined by applying the BET method to the corresponding nitrogen adsorption isotherms, with

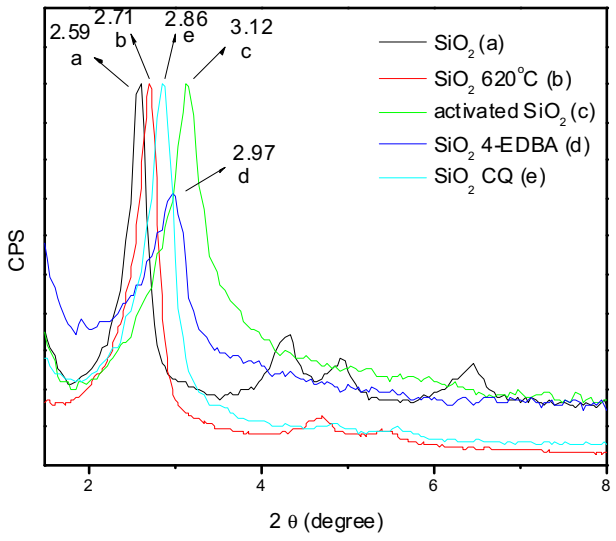

Fig. 2. XRD of mesoporous silica without calcinating (SiO_2), mesoporous silica treated at 620 °C (SiO_2 620 °C), mesoporous silica activated with acid treatment (activated SiO_2), mesoporous silica incorporated with 4-EDBA (SiO_2 4-EDBA), and mesoporous silica incorporated with CQ (SiO_2 CQ).