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A friendly environmental approach for the controlled release of Eucalyptus essential oil

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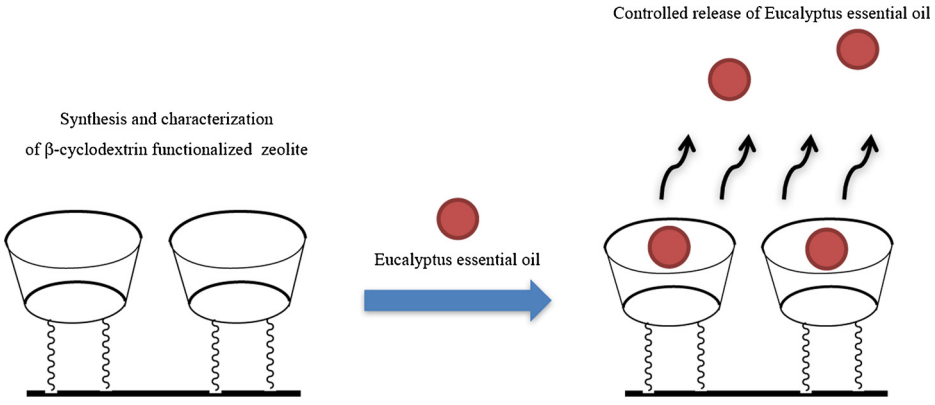
GRAPHICAL ABSTRACT



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ABSTRACT

The latest health scandals lead to improve treatment of patients using alternative ways more concerned with the environment and human health. The use of ecological systems represents a safe approach for their uses in medical application. Delivery system encapsulating Eucalyptus essential oil (EEO) could be an alternative approach to fight against bacterial, inflammatory, pyretic and respiratory infections. In this study, we report the synthesis of three zeolites Y covalently grafted with β-cyclodextrins using succinic, adipic and citric acid as croslinker. The morphology, thermal property, porosity, chemical composition and yield of grafting were determined to fully characterize these new materials. The values obtained in BET show a marked decrease of specific surface area, characteristic of a change in the zeolite structure. The ability of the obtained zeolite to progressively release EEO was investigated by multiple headspace extraction (MHE). The results demonstrated that obtained zeolites were able to encapsulate EEO more efficiently than free β-cyclodextrin and to decrease their release kinetics. Thus, these new friendly materials can find applications to improve the use of essential oils in aromatherapy, cosmetic or medicine.

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1. Introduction

Since antiquity, nature has been an inexhaustible source of medicines to cure various pathologies without knowing the origin of their beneficial actions. In recent years, the world population has had a renewed interest in natural products. As a consequence, manufacturers are developing more and more processes using extracts and active substances of natural origin. Although the nature offers a rich diversity in plant species, only 10% of these contain essential oils (EOs) [1]. Hydrocarbons and oxygenated monoterpenes, sesquiterpenes, diterpenes, aromatic and aliphatic compounds are the major components of EOs. A lot of them have been approved as food additives [2,3], in cosmetic formulations [4] and in traditional medicine [5–8]. However, their uses are limited due to their volatility, stability and lower water solubility [9]. To overcome these drawbacks, various encapsulation systems have been suggested.

The last past decade, numerous reports described the use of cyclodextrins (CDs) as encapsulation agents for EOs [10–15]. Due to their ability to form inclusion complexes with hydrophobic guests, CD-assisted encapsulation systems provide many benefits. The formation of inclusion complex with EOs allows their subsequent controlled release in time [16], could protect EOs from temperature, light, oxidation and degradation [17,18] and therefore increases their stability allowing an enhancement of its antibacterial and antioxidant activities [19–21]. Another alternative to CD is the use of organic or inorganic scaffolds, in particular silica supports, for the storage and release of essential oils in solid form for different purposes [22–26]. The most important requirements of host supports are a large specific surface area to facilitate the adsorption of EOs, cheap cost, biocompatibility, high inertness, low cytotoxicity and environmental friendly agent. Previous studies have reported the association of these two encapsulation systems in electrospun ultrafine fibers from zein [27], electrospun poly (ethylene oxide) [28] and silica mesoporous supports [29]. In each case, the preparation of inclusion complex between essential oil and β-cyclodextrin (β-CD) was realized followed by the embedding into the solid matrix.

Based on these results, we decided to combine the advantages of a solid support and the ability of β-CD to form inclusion complexes to allow the gradual release of EOs. An alternative way to silica may be found in the use of zeolite. Zeolite is a candidate of choice for biomedical applications, because it is natural, non-toxic and considered as green. For example, loading of a drug on zeolite Y (Faujasite) was shown to be more efficient than administration of pure drug alone because of the slow release of the drug [30]. Zeolites are aluminosilicate minerals characterized by a uniform structure consisting of cages and channels. Zeolites exhibit high performance in ion exchange [31] or remediation [32–34]. Moreover, literature reports the use of zeolite with essential oil for plant growth [35,36] or green catalysis [37,38]. To avoid its loss during regeneration process, CD was linked covalently to zeolite. Previously, we reported the linkage of β-CD onto zeolite Y via the use of 3-glycidyloxypropyl spacer [34]. In this study, polycarboxylic acids were chosen to act as crosslinkers. These polyacids have been selected according to their non-toxicity, and are biocompatible [39] with β-CD and zeolite. For example, citric acid is currently used in the synthesis of CD polymers with medicinal applications [40,41].

Lastly, the last health scandals have lead medicine to use natural treatment. Consequently, the synthesis of cartridge based on modified zeolite for EOs should be an alternative for biomedical applications. Here, Eucalyptus essential oil (EEO) was chosen for its broad scientifically proven medicinal benefits and for its non-toxic classification: this oil presents antibacterial, anti-inflammatory and antipyretic effects, and is more particularly employed for the treatment of respiratory infections [42]. In addition, EEO is already used as a natural food preservative [43] Although, some studies evaluated the formation of inclusion complex and controlled release of EEO with β-CDs [44,45], no paper reports the encapsulation and release of EEO from a β-CD modified-zeolite material.

The aim of this work was to synthetize new β-CD functionalized zeolite materials and to evaluate them for the controlled release of EO. The obtained new materials were characterized by complementary analysis including TG-TDA, SEM, BET and FTIR. For the fist time, the release of EEO from these new supports was evaluated as a function of time by using multiple headspace extraction (MHE) coupled to gas chromatography.

2. Materials and methods

2.1. Reagents and chemicals

Zeolite Y (Si/Al: 2:3, Faujasite) was obtained from Zeolyst International. Prior to use, zeolite was washed with 100 mL of water, dried and calcinated one day at 500 °C in a furnace. β-CD was obtained from Wacher-Chemie (Lyon, France). To eliminate residual water, β-CD was dried at 100 °C for 24 h before use. Xylene, polycarboxylic acids (adipic, succinic and citric) were purchased from Sigma Aldrich and used without further purification. Eucalyptus essential oil (*Eucalyptus Citriodora*) was obtained from Herbes et Traditions (Comines, France). Eight major components were identified for this EO: α-pinene (1.32%), β-pinene (1.04%), limonene (0.45%), eucalyptol (0.38%), *p*-cymene (0.83%), linalool (0.29%), citronellal (74.77%) and β-caryophyllene (0.93%) [11].

2.2. Synthesis of hybrid materials

Zeolite (2 g) was swelled with 50 mL of xylene during 1 h. Then 2 g of β-CD and 2 g of polycarboxylic acid were incorporated and the mixture was refluxed for 6 h. The product was filtered and washed abundantly with water and then subjected to dimethylformamide Soxhlet extraction to eliminate unreacted residual compounds. The resulting material was dried under vacuum to eliminate the solvent. **ZEOCDcit** (1.90 g), **ZEOCDsuc** (1.86 g) and **ZEOCDadi** (1.95 g) have been respectively obtained from citric acid, succinic acid and adipic acid.

2.3. Characterization of hybrid materials

Infrared spectra were recorded between 600 and 3600 cm^{-1} at a resolution of 4 cm^{-1} with a Bruker Equinoxe 55 Fourier Transform Infrared Spectrometer equipped with a Golden Gate diamond ATR reflexion unit.

BET surfaces areas of the solids were measured by nitrogen adsorption at −196 °C using a Surface Area analyser 2010, ASAP apparatus. The samples were outgassed for 1 h at 120 °C.

TG-TDA experiments were realized with a Netzsch STA 409 apparatus. A sample mass of catalyst was loaded in an alumina crucible and heated from room temperature to 1000 °C (heating rate: 5 °C min^{-1}) in air flow (75 mL min^{-1}).

Elementary analysis were performed on triplets of 2–3 mg were analysed on a Perkin Elmer 2400 Series II CHNS/O System using standards of low and high organic content and with every sixth sample being sulfamic acid for conditioning of the system. Prior to the analysis all samples were dried under vacuum at 80 °C for 48 h.

SEM characterization was obtained with a FEI QUANTA FEG 200 environmental scanning electron microscope (ESEM) equipped with a gaseous secondary electron detector (GSED). Experiments were performed at 100 Pa and an accelerating voltage of 15 kV.

Powder X-ray diffraction (XRD) patterns were recorded at ambient temperature on a Brucker D8 ADVANCE powder diffractometer using Ni filtered CuK_{a1} (λ = 1.5406 Å) radiation. Data were collected in the range 5–60° (2θ), with a step of 0.05°, and a scanning rate of 0.1°/min.