Arabian Journal of Chemical and Environmental Researches

Vol. 01 Issue 1 (2014) 41–48

www.mocedes.org/ajcer

Synthesis of hydroxyethylcellulose and hydroxyapatite composite for analysis of bisphenol A

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Received 18 Dec 2014, Revised 26 Dec 2015, Accepted 26 Dec 2014

Abstract

Abstract This study evaluates solid-phase micro-extraction (SPME) coupled with gas chromatography–mass spectrometry (GC–MS) to determine trace levels of bisphenol A in water and leached from plastic containers. In our study, we used very thin composite membranes prepared in the laboratory. The extraction using headspace post-derivatization with bis (trimethylsilyl) trifluoroacetamide (BSTFA), containing 1 % trimethylchlorosilane (TMCS) vapor, following SPME was compared with extraction without derivatization. The SPME experimental procedures to extract bis-phenol A in water were optimized with a relatively of the composite a based of the hydroxyapatite, an extraction time of 50 min, and desorption at 300 C for 2 min. Headspace derivatization following SPME was performed using 7 µL of BSTFA with 1 % TMCS at 65 C for 30 s. The precision was 5.2 % without derivatization and 9.0 % headspace derivatization. The detection limit was determined to be at the nanogram per liter level. When SPME wasused following headspace derivatization, the detection limit was one order of magnitude better than that achieved without derivatization. The results of this study reveal the adequacy of the SPME–GC–MS method for analyzing bisphenol A leached from plastic containers. The concentrations of bisphenol A leached from plastic containers into water ranged from 0.7 to 78.5 mg L^{-1}.Used with different percentages. Then inorganic-organic films were fabricated by evaporation of solvent. The composite films were characterized using emission scanning electron microscopy (SEM), and Fourier transform infrared (FT-IR) spectroscopy. The results showed that these films are uniform and have good ductility. A strong interaction existed between HAp and cellulosic polymers, and the method allows the production of composite with very fine particles size of about 90 nm, that is appropriate for medical applications. As an application we study the absorption of Bisphenol A (noted PBA) by the composite HEC / HAp. The study of the extraction of bisphenol A (BPA) with HEC/ HAp composite has achieved a satisfactory extraction with a very good yield.

Keywords: Composite, Hydroxylapatite, hydroxyethylecellulose, Bisphenol A, Adsorption, Derivatization, GC/MS/SIM

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1. Introduction

There have been numerous composites developed based on hydroxyapatite and polymers such as cellulose [1, 5]. Cellulose is most abundant in nature and its derivatives can be obtained in large scale.

They possess various industrial applications, because they are produced in a sustainable way, also they are renewable, biodegradable and biocompatible. Though, some limits appeared the forest cannot satisfy the perpetual growth of demand, because 30 Million Hectares of trees disappeared every year (FAO, 1997). Actually,the researchers are looking to exploit new sources of cellulose such as (residues of Maize [6]. Hibiscus cannabinus L [7], OpuntiaFicusindica [8]). Many attempts were made to use the biomass efficiently to obtain a new class of high performance green polymers [9]. Esparto ‘‘Stipatenacissima’’ plant is a easily cultivated with short renewal times [10] and their annual worldwide production is about 1014 kg [11] and in Morocco about 5.71.

In this work, calcium phosphate nanocomposite, especially hydroxyapatite (HAp), was selected for bone regeneration applications. Their biocompatibilities are thought to be due to their chemical and structural similarity to the mineral phase of bone [12]. Biomineralized tissues are often found to contain polymorphs and individual minerals whose crystal morphology, size, and orientation are often controlled by local conditions and, in particular, by organic macromolecules such as proteins and polysaccharides. The processes and materials that control such crystal nucleation and growth are of great interest to material scientists to learn about the architecture, morphology, and patterning of inorganic materials by mimicking the process of bio- mineralization25 108 kg (Moroccan Society of Agricultural and Management; SOGETA, 1983).

The technology employed for the extraction of BPA from aqueous samples includes solid phase micro-extraction (SPME) [13], liquid–liquid extraction (LLE) [14] and solid-phase extraction (SPE) [15].

News stories about contamination with BPA, and the situation has since, have become an international health scare. In this work, a novel analytical method based on enrichment and pretreatment of analytesin the water sample, HEC/ HAsorptive extraction and gas chromatography–mass spectrometry SIM mode have been developed for the rapid analysis of BPA in water. The obtained results demonstrated that HEC/ HAp combined with GC–MS is a simple, rapid and solvent-free method for the analysis of BPA in water.

The aim of this work was then to choose the best stationary phase (TFME) and best chromatographic method for the quantification of BPA in samples of baby food matrices, which could be used for routine controls.

2.Experimentalprocedures

2.1. Materials

Hydroxyapatite (HAp) was synthetised in our laboratory, The composite HEC/ HAp was prepared by a wet chemical method at low temperature, all of analytical grade, trimethylsilyl trifluroacetamide (BSTFA,

1 % TMCS), purity [98 %, and BPA (bisphenol A purity [99 %) were purchased from Somaprol (Casablanca, Morocco). The hydroxyethyl cellulose (HEC) (99%), Calcium Nitrate $Ca(NO_3)_2{\cdot}4H_2O$ (99%), Ammonium Hydrogen Phosphate $(NH_4)_2{\cdot}HPO_4$ (99%), DMF (Dimethylformamide) and acetone were purchased from Aldrich. All other chemical reagents were of reagent grade and used as received and purchased also from Aldrich.

2.2 Extracting the cellulose from alfa

The Cellulose is extracted from the rods alfa collected from Hoceima sites in eastern Morocco as the Kraft process illustrated in Figure 1.

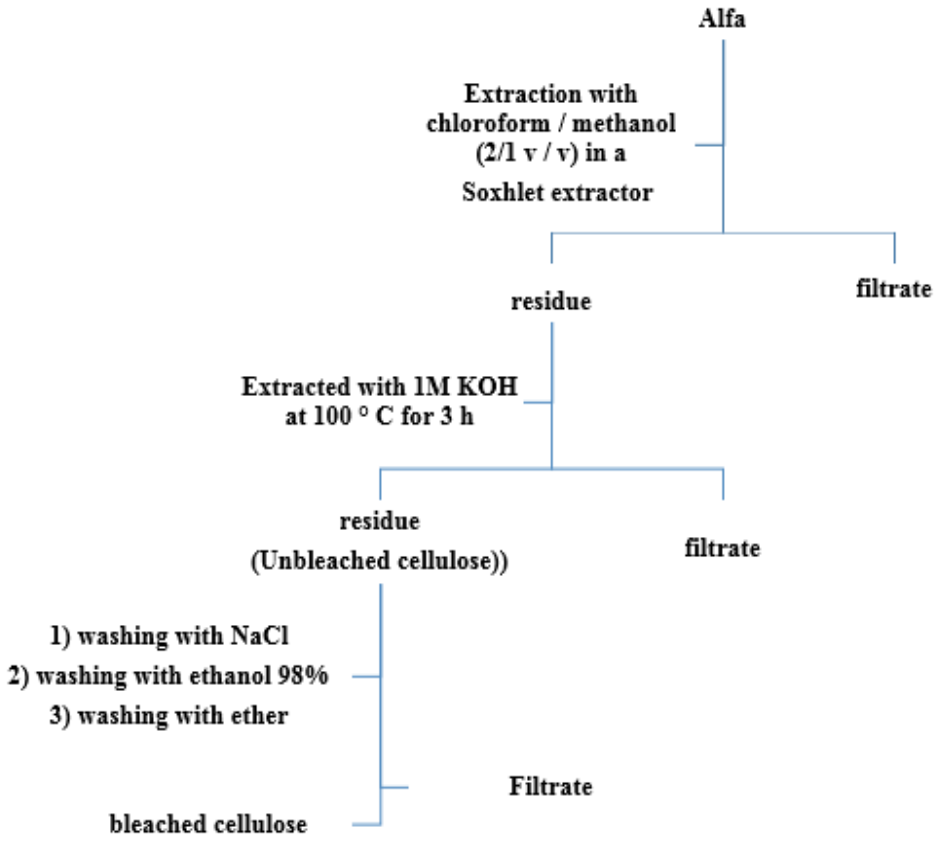

Figure 1. Different cellulose extraction steps

2.3. Synthesis thin film HEC/ HAp composite

HEC polymer were dissolved in water at room temperature to from solution and assed to from solution A . Solution B was hydroxylapatite (HAp) dispersed in DMF at room temperature and added to solution A. The solution turned to opaque milky white after about half an hour. Thin films were obtained by during the procedure with careful temperature control to 120 C at the temperature rate of 2 C minand maintained for 2 h, and then cleaned in absolute ethanol to remove any possible impurities in the film.

2.4. Gas chromatography coupled to mass spectrometry (GC-MS)

2.4.1. Adsorption study of PBA by the composite HEC/HAp

The work was performed in Laboratory of Solid Mineral and Analytical Chemistry. It consists in developing a method of analysis of bisphenol A by GC-MS in various samples of food matrices.

Extraction of the films (TFME) made from the polymer as HEC and hydroxyapatite (HAp) were tested. Due to their polymeric nature, these films (diameter 100 μm) are capable of adsorbing a wide variety of active molecules in a stable and reproducible way, and can be used to improve the mass transfer of an aqueous sample [16, 17]. Bisphenol A (the target molecule used in this study) is an organic compound disruptive endocrine system, used in the industrial manufacture of plastic bottles. It is a toxic and carcinogenic active ingredient, its metabolism is well known. To study the degradation of this organic compound, it is necessary to control the amount of BPA released plastics.

Chromatographic methods GC-MS and HPLC-UV were used for determination of BPA in food matrices for babies. The TFME-GC-MS method (developed in our laboratory) could be a good alternative method, which not only allows the control of the BPA but also the identification of metabolites and degradation products.

Composite membranes HEC / HAp combined with GC-MS method is a simple, economical, fast and does not use solvents to the GAP analysis in water. We conducted a comparative experimental study of BPA extraction between two phases-based composites HEC/HAp and commercial Florisil.

2.4.2. Preparation of standards and sample solution

Standard solution S0 is prepared by accurately weighing 100 mg of BPA. This mass is then dissolved in distilled water by adjusting the pH = 3 using a volumetric flask (1 litre). Dilutions in distilled water are carried out respectively to obtain solutions S1 and S2 at concentrations 10 and 1 mg / L The membranes were washed with deionized water and absolute ethanol, then dried at 100 ° C for 10 minutes. The steps of extraction and desorption are performed as follows: the membranes are immersed stirred in 50 ml of solution S1. After extraction, the membranes were dried at 40 ° C for 40 minutes. Finally, the stationary phases are directly placed in a centrifuge tube (1.5 ml) for desorption of BPA with the derivatizing reagent TMCS- BSTFA 1% (200 μl) under ultrasound and heating at 70 ° C for 30 minutes. 1 ml of this solution is injected directly into the GC / MS chromatograph. The solutions are analyzed in triplicate, to evaluate coefficients variation [16].

3. Results and discussion

3.1. Chemicalstructure

The spectrum alfa, it is observed the presence of a band at 2858 cm-1 due to stretching of the aromatic

CH bonds of the lignin. The band centered at 1732 cm^{-1} is attributable to vibration of the acetyl ester of uronic hemicelluloses or the nucleus of the carboxylic ester moiety of ferulic and p-coumaric acid to lignin and / or hemicellulose. Sun et al also report that the band at 1512 cm^{-1} is attributed to the elongation of the C = C bond of the aromatic nucleus of lignins. The peak at 1643 cm^{-1} is assigned to the presence of water molecules in alfa.The spectrum of the extracted cellulose, it is observed that there is disappearance of these bands, indicating that the extraction of lignin and hemicelluloses by the Kraft method is effective. In addition, the spectrum of the extracted cellulose is identical to that of the commercial cellulose. In these spectra, it is noted the presence of all the absorption peaks characteristic of the cellulose. The broad band centered at 3400 cm^{-1} corresponds to the OH bond of elongation vibration, the band 2915 cm^{-1} characteristic of the CH bonds of cellulose, 1031cm^{-1} band is due to the connections of elongation mode CO alcohols and ethers functions. There is also a smaller band at 896 cm^{-1} characteristic of β-glycosidic bonds between glucose units as shown in **Figure 2.a.**

The bands of the groups PO_4^{3-} apatitic structure is characterized by two absorption areas: 1100- 900 cm^{-1} (especially the bands located at 1090, 1050 and 962 cm^{-1}) and 600-500 cm^{-1} (particularly the bands located at 603 and 571 cm^{-1}) [17].

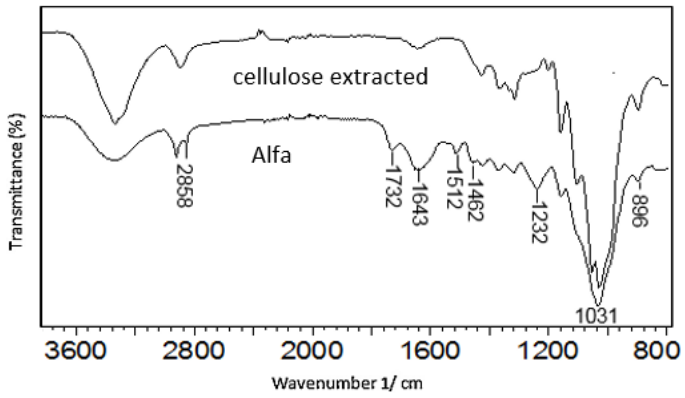

Figure 2.a. FTIR spectra of Alfa and extracted cellulose

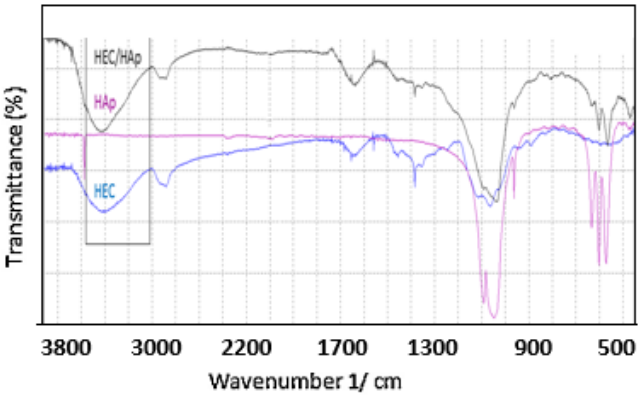

Figure 2.b. The infrared spectra of the HEC, HAp and HEC/HAp composite

The strips of the first field correspond to symmetric and antisymmetric vibration of the PO bond, and those of the second field are due to deformation vibrations of the bond O-P-O. Another vibrational band is observed around 1635 cm^{-1}, which is assigned to CO vibration. This band is shifted to 1623 cm^{-1} to low frequency, when the rate increases apatite. The peak between 2900 and 2980 cm^{-1} corresponds to the stretching vibration of alkyl (CH_3) groups of HEC [17] as shown in **Figure.2.b.**

3.2. Microscopic observation SEM

The **Figure 3** shows the SEM micrographs of HAp and HEC/ HAp prepared. It allows visualizing the morphology and distribution of the grains. The pure HAp sintered at 900 °C for 2 h has a structure of

individual platelets, the powder Hap modified by PEG 1000 obtained after heat treatment at 900 °C for 2 h, shows the fineness and spherical structure of grain .

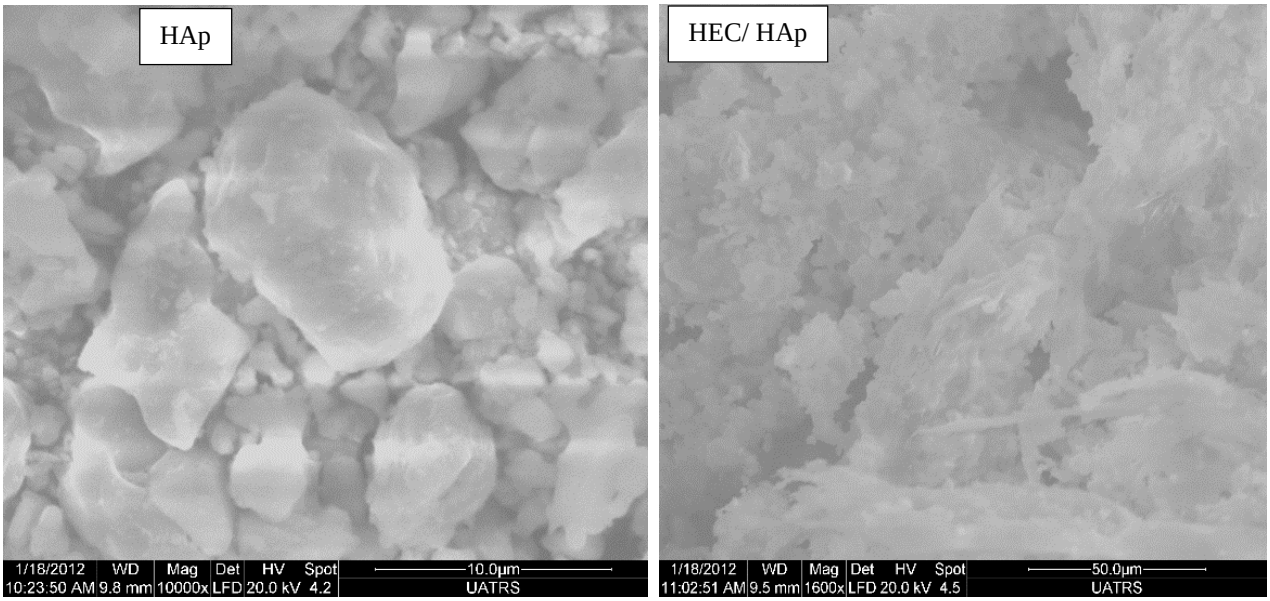

Figure. 3. The SEMof HAp and HEC/HAp/composite.

The results indicate that the modified particles of hydroxylapatite have relatively small grain size (about 90 μm). All membranes used have homogeneous structures, with the exception of rare agglomerate which are caused by the surface energy of hydroxylapatite.

3.3. Chromatogram of BPA desorbed from the HEC/HAp/PEG 1000 composite

Adsorption performance for the membranes HEC/ HAp composite are compared with thos of the commercial Florisil. The results obtained are shown in (**Figure .4**). The figure shows the evolution of the shape of the chromatographic peaks BPA desorbed by these membranes. Best BPA recovery rate is achieved with the stationary phase 50% of the organic phase 50% of HEC and 50% of HAp.

The result of florisil also leads to very interesting results with comparable recovery rates than those recorded by the studied composites.

The study of BPA extraction composites based HEC/ HAp composite has achieved a satisfactory extraction with a very good yield. These results contribute to the enhancement of calcium phosphate matrices in the extraction of organic pollutants.

The thin films made in our laboratory can be used for the qualitative and quantitative analysis of bisphenol A in different and various matrices of children and baby foods.

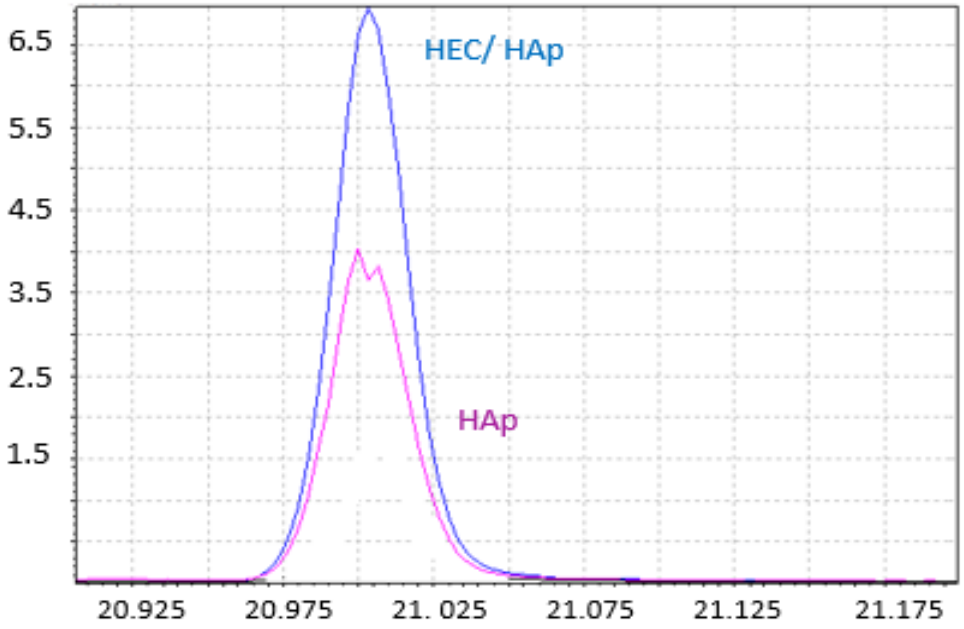

Figure 4. Chromatogram of BPA desorbed from composite HAp and HEC/ HAp

Conclusion

The preparation of HEC/ HAp composite was successfully achieved through dispersion of HAp particles homogeneously in the composite. The composite was characterized by IR and SEM. The results showed a weak interaction between the organic matrix and the HAp matrix. The morphology showed that the composite has good compatibility between the organic matrix and the inorganic matrix composite. We have developed very thin membranes that can be used for the extraction of various elements and compounds. The chemical study of these membranes showed some interaction between the polymers and the inorganic matrix. The Chromatogram of BPA desorbed from composites showed that the polymer alone has the lowest amount adsorbed.

Conflict of Interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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