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Research paper

Anionic clays for sunscreen agent safe use: Photoprotection, photostability and prevention of their skin penetration

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Abstract

The use of sunscreen preparations is recently growing and their efficacy and safety must be taken into account since they are applied on the skin frequently and for many hours. Exposition to sunlight, in fact, can cause sunscreen photodegradation and determine their decrease in UV protection often with the occurrence of allergic and/or toxic degradation products. A high photostability is hence very important for their effectiveness and safety.

The aim of this work is to obtain new sunscreen formulations stabilized by intercalating PABA, within the lamellar structures of two kinds of hydrotalcite. PABA was chosen as model sunscreen because of its high photoinstability and photosensitizing properties that nowadays bar its utilization. Both intercalated products showed an increased protection range and, in one case, an improved sunscreen photostability.

Sunscreen release from creams containing intercalated or free PABA was evaluated as well. The very low or negligible sunscreen release, obtained from the intercalated product loaded formulations, resulted in a lack of a close contact between skin and filter with the consequence that cutaneous reactions and allergy problems are eliminated.

The use of these materials resulted in a good strategic technological approach in order to increase efficacy and safety of solar products.

Keywords: Sunscreen agent; *para*-Aminobenzoic acid; Hydrotalcite; Intercalation; Photoprotection; Photostability

1. Introduction

The harmful effects of sunlight, especially the solar UV radiation, on human skin are well known [1]. Adverse reactions to the sun UV rays include short-term inflammatory responses (erythema, sunburn) and long-term effects (cutaneous photoageing, immunosuppression and skin cancers) [1–3], which are increasing throughout the world. Public hazard awareness to sunlight exposure brought to an increasingly widespread use of sunscreen agents [1,4,5]. Chemical sunscreens are compounds that absorb UV light and thereby decrease the amount of the solar radiation energy reaching the stratum corneum [1]. Most sunscreen preparations on the market are appropriate only for UV-B rays, but protection from UV-A rays assumed increasing importance too since more is known about their adverse effects on human skin [1,6,7]. The electronically excited sunscreen molecule can decay through different pathways: in the form of heat, by fluorescence, phosphorescence, interaction with neighbouring molecules or by undergoing photoinduced decompositions [8,9]. The latter reactions decrease the sunscreen UV-protective capacity during its use [9–11] and can also produce allergic or toxic degradation products [4,12]. Therefore a high photostability is a prerequisite for the effectiveness of sunscreen products.

The *p*-aminobenzoic acid (PABA) is a UV-B absorber (200–313 nm) [13] used as a sunscreen component as early as the 1920 s and lasted since when dermatologists became aware that it was a fearly photosensitizer. In fact it tends to cross-sensitize with other *para*-molecules [14] and it is responsible for adverse cutaneous reactions like irritation, contact orticaria and allergic and photoallergic dermatitis

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[15,16]. PABA can decompose to a nitrosamine degradation product with a known potential carcinogenic effect, so that, since the late 1980 s, it has been practically withdrawn from the sunscreen and cosmetic market, and most products proclaim that they are ‘PABA-free’ [14].

In the time, photodegradation of chemical sunscreens has been reduced by providing a protective film around the reacting molecule, by incapsulation in liposomes, microspheres [17] and in glass beads [18], incorporation in nanoparticles [19] or by complexation with cyclodextrines [20]. Recently, we demonstrated that intercalation in inorganic materials as hydrotalcite (HTlc) [21] could represent a new strategy to improve sunscreen photostability and to avoid a direct contact with skin. Hydrotalcites, natural anionic lamellar solids with positively charged layer balanced by exchangeable anions [22], are rare in nature, but quite easy to prepare in laboratory. They have the general formula $[M(II)_{1-x}M(III)_{1-x}(OH)_2]^{x+}[A^{n-}_{x/n}]^{x-}\ m\ S$ where M(II) is a bivalent metal cation, usually Mg, M(III) is a trivalent metal cation, usually Al, A^{n-} is an exchangeable inorganic or organic anion that compensates the positive charge of the layer and *m* are the moles of solvent S, usually water, co-intercalated for mole of compound [22]. An intercalated anion can be replaced by another via ion-exchange, with consequent variation of the interlayer distance [23]. Consequently, the interlayer region of a lamellar host can be considered a microvessel in which an anionic molecule may be stored.

The aim of this research is to store the sunscreen in the interlayer region of a lamellar host and for this purpose we have chosen HTlc containing magnesium and aluminium (MgAl–HTlc) or zinc and aluminium (ZnAl–HTlc) cations. These metals are largely used in cosmetic formulations both as salts (antiperspirants) and as oxides (ZnO is a physical sunscreen) [24–30]. PABA has been chosen as sunscreen model because of its high photoinstability and photosensitizing properties. The expected advantages of sunscreen intercalation in hydrotalcites are: (i) sunscreen stabilization, (ii) absorption of ultraviolet lights in both the UV-A region and the UV-B region and (iii) absence of a close contact between skin and filter with the consequent elimination of allergy problems. With this assumption, a new protection model has been designed. Thus, the present paper reports the studies on the intercalation products of PABA into MgAl–HTlc and ZnAl–HTlc lamellar structures and the properties of the relative cosmetic formulations.

2. Materials and methods

2.1. Materials

Well crystallised $[Mg_{0.66}Al_{0.34}(OH)_2](NO_3)_{0.34}\cdot 0.4H_2O$ and $[Zn_{0.66}Al_{0.34}\ (OH)_2](NO_3)_{0.34}\cdot 0.4H_2O$ was obtained by co-precipitating, from ‘homogeneous solution’, Mg(II) or Zn(II) and Al(III) hydroxycarbonate (HTlc–CO_3) [31] and successive CO_3^-/NO_3^- ion exchange by titration with HNO_3 0.1 N [32].

PABA was kindly provided by Farmalabor, Bari (Italy), polygliceryl-4-isostearate cetyl dimethicone copolyol hexyl laurate (Abil WE 09) and polygliceryl-3-isostearate (Isolan GI 34) and cetyl dimethicone (Abil wax 9801) by Goldschmidt, Cremona (Italy), cyclomethicone (Silicone DC 245) by Dow Corning, Seneffe (Belgium), Ceresine (Ceresine wax SP 252) by Rossow Cosmétiques, Gennevilliers (France), Mineral oil was purchased from Carlo Erba, Milano (Italy). Other chemicals and solvents were of reagent grade and were used without further purification.

2.2. Methods

2.2.1. Preparation and characterization of intercalation products

A carbon dioxide free 0.1 N NaOH water solution (474 ml) was added to a suspension of 65 g (474 mequiv) of PABA in degassed water (710 ml) to obtain a sodium salt solution to which 5 g (19.5 mequiv) of MgAl–HTlc–NO_3 were added. The same procedure was followed to intercalate the sunscreen in ZnAl–HTlc–NO_3 by adding a carbon dioxide free 0.1 N NaOH water solution (569 ml) to a suspension of 78 g (569 mequiv) of PABA in degassed water (854 ml). Then 5 g (14.8 mequiv) of ZnAl–HTlc–NO_3 were added. The resulting suspensions were stirred at 60 °C, 140 rpm for 7 days in an orbital incubator. After cooling, the reaction mixtures were centrifuged at 5000 rpm for 5 min, washed three times with degassed water, three times with ethanol and finally dried at room temperature over P_2O_5. The intercalation reactions were performed in an orbital incubator Gallencamp type INR 2000, Leicestershire, UK, and the mixtures were centrifuged with a A.L.C. centrifuge (Milano, Italy) mod. 4236A.

X-ray powder diffraction patterns (XRDP) were performed with a PW 1710 Philips diffractometer (Lelyweg, Netherland), using the Ni-filtered Cu Kα radiation. Thermogravimetric analyses were carried out using A Stanton-Redcroft STA 780 (England) thermoanalyzer at heating rate of 5 °C min^{-1} in air flow to determine the weight loss of water and drug as a function of increasing temperature.

PABA content was also determined by UV analysis at $\lambda_{max}=268.0$ nm using a spectrophotometer Jasco-V-520 (Tokyo, Japan) after dissolution of a known amount of intercalation compound in HCl solution and successive dilution with phosphate buffer at pH 7.5.

Differential scanning calorimetry analyses (DSC) were performed using an automatic thermal analyser (Mettler Toledo DSC821e, Italy). Temperature calibrations were performed with indium as a standard. Sealed and holed aluminium pans were used for all the samples and an empty pan prepared in the same way was used as a reference. Samples of 3–6 mg were weighted directly into the aluminium pans and thermal analyses were conducted at a scanning rate of 10 °C/min from 20 to 500 °C.

FT-IR spectra were recorded by mean of a Bruker IFS 113 V with source Globar and DTGS rilevator on KBr tablets and discs of CsI.

Scanning electron microscopy (SEM) photographs were taken with a Philips SEM 501 (PW 6703) (Holland). Before observation, the dried samples were sputtered and coated, for ca. 5 min under an argon atmosphere, with gold–palladium.

2.2.2. Intercalated product water-stability

Stability of intercalated products in water [33] was performed pouring 100 mg of intercalated products in 50 ml of deionized water. The suspension was stirred for 2 h at room temperature and then centrifuged with a 4236A ALC centrifuge (Milan, Italy) at 4000 rpm for 5 min. The PABA content in the supernatant was determined by UV absorption at 268.0 nm.

2.2.3. Preparation of sunscreen creams

The waterproof silicone cream [34] used for the sunscreen formulations had the following composition:

1. polygliceryl-4-isostearate cetyl dimethicone copolyol hexyl laurate (Abil WE-09) 5%, polygliceryl-3-isostearate (Isolan GJ-34) 1%, cyclomethicone (silicone DC-245) 7.50%, cetyl dimethicone (Abil wax 9801) 3%, castor oil 0.50%, ceresin (Ceresine wax SP 252) 1%, mineral oil 2%,
2. HTlc–PABA 10%,
3. deionized water q.b. a 100 g.

The components 1 and 3 were mixed at 80 °C, cooled down to 60 °C, then the intercalated product (10%) were added. The resulting PABA content was 2.48% for the MgAl–HTlc formulation and 2.47% for the ZnAl–HTlc formulation. Creams containing the same amount of free PABA (nonintercalated) were prepared as well.

2.2.4. In vitro PABA release from sunscreen creams

The sunscreen release was performed in a dissolution apparatus for semisolid preparation (Steroglass, Perugia, Italy) using the Petri disk method [35]. 300 mg of sunscreen cream were spreaded on the Petri disk (50 mm diameter) with a spatula to produce an even, uniform surface of constant dimensions. The paddle rotation speed was kept at 60 rpm and the dissolution medium volume was 100 ml [36]. The dissolution vessels, closed on the top, were kept in a thermostatically controlled circulation water bath at 32 ± 0.5 °C. The dissolution media consisted in deionized water, phosphate buffer pH 5.5 (Farmacopea Ufficiale Italiana XI Ed.) to simulate the pH skin and NaCl solution (0.4 mg/100 ml) [33] in order to simulate the sea water. At predetermined times, aliquots of 2 ml were removed, appropriately filtered (13 mm Filter UNIT 0.45 μm NY PP, Lyda, WI, USA), diluted when necessary and analysed by UV at $\lambda_{max} = 268.0$ nm in the case of water and saline solution and at $\lambda_{max} = 266.4$ nm in the case of phosphate buffer pH 5.5. The removed aliquots were immediately replaced with the same volume of medium. Tests were made in triplicate and the results were recorded as an average. Sunscreen releases from the formulation and from the cream

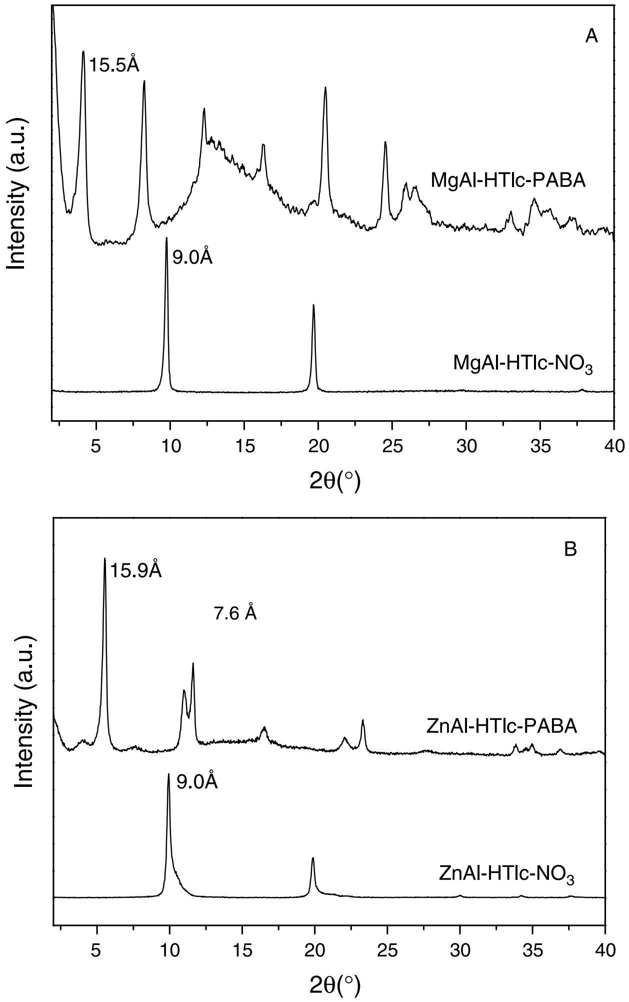


Fig. 1. X-ray powder diffraction pattern of MgAl–HTlc–NO_3 and MgAl–HTlc–PABA (A); ZnAl–HTlc–NO_3 and ZnAl–HTlc–PABA (B).

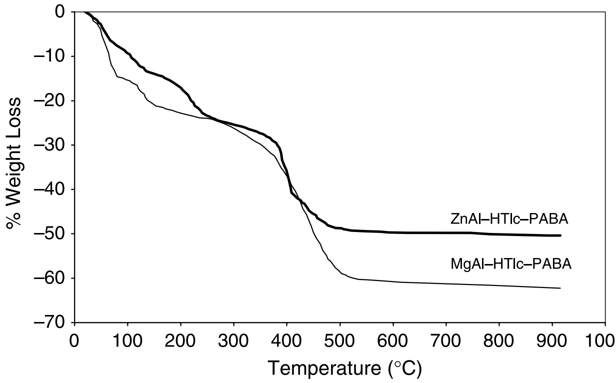


Fig. 2. Thermogravimetric analysis curves of MgAl–HTlc–PABA and ZnAl–HTlc–PABA.

containing not intercalated PABA were performed. For this reason a silicon cream containing 2.47% of free (not intercalated) PABA was prepared and the release profiles of all formulations were observed.

2.2.5. Photochemical and photophysical studies

Absorption spectra of the solid samples were recorded by a spectrophotometer (Perkin–Elmer Lambda 16, England) equipped with an integration sphere. The spectra recorded were analysed with the Kubelka–Munk equation in order to make possible the comparison. The fluorescence spectra and intensity vs. time for all samples were recorded through a fluorimeter (Spex Fluorolog 2, USA) using the front face configuration between the excitation and the emission light. Spectra were corrected for the instrument response at each wavelength. The fluorescence intensity vs. irradiation time was recorded by fixing excitation and emission wavelengths and by monitoring the emission intensity as function of the irradiation time.

3. Results and discussion

3.1. Preparation and characterisation of intercalation products

Synthetic MgAl–HTlc and ZnAl–HTlc in the carbonate form, prepared as previously described, were not suitable for PABA intercalation because it is well known [22] that carbonate ions are strongly held in the interlayer region and it is very difficult to replace them with other anions using simple ion exchange procedures. It is also known that the monovalent anions as NO_3^- [22] can be more easily replaced than carbonates; therefore MgAl–HTlc–CO_3

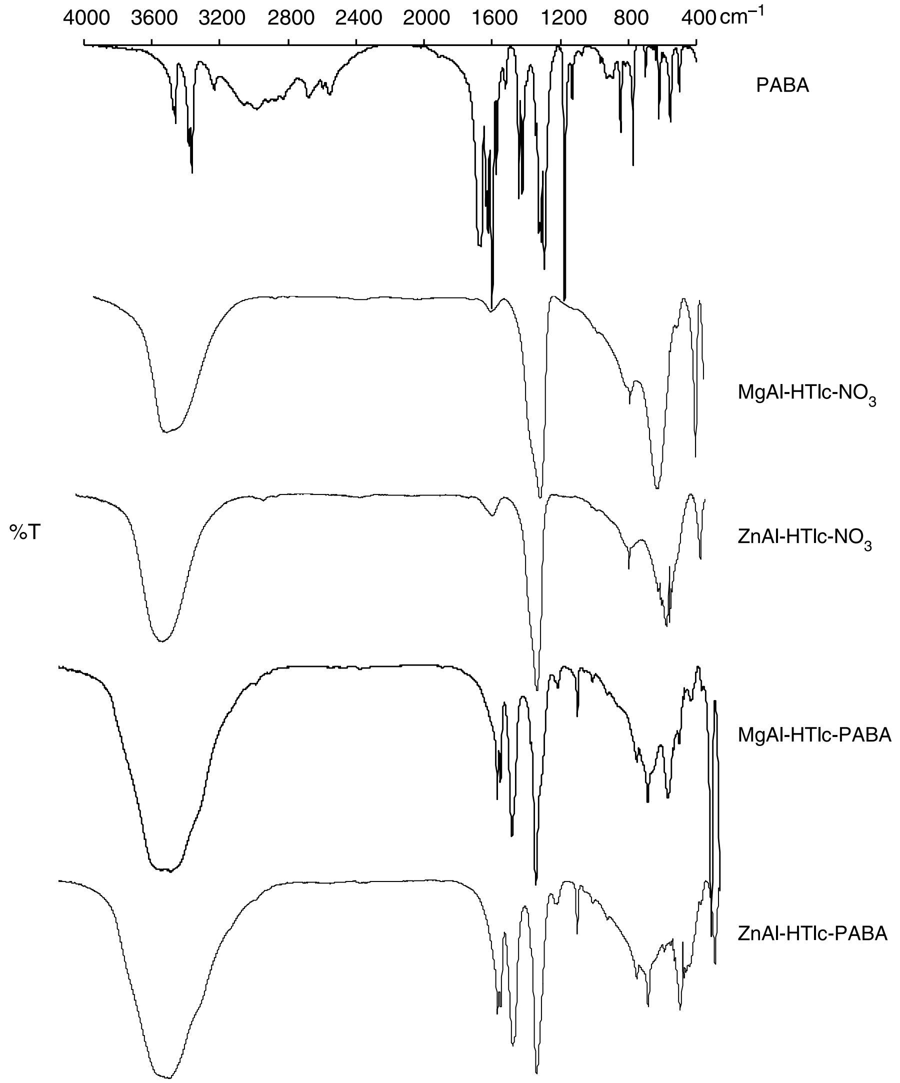


Fig. 3. FTIR spectra of free PABA, MgAlHTlc–NO_3, ZnAlHTlc–NO_3, MgAlHTlc–PABA, ZnAlHTlc–PABA.

and ZnAl–HTlc–CO_3 have been converted into the nitrate forms [32]. The PABA intercalation has been successfully obtained by an anion exchange process as described in the experimental part. The formation of both intercalated compounds, MgAl–HTlc–PABA and ZnAl–HTlc–PABA, was confirmed by X-ray powder diffraction spectra (Fig. 1(A) and (B)) where an increase of the interlayer distances was observed as a consequence of PABA intercalation. In the case of MgAl–HTlc–PABA it was possible to observe the lack at 9.0 Å due to MgAl–HTlc–NO_3 and the presence of the peak at 15.5 Å relative to the intercalation of PABA in MgAl–HTlc. Similarly, in the spectrum of ZnAl–HTlc–PABA the interlayer distance increased from 9.0 to 15.9 Å. In this spectrum, it was possible to note also a residual peak at 7.6 Å due to the CO_3^- ions entrapped between the lamellae.

Fig. 2 shows the thermogravimetric curves of the intercalation compounds, previously stored in a dessicator at room temperature and 75% relative humidity. Taking into account that patterns of the sample heated at 1000 °C indicate the presence of MgO and $MgAl_2O_4$ in the case of MgAl–HTlc–PABA and ZnO and $ZnAl_2O_4$ in the case of ZnAl–HTlc–PABA, the weight loss curves, as function of temperature, may be interpreted as follows: from room temperature to ca. 200 °C samples loose the co-intercalated water; the great weight losses between 200 and ca. 500 °C is attributable to the sunscreen decomposition and to the loss of water due to dehydroxylation of the inorganic layers. The derived formulas resulted: $[Mg_{0.66}Al_{0.34}(OH)_2]PABA_{0.212}(NO_3)_{0.128}\cdot 1.13H_2O$ (sunscreen content 24.8%) and $[Zn_{0.66}Al_{0.34}(OH)_2]PABA_{0.258}(CO_3)_{0.041}\cdot H_2O$ (sunscreen content 24.7%). This means that 248 and 247 mg of PABA were present, respectively, in 1000 mg of the intercalated compound. The PABA content was confirmed by UV analysis after HTlc destruction in acidic medium.

FT-IR spectrum of PABA (Fig. 3) showed two peaks between 3365 and 3475 cm^{-1} due to the amine group and a peak at 1667 cm^{-1} due to the carboxylic groups. However, the IR spectrum of MgAl–HTlc–NO_3 and ZnAl–HTlc–NO_3 showed a broad band between 3200 and 3800 cm^{-1}, due to the stretches of hydrogen-bonded hydroxyl group of both hydroxide layers and interlayer water, and a peak at 1363 cm^{-1}, due to the nitrate group. The lack of carboxylic group absorption and the presence of two peaks at 1401 and 1532 cm^{-1} for MgAl–HTlc and at 1397 and 1527 cm^{-1} for ZnAl–HTlc, due to the carboxylate asymmetric and symmetric stretches relative to the intercalated anions, were observed as well.

DSC thermogram (Fig. 4) of PABA ((A) and (B)) showed an endothermic peak at ca. 189 °C relative to the melting point of pure crystalline substance. Thermograms of HTlc in nitrate form show a large peak around 250 °C for MgAl–HTlc–NO_3 (A) and 380 °C for ZnAl–HTlc–NO_3 (B) due to the loss of hydroxyl groups present in HTlc. In the intercalation compound thermograms, the lack of the endothermic peak at 189 °C is a confirmation that the sunscreen intercalation process occurred.

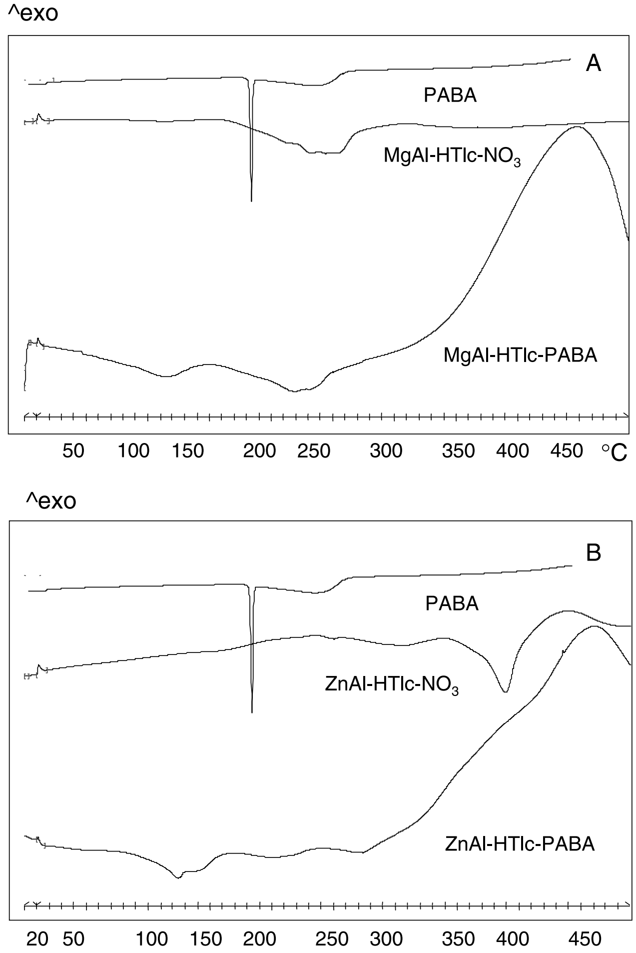


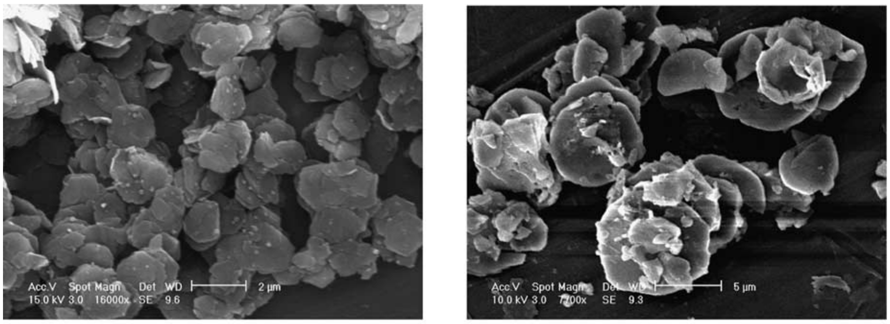
Fig. 4. Differential scanning calorimetry thermograms curves of free PABA, MgAl–HTlc–NO_3 and MgAl–HTlc–PABA (A) and PABA, ZnAl–HTlc–NO_3 and ZnAl–HTlc–PABA (B).

SEM of HTlc–NO_3 and HTlc–PABA powders are also reported (Fig. 5). The images relative to the intercalated products revealed microcrystals in a nearly hexagonal form and, in comparison to hydrotalcites in nitrate form, it is noteworthy to point out that the intercalation process did not modify either the microcrystal size or the morphology.

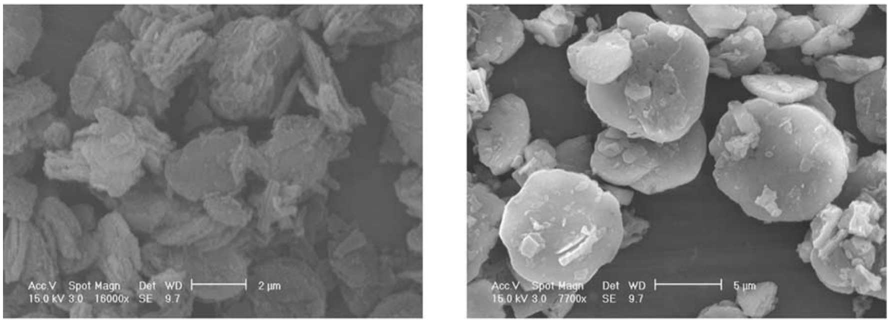
3.2. Preparation of sunscreen creams

Sunscreen formulations are generally gels, oils, creams, milks or sticks; in our case the ideal formulation should have the following requirements:

1. least presence as possible of water to prevent the filter deintercalation from hydrotalcite and consequently to avoid its contact with the skin;
2. absence of dissolved ions, whose presence could cause filter deintercalation from hydrotalcite via ionic exchange during the cream preparation and storage;



($MgAl\text{-}HTlc\text{-}NO_3$) ($ZnAl\text{-}HTlc\text{-}NO_3$)



(MgAl-HTlc-PABA) (ZnAl-HTlc-PABA)

Fig. 5. Scanning electron micrography of HTlc–NO_3 and intercalation compounds.

3. consistency, spreading, cosmetic pleasantness, water resistance as requested from a good sunscreen formulation.

To fulfil these requirements a silicon cream was chosen because it is not oily and water proof [37].

3.3. Studies of sunscreen release from formulations

The release of PABA in water was evaluated (Fig. 6(A)). The PABA is released from cream in a quantity of 20% after 15 min, 43% after 5 h and the release increased up to 81% after 8 h. The intercalated PABA is released in a much smaller manner. In fact, the release is less than 5% for the first hour, less than 10% in 5 h and less than 12% in 8 h.

The same release differentiations were observed in presence of a phosphate buffer (Fig. 6(B)). The release of PABA, when in free solid state, is 25% in 15 min., around 50% in 6 h and increased up to 67% in 7 h. The PABA release from both intercalated compounds is around 20% after 3 h and less than 31% after 8 h.

The nonintercalated PABA release from the cream in sea water (NaCl salt solution) (Fig. 6(C)) is more than 30% after 15 min and rises to 50% after 2 h, while from the intercalated formulation is less than 10% after 6 h and less than 12% in 8 h. These results show that, even after the contact with sea water, the sunscreen is barely released while most of it remains entrapped inside the inorganic host practically avoiding any its skin contact.

3.4. Studies of photophysical and photochemical properties

The absorption spectra of free solid and intercalated PABA (Fig. 7), are strongly affected by the microenvironment. The spectrum obtained from the free solid PABA presents a maximun at 320 nm and a shoulder at 415 nm. In the case of MgAl–HTlc–PABA the main absorption maximum is centered at 300 nm and the shoulder in the visible region is more evident than when PABA is in the free solid state. For the system ZnAl–HTlc–PABA, the absorption spectrum is markedly red shifted since the main maximum is at 425 nm and a shoulder at 580 nm was observed. These effects on the absorption spectra can be due to specific interactions between PABA and ZnAl–HTlc matrix likely because of the formation of complexes between the nitrogen of the sunscreen and the Zn atoms present in the inorganic phase [38,39]. The broadening of the absorption bands observed for ZnAl–HTlc–PABA leads to an increase of the protection range for the intercalation compound compared to the free compound. So, the establishment of these specific interactions between the sunscreen and the matrix is wanted to extend its protection range.

The emission spectra of samples under investigation are recorded. The spectrum of free solid PABA shows a broad band centered at 420 nm while the spectra obtained from the intercalated samples show a main maximum at 345 nm and a broad band between 400 and 550 nm. It is likely that the band centered at 345 nm is due to the chromophore externally adsorbed on the hydrotalcite, while the red-band is the contribution of the intercalated molecules, as already observed for other dye–hydrotalcite composite [40]. It is noteworthy to point out that excitation of the inorganic matrix alone did not lead to a detectable emission (data not shown).

The high sensitivity of the emission measurements was used to test and compare the photostability of the samples under investigation. In particular, emission spectra of all samples, were recorded in the same experimental conditions, before and after irradiation at 297 nm for 2 h. No changes in the spectral shape were observed. However, an emission intensity decrease was detected in the not normalized spectra (see below) indicating the occurrence of photodegradation processes leading to products that do not emit in the used experimental conditions. Since the photoproducts did not interfere with the emission properties of PABA-compounds, the photostability analysis was pushed further considering that all samples absorb a similar amount of the excitation light (297 nm, Fig. 7). In order to have kinetic information on the chromophore concentration change in the irradiated area, the decrease of emission intensity was followed as function of irradiation time for all compounds under investigation. In particular, the emission traces (Fig. 8) were recorded during the irradiation at 297 nm by collecting the emission at the maximum for each

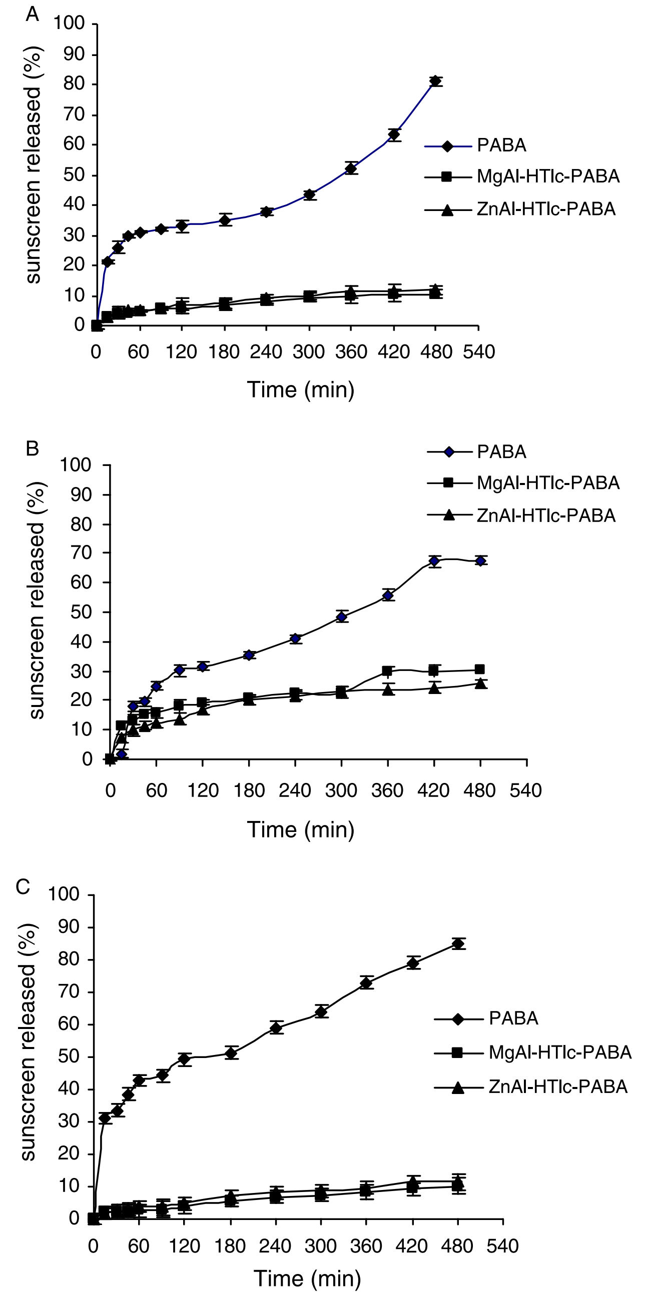


Fig. 6. Release of PABA from creams containing free PABA, MgAl–HTlc–PABA and ZnAl–HTlc–PABA in water (A), in phosphate buffer at pH 5.5 (B), in sea water (C).

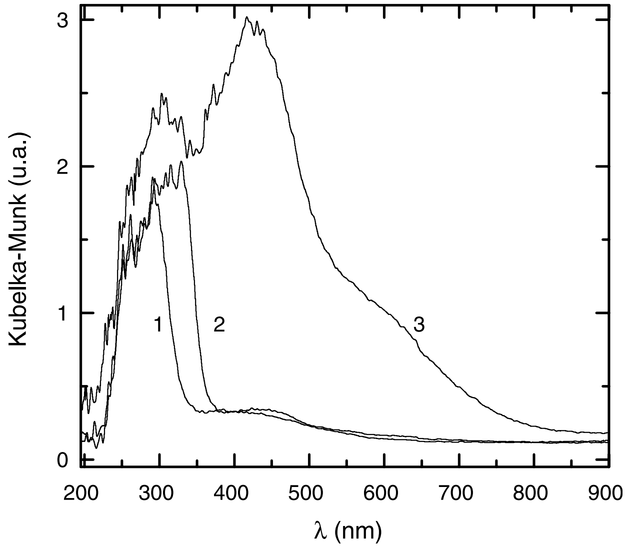


Fig. 7. Absorption spectra of MgAl–HTlc–PABA (1), free PABA (2) and ZnAl–HTlc–PABA (3).

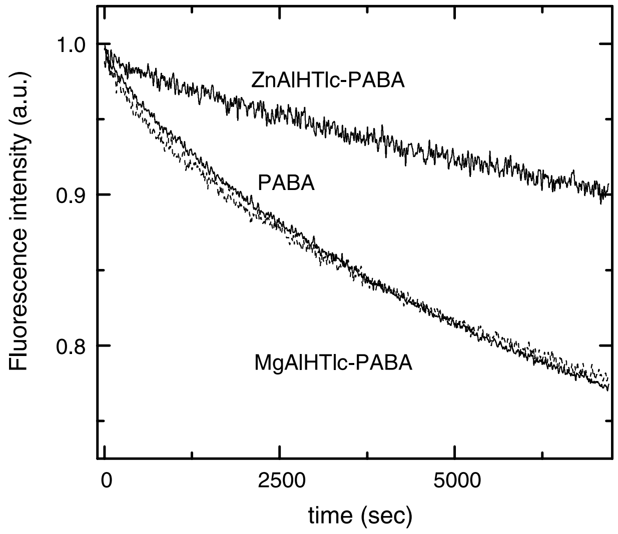


Fig. 8. Fluorescence decay of free PABA, ZnAl–HTlc–PABA and MgAl–HTlc–PABA.

sample. The traces shown in Fig. 8 indicated that the emission of free PABA and of MgAl–HTlc–PABA decreases with a similar behavior to reach 78% of the initial value during the irradiation. In the case of ZnAl–HTlc–PABA, the emission decreases slower and in 2 h only 10% reduction was observed. Thus, the ZnAl–HTlc matrix well improves the photochemical stability of PABA, protecting the molecule from photodegradation reactions. The comparison of the data obtained from the two intercalation compounds suggests that the higher stability of ZnAl–HTlc–PABA system is not only due to a physical screen (similar for both matrices), but also to a chemical protection of the photoactive chromophore.

The spectrofluorimetric investigation was then carried out on the samples obtained by dispersing the intercalation compounds in the siliconic cream. The absorption and emission spectra of these samples were recorded to investigate the occurrence of specific interactions among the intercalation compounds and the formulation components. The absorption spectra of creams loaded with the intercalated sunscreen presented a shape similar to those of not formulated intercalation compounds (Fig. 7) but they have an intensity 2–3 fold higher. This effect is due to the contribution of cream ingredients to the screening properties of the intercalation compounds, leading to a higher protection factor. The emission spectra of the intercalation compounds in the cream formulation are similar to those of the intercalated compounds with the same maxima. This observation indicates that the energy of the emitting state does not change when HTlc–PABA is dispersed in creams probably because the interactions between the chromophore and the cream components are negligible.

To evaluate the photostability of the creams with the intercalated solar screen, their emission signal was recorded as function of the irradiation time (Fig. 9). Both creams showed a reasonable photostability since, after 1 h of irradiation, only a reduction of ca. 20% of the signal, attributable to degradation of the chromophore, was observed. In particular, as already noticed for the intercalation compounds, ZnAlHTlc–PABA formulation appeared slightly more stable as well.

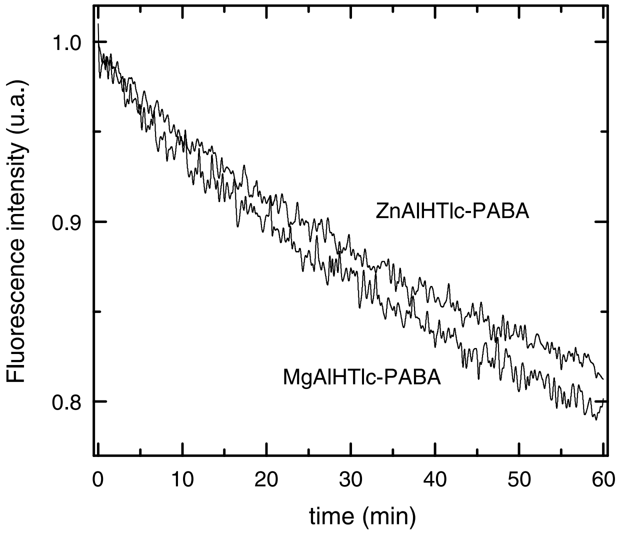


Fig. 9. Fluorescence decay of formulations containing 10% intercalation products MgAl–HTlc–PABA and ZnAl–HTlc–PABA.

4. Conclusion

The aim of the present research was to store a model compound sunscreen, such as PABA, whose high instability and photoreactivity is well known, in the interlayer region of the lamellar host to study the protection and the sunscreen modified release offered by HTlc lamellar structures.

It was thus observed that

1. The intercalation process leads to nanocomposite materials that extend the solar screen protection range.
2. In the case of the ZnAlHTlc–PABA system, a high photostability is observed due probably to the establishment of specific interactions between the matrix and the solar filter.
3. The intercalation compound, when dispersed in the formulation, maintained its spectral properties (absorption and emission) suggesting that the interaction among the solar filter and the components of the creams are negligible.
4. The photostability of the intercalated PABA creams was remarkably increased.
5. The release of PABA from creams containing HTlc–PABA was negligible (in water and sea water) or very low (in phosphate buffer) and always much lower than from creams containing not intercalated PABA.

It is possible thus, to conclude that the intercalation of PABA into hydrotalcite proved to be very useful to enhance its sunscreen properties in terms of protection range and photostability. In fact the use of these new systems represents a promising, good, efficient way to protect other chemical filters having similar photoinstability. Moreover, since these novel formulations allow a very low sunscreen release from the formulations, they avoid a close contact between skin and filter and hence prevent any cutaneous reactions and allergy problems that may occur.

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