

Research article

Intercalation compounds of a smectite clay with an ammonium salt biocide and their possible use for conservation of cultural heritage

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ABSTRACT

Ordered intercalation compounds between a smectite mineral clay (montmorillonite, Mt) and the ammonium salt mainly used for stone material disinfection procedures (i.e. N-Alkyl-N-benzyl-N,N-dimethylammonium chloride, shortly known as benzalkonium chloride, BAC), leading to an increase of interlayer distance from 1.3 nm up to 3.4 nm, have been prepared. The used clay/ammonium salt ratios are close to (or higher than) those often used for stone materials disinfection procedures for the conservation in cultural heritage. The prepared intercalated compounds have been studied as for their possible cation release in suitable aqueous media. Mt/BAC intercalated compounds are able to release only a fraction (if any) of the intercalated cations, eventually leading to a stable intermediate intercalated structure with interlayer distance not far from 1.9 nm, with a Mt/BAC ratio roughly equal to 4/1. The overall results indicate that Mt/BAC intercalates are possibly suitable for biocide applications in stone conservation procedures requiring both fast antimicrobial release and long-term biostatic effect.

1. Introduction

The biological degradation of stone in buildings and monuments is well known since the mid-1960s but the topic has received increasing attention from conservators and conservation scientists only within the last two decades. Cleaning of stone artifacts is a necessary operation for the prevention from deterioration of materials and is usually carried out with a large number of methods widely known in the field of conservation, such as mechanical and chemical cleaning [1, 2, 3]. Specifically, washing or poultices with ammonium salts and biocide products are mostly used [1, 2].

Ammonium salts, mainly benzalkonium chloride (BAC, N-Alkyl-N-benzyl-N,N-dimethylammonium chloride, with the alkyl chain length being variable between 12 and 16 carbon atoms), are widely known for their effectiveness on autotrophic and heterotrophic microorganisms and hence are commonly used in stone material disinfection and cleaning procedures [4, 5, 6, 7] also in underwater environment [8].

In cases of more persistent deposition, more concentrated solutions may be used and possibly suspended in paste, generally using cationic clays, and left to work for one or two days [9, 10]. Analogous procedures based on clays and ammonium salts are used to remove cuprous metal stain, mainly from marble and limestone [1].

The used cationic clays are generally 2/1 phyllosilicates, e.g. sepiolite or attapulgite [1, 9, 10], i.e. clay minerals being formed by 2 external sheets of silicon-based tetrahedra and 1 internal sheet of metal-based (Al, Mg) octahedra.

It is well known that 2/1 mineral clays of the smectite group are expanding clays, which are able to form stable intercalated compounds with ammonium cations. The interlayer space of pristine clay, d_{001} , typically in the range 1.2–1.3 nm, can increase up to 1.8–4.0 nm by compounding with either single chain or double-chain amphiphiles with n carbon atoms (C_n), such as the ammonium cations $[(CH_3)_3 N^+ C_n]$ or $[(CH_3)_2 N^+ (C_n)_2]$, respectively [11, 12, 13, 14, 15, 16, 17].

The formation of these intercalation compounds leads to very large increases of distances between clay layers, when the organic cation includes long hydrocarbon chains (in particular for montmorillonite, from 1.2 nm up to 6 nm) [18, 19, 20, 21, 22]. The ability of ammonium cations, with one or two long hydrocarbon chains, to form intercalated compounds has also been demonstrated by the achievement of intercalated compound with graphene [23, 24] as well as with oxidized carbon black [25], with very high interlayer space (from 0.8 nm up to 5.8 nm) [24].

In this work, the formation of intercalated compounds of montmorillonite and benzalkonium chloride (a commercial product commonly

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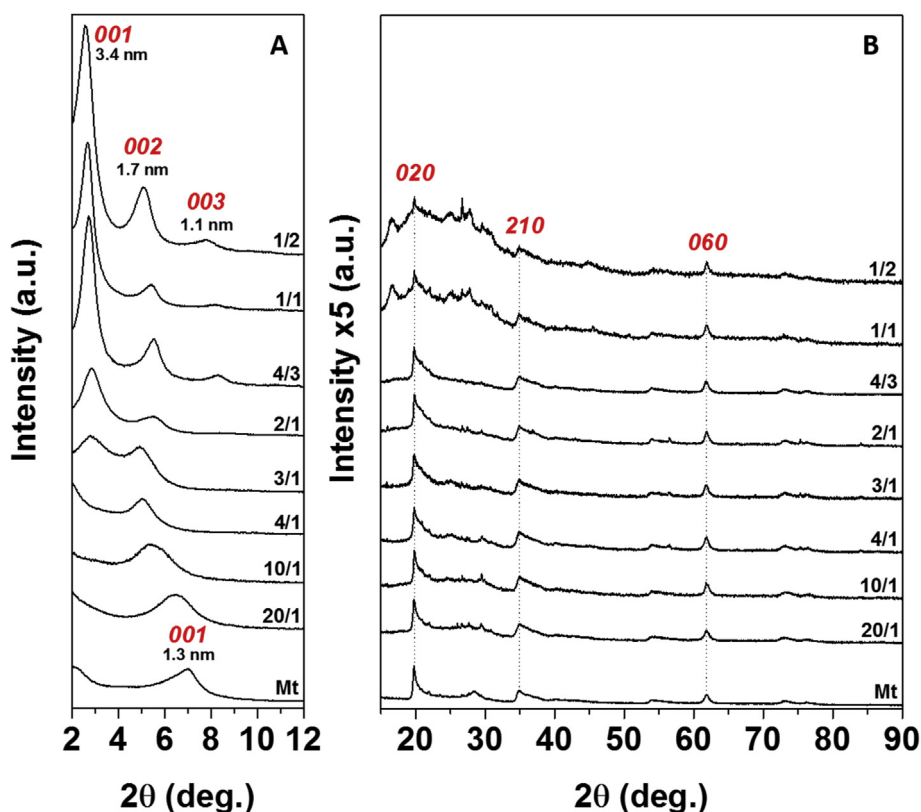


Figure 1. WAXD patterns (Cu-K α radiation) of the starting montmorillonite (Mt) and of Mt/BAC compounds, as prepared with the indicated wt/wt ratios. WAXD patterns are reported in the 2θ range between 2–12 (A) and 15–90 (B), respectively.

used as biocide for stone materials, known as Preventol® RI80 [4,8]) and corresponding desorption kinetics of the ammonium salt, have been studied. Wide-angle X-ray diffraction (WAXD) and thermogravimetric analysis (TGA) measurements were carried out to detect the structure and the stability of the intercalated compounds, respectively. The release of the ammonium salt from the montmorillonite was conducted in different desorption conditions and the overall results could be relevant for stone materials preservation.

2. Materials and methods

2.1. Materials

Layered sodium montmorillonite (Mt) was purchased by Laviosa Chimica Mineraria S.p.A. with Dellite® HPS as the trade name.

N-Alkyl-N-benzyl-N,N-dimethylammonium chloride (BAC) used for this work is an ammonium salt aqueous solution with the alkyl chain length variable between 12 and 16 carbon atoms. It was purchased by An.T.A.Res s.r.l., with Preventol® RI80 as the trade name.

Sodium chloride (NaCl, 99.5%) was purchased by Biochem Chemopharma. Hydrochloric acid (HCl, 37 mass%) was purchased by Sigma-Aldrich.

All chemicals were used without any purification.

2.2. Organoclays preparation

Mt was not dried prior to the organoclay preparation. Powders were prepared by mixing Mt and BAC solution in different ratios in a FRITSCH Pulverisette 7 ball miller. For each sample, 3 g of Mt were mixed with the ammonium salt BAC in 80 mL jar containing stainless steel balls. The jar was rotated at 500 rpm for 20 min at room temperature. Samples were washed with distilled water and then dried at 100 °C for 1 h.

2.3. Organoclays characterization

Wide-angle X-ray diffraction (WAXD) patterns with nickel filtered Cu-K α radiation were obtained in reflection, with an automatic Bruker D8 Advance diffractometer. Patterns were recorded in the diffraction angle range $2^\circ < 2\theta < 90^\circ$ and normalized respect to the 060 reflection, corresponding to $2\theta = 61.8^\circ$.

Thermogravimetric analyses (TGA) were performed with a TA Instruments Q500 thermal analysis system, under a flowing nitrogen atmosphere at scan rate of 10 °C/min from 20 to 800 °C.

Cation release kinetics for Mt/BAC intercalates were analyzed by UV-Vis spectroscopy on different aqueous solutions, after different desorption times (in the range 0.5–44 h). UV-Vis spectra were recorded by using a single cell Varian Cary 50 Probe UV-Vis spectrophotometer, in the wavelength range 190–300 nm. To avoid saturation of the intense UV band of BAC, low amounts of Mt/BAC intercalates were used in out release tests. In most tests, the amount of BAC in the Mt/BAC intercalates was $26,49 \pm 0,01$ mg and the release was studied toward 1000 mL of aqueous solution at room temperature, maintaining the system constantly stirred.

The used neutral solutions contain NaCl in molar ratio 2/1 with respect to the BAC. Cation release is not altered by increasing this molar ratio, at least up to 10/1. Acidic solutions at pH = 3 and pH = 1 were obtained by adding HCl to water.

3. Results and discussion

Wide Angle X-ray Diffraction (WAXD) patterns of the starting montmorillonite (Mt) and of Mt/BAC wt/wt compounds, as prepared according to the procedure described in the experimental section, are compared in Figure 1.

As already observed for compounding with different organic ammonium salts with single or double long alkyl chains [24], for low

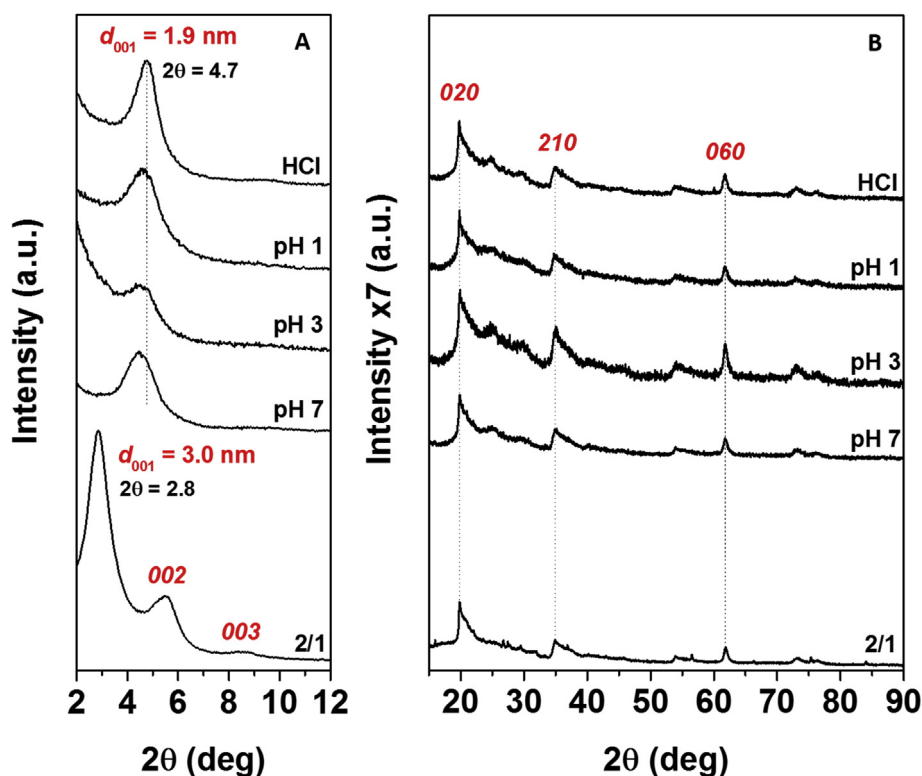


Figure 2. WAXD patterns (Cu-K α) of the Mt/BAC 2/1 wt/wt compound, as prepared and after 44 h of immersion in different aqueous solutions at pH = 7, 3, 1 and in 37 mass% aqueous HCl, respectively. WAXD patterns are reported in the 2θ range between 2–12 (A) and 15–90 (B), respectively.

ammonium content there is a progressive shift of the 001 reflection to lower diffraction angles, indicating a progressive increase of the interlayer spacing. For higher ammonium contents, additional 00 ℓ reflections appear (up to $\ell = 3$), which clearly indicate an increase of the interlayer clay spacing from 1.3 nm up to 3.4 nm, associated with an increase of structural order. It is worth adding that this Mt/BAC intercalate compound with $d = 3.4$ nm is a sort of limit ordered structure, because it remains nearly unaltered by increasing the Mt/BAC preparation mass ratio from 1/1 up to 1/2.

Reflections corresponding to the in-plane order of the starting Mt (e.g., those with Miller indexes 020, 210 and 060) remain essentially unaltered as consequence of formation of intercalates with BAC. This indicates that the used procedure does not reduce the in-plane structural order of the clay.

It is worth adding that WAXD patterns of Figure 1 do not show the intense reflection at $2\theta = 21.2^\circ$ ($d = 0.42$ nm), which clearly appear for many intercalate compounds with clays (as well as with graphene) [24, 25] of ammonium salts with two long hydrocarbon chains [18]. This indicates that in the used conditions, for ammonium salts with only one long hydrocarbon chain, the hexagonal rotator order is not achieved.

To study the possible release of the ammonium salt in aqueous media, Mt/BAC intercalate compounds have been treated by aqueous solutions at pH = 7 (neutral with NaCl), pH = 3 and pH = 1 (with HCl).

Just as an example, WAXD patterns of the Mt/BAC 2/1 wt/wt compound, before and after cation release in aqueous solutions at pH = 7, 3 and 1 are compared in Figure 2. It is clearly apparent that after these treatments, 003 and 002 reflections disappear while the 001 reflection is shifted to $2\theta \approx 4.7^\circ$, corresponding to $d_{001} \approx 1.9$ nm. Hence, already based on the WAXD patterns, it is apparent that the desorption of BAC is not complete, because the interlayer periodicity remains much higher than for the starting Mt (1.3 nm). It is worth adding that the intercalate structure with $d \approx 1.9$ nm is particularly stable. In fact, its pattern remains unaltered even after treatment by a concentrated strong acid, like 37 mass% aqueous HCl (upper WAXD pattern in Figure 2).

Relevant information on the Mt/BAC intercalate structures is also obtained by thermogravimetric analysis (TGA). A comparison between the TGA scans of the starting Mt and of the Mt/BAC 2/1 intercalate compound is shown, for instance, in Figure 3. As expected, the water content of the starting clay (≈ 10 mass%) is much higher than for the organically modified clay (not far from 2 mass%). A decrease of the water content for organo-modified montmorillonite with quaternary ammonium salts was already observed in previous studies [26, 27].

Moreover, the mass loss in the temperature range 100 °C–400 °C is negligible for Mt while is ≈ 35 mass% for the intercalate 2/1 compound, not far from the amount of BAC (33.3 mass%). TGA scans of the

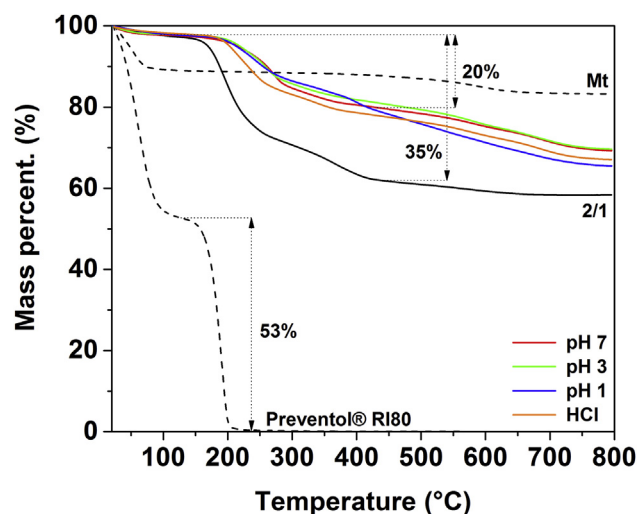


Figure 3. TGA scans of the Mt/BAC 2/1 wt/wt compound, as prepared and after 44 h of immersion in different aqueous solutions at pH = 7, 3, 1 and in 37 mass% aqueous HCl, respectively.

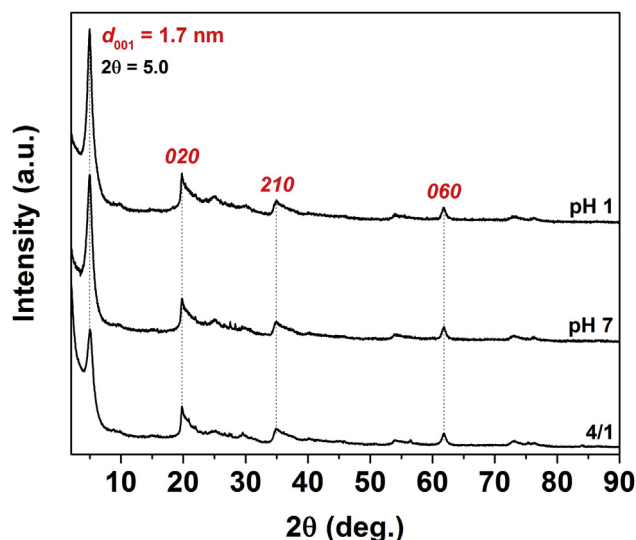


Figure 4. WAXD patterns (Cu-K α) of the Mt/BAC 4/1 wt/wt compound, as prepared and after 44 h of immersion in different aqueous solutions at pH = 7 and pH = 1, respectively.

intercalate 2/1 compounds, after treatments in completely different aqueous media (pH = 7, 3, 1 and 37 mass% aqueous HCl), are very similar to each other (intermediate scans in Figure 3). The mass loss in the temperature range 100 °C–400 °C indicates a BAC content close to 20 mass%. In good agreement with the WAXD patterns of Figure 2, these results indicate that the ordered Mt/BAC intercalate structure can easily lose less than 50% of the BAC content originally present, while a large fraction of BAC remains strongly bonded to the clay. All the considered BAC release procedures lead to a limit structure with $d_{001} \approx 1.9$ nm, whose residual BAC content is not removed by additional aqueous solution treatments.

The occurrence of a lower limit BAC content which allows BAC release in aqueous solutions is confirmed by the behavior of intercalate structures with a lower BAC content. It is worth noting that cleaning operations of stone materials are generally carried out by using clay poultices systems with a lower BAC content, typically till Mt/BAC 4/1 ratio [1]. WAXD patterns and TGA scans, analogous to those reported in Figures 2 and 3 for the Mt/BAC 2/1 compound, are reported in Figures 4 and 5, for the Mt/BAC 4/1 compound.

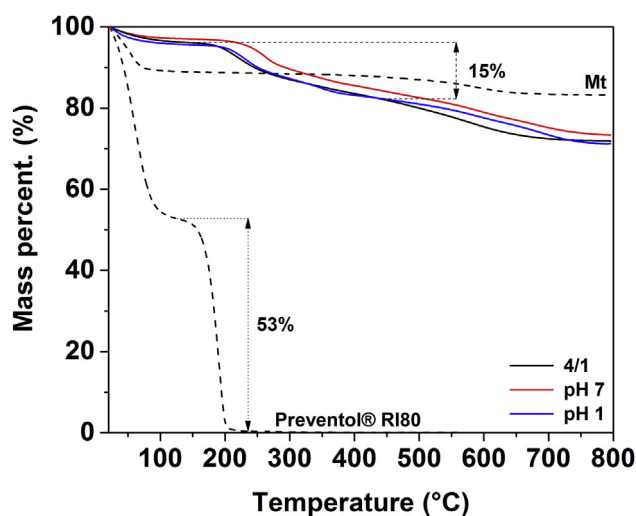


Figure 5. TGA scans of the Mt/BAC 4/1 wt/wt compound, as prepared and after 44 h of immersion in different aqueous solutions at pH = 7 and pH = 1, respectively.

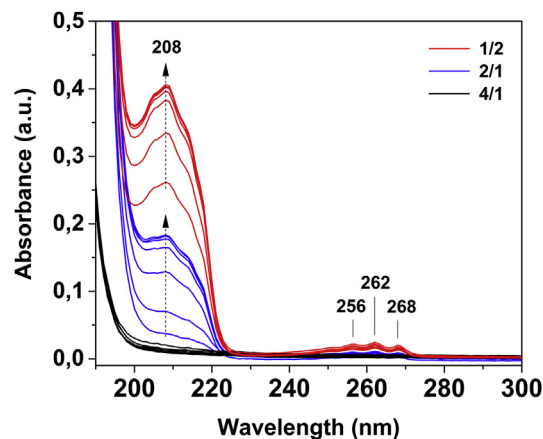


Figure 6. UV spectra of neutral saline water after different desorption times (1, 2, 4, 8, 16, 28 and 44 h) from 4/1, 2/1 and 1/2 Mt/BAC (wt/wt) intercalate compounds.

WAXD of Figure 4 show that treatments with aqueous solutions do not change the spacing as obtained by the intercalation procedure ($d \approx 1.7$ nm). TGA of Figure 5 confirm that in this case the used treatments in aqueous solutions do not lead to BAC release. WAXD and TGA data suggest the occurrence of thermodynamic stability for the Mt/BAC 4/1 intercalate structure, in acidic conditions.

Kinetics of release of BAC in pH 7 aqueous solutions have been studied by collection, after different desorption times, of UV spectra of the extracting aqueous solutions. UV spectra of neutral saline water after different desorption times (1, 2, 4, 8, 16, 28 and 44 h) from 4/1, 2/1 and 1/2 Mt/BAC (wt/wt) intercalate compounds are shown in Figure 6.

A comparison of kinetic cation desorption curves, for Mt/BAC 4/1, 2/1 and 1/2 compounds, as obtained by the UV spectra of Figure 6 and evaluated by considering the UV peak at 208 nm, are shown in Figure 7, by reporting the BAC mass percent loss versus the soaking time.

Kinetic cation desorption curves, as obtained by the UV spectra of Figure 6, were evaluated by considering the UV peak at 208 nm and are compared in Figure 7, by reporting the mass percent loss versus the soaking time. It is apparent that the BAC loss is negligible for 4/1 intercalate, whereas for 2/1 and 1/2 intercalates is 35% and 75%, respectively. Moreover, as for these last two intercalate compounds, the maximum BAC loss has been reached after nearly 13 h (circle and square symbols in Figure 7).

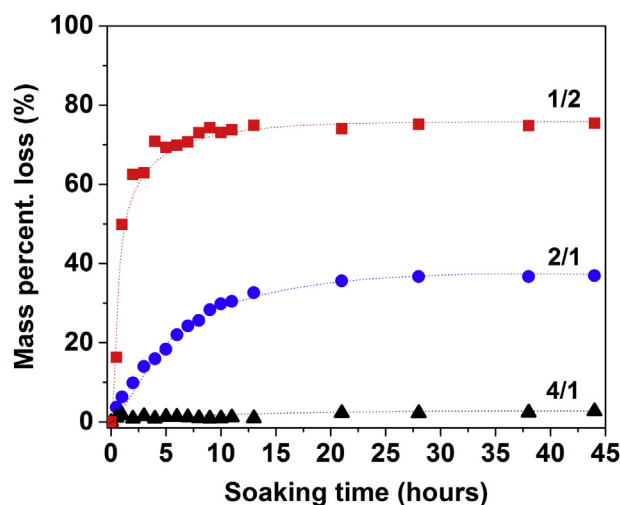


Figure 7. Kinetics of BAC cation release from 4/1, 2/1 and 1/2 Mt/BAC (wt/wt) intercalate compounds in neutral saline water, as obtained by UV spectra of Figure 6.

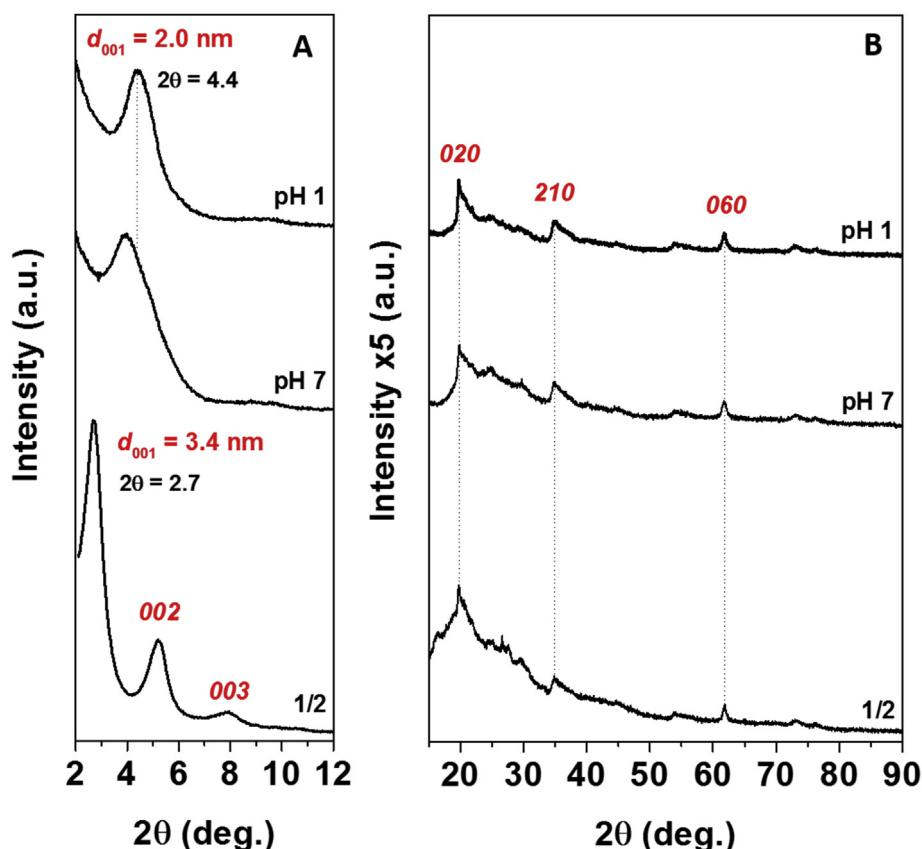


Figure 8. WAXD patterns (Cu-K α) of the Mt/BAC 1/2 wt/wt compound, as prepared and after 44 h of immersion in different aqueous solutions at pH = 7 and pH = 1, respectively. WAXD patterns are reported in the 2θ range between 2–12 (A) and 15–90 (B), respectively.

For sake of completeness, WAXD patterns for the Mt/BAC 1/2 compound, before and after cation release in aqueous pH 7 and pH 1 solutions, are reported in Figures 8. It is apparent the formation of the limit structure with $d_{001} \approx 2.0$ nm, containing a relative amount of BAC close to 22%, similar to those obtained for Mt/BAC 2/1 intercalate compound, shown in Figure 2.

The occurrence of a lower limit clay-organic cation intercalate structure, for which the cation substitution is difficult, was already described in Figure 9 of Cipolletti and co-workers [18], for a different clay-organic cation intercalate, by extracting with ethyl acetate.

The overall results indicate that Mt/BAC 4/1 compound, typically used for cleaning operation of stone materials [1], is particularly stable also in strong acidic conditions and could be used for long-term biostatic applications in the field of preservation of cultural heritage.

4. Conclusions

Compounds of montmorillonite, a smectite mineral clay being an expanding phyllosilicate, with N-Alkyl-N-benzyl-N,N-dimethylammonium chloride (shortly known as benzalkonium chloride, BAC), i.e. the ammonium salt mainly used for stone material disinfection procedures, have been prepared and characterized by different techniques.

By increasing the BAC content in the compounds, the formation of intercalate compounds is clearly proved by the observed increase of the interlayer distance from 1.3 nm up to 3.4 nm. The limit intercalate structure with maximum spacing value ($d = 3.4$ nm) exhibits increase of structural order, as indicated by the sharpening of the 001 reflection as well as by the appearance of 002 and 003 reflections.

The prepared intercalate compounds have been studied as for their possible cation release in suitable aqueous media. In particular, a saline solution at pH = 7 (with NaCl in molar ratio 2/1 with respect to the BAC)

as well as acidic solutions based on HCl (pH = 3, pH = 1, and HCl 37 mass %) have been used as extracting media. The reported results indicate that cation release from Mt/BAC intercalate compounds with interlayer spacing lower than $d_{001} \approx 1.9$ nm is negligible while, from Mt/BAC intercalate compounds with higher interlayer spacing, cation release occurs only till the spacing reduces down to $d \approx 1.9$ –2.0 nm.

Hence, this study indicates the occurrence for the Mt/BAC system of an upper limit intercalate structure with $d_{001} \approx 3.4$ nm as well as lower limit intercalate structure with $d_{001} \approx 1.9$ nm.

The reported cation release studies indicate that the Mt/BAC intercalate structure with $d_{001} \approx 1.9$ nm is possibly suitable for biostatic applications, i.e. for long-term applications requiring the presence of a non-leachable active agent. Mt/BAC intercalate structure with $d_{001} \approx 3.4$ nm appears, instead, to be suitable for applications requiring both fast antimicrobial release and long-term biostatic effects.

Declarations

Author contribution statement

Chiara Gallo: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Paola Rizzo, Gaetano Guerra: Conceived and designed the experiments; Analyzed and interpreted the data; Wrote the paper.

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Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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