Original Article

Zn–Al-based layered double hydroxides (LDH) active structures for dental restorative materials

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\textbf{A B S T R A C T}

The development of smart dental materials able to react to its environment and release remineralizing ions is attractive point of research. The phosphate interaction with Zn–Al layered double hydroxide was evaluated by the reconstruction method, at 300 °C and 600 °C. In a general way, thermal stable zinc-phosphate compounds are formed with the increase of the phosphate concentration. To assess the potential to act as bioactive dental restorative materials, phosphate-loaded samples were incorporated on photopolymerizable dental resin (Fill Magic, Coltene) at 2.5\% and 4\% (m/m) evaluating the phosphate release at artificial saliva medium. After 58 days, the materials showed a useful continuous release of phosphate which in conjunct with other mineralizing elements, could contribute to remineralization of dental tissues and protection against caries and other dental health problems.

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1. Introduction

Dental caries is one of the most common clinical diseases in oral health worldwide. Depending on the extent of tooth damage, different approaches can be used to restore the damaged tissue. The most commonly used restorative materials are amalgam, dental porcelain (dental ceramic), gold, glass ionomer, and resin-based composites [1].

Resin composites are one of the important materials developed that can be used as restorative material and keep the appearance and function of the biological tissues [2]. Besides the restorative function, these materials are used on cavity liners and provisional restorations [3]. This composites are formed by three phases, the first one is the resin composed of polymerizable monomers, which after exposure to UV or visible light create a highly cross-linked polymer; the second phase is the filler, important to enhancement of mechanical properties, radiopacity and alteration of thermal expansion behavior; the last phase is the silane coupling agent, which acts as a binder between the coupling polymerizable moieties and the particle surface [4].

The resin composites restorations interact with the collagen fibrils meshwork of the dentin matrix, reached from dental procedures, forming the so-called hybrid layer [5]. However, this hybrid layer may be degraded over time, leading to the failure, which turn in microgaps that are readily
penetrated by pathogens, allowing the development of secondary cavities and dental plaque biofilm [6–8]. The main aging mechanisms involved in the degradation of resin-bonded interfaces are (a) hydrolysis and leaching of the resin composite that has infiltrated the demineralized dentin matrix, and (b) degradation of the collagen matrix of the hybrid layer [5,9]. On the other hand, the collagen matrix of pathogen-affected dentin is physiologically remineralizable [10]. Phosphate is an important ion in the process of tissue mineralization, which deposition in conjunct with other elements, leads to remineralization of the resin-dentin bond [11]. Therefore, the incorporation of a phosphate releasing material as a component of dental resin is an important technique that can be used to avoid dental health problems [12].

Layered double hydroxides (LDH) known as “anionic clays” due to structural resemblance with the cationic clays has the general formula [M\textsuperscript{2+}_1−xM\textsuperscript{3+}_x(OH)\textsubscript{2}]\textsuperscript{x+}[A\textsuperscript{−}_n]m−⋅yH\textsubscript{2}O, where M\textsuperscript{2+} is a divalent cation such as Mg\textsuperscript{2+}, Ni\textsuperscript{2+}, Zn\textsuperscript{2+}, Cu\textsuperscript{2+}, or Co\textsuperscript{2+}; M\textsuperscript{3+} is a trivalent metallic cation such as Al\textsuperscript{3+}, Cr\textsuperscript{3+}, Fe\textsuperscript{3+}, or Ga\textsuperscript{3+}; A\textsuperscript{−} is a charge-balancing anion; and x is the molar ratio M\textsuperscript{2+}/(M\textsuperscript{2+}+M\textsuperscript{3+}), ranging from 0.1 to 0.5 [13]. LDH exhibit high anionic exchange capacity, with affinity for phosphate and other multivalent anions [14]. Thermal treatment confers important physicochemical properties to LDH [15]: (a) a “memory effect” of the hydroxide lattice, which allows different anionic species to be incorporated into the LDH interlamellar spaces; and (b) higher surface area, which increases anion adsorption [13,16]. LDH have been used in different areas, such as the reinforcement of polymers in order to improve their mechanical properties or thermal stability [17–19], reduction of corrosion in steel materials [20], and reinforcement and protection against corrosion of concrete [21]. Additionally, LDH anion exchange property allows using this material class for ions slow/controlled release. In fact, the use of LDH as matrices for phosphate release was studied at different fields [22,23]. However, the effects of LDH as fillers in resin composites for phosphate release have received little attention [24].

Considering that zinc has antimicrobial properties, ability to inhibit the crystallization (acting as anti-calcus agent), ability to increase demineralization resistance [25–28] and given the potential of LDH to act matrix for phosphate release [29] here we demonstrate the potential of LDH, where M\textsuperscript{2+} is zinc ([Zn–Al]-LDH), for loading with high amounts of phosphate anions by means of the memory effect for eventual application of these materials on dental field, as fillers of dental polymer resins with potential for slow phosphate release.

2. Materials and methods

2.1. Materials

Zinc chloride (ZnCl\textsubscript{2}), aluminum chloride hexahydrate (AlCl\textsubscript{3}·6H\textsubscript{2}O), sodium hydroxide (NaOH), sodium carbonate (Na\textsubscript{2}CO\textsubscript{3}), and potassium phosphate monobasic (KH\textsubscript{2}PO\textsubscript{4}) were purchased from Synth (Brazil). All reagents were used as received. Decarboxylated deionized water (\(\rho = 18.2\) \(\mu\)Ω·cm) obtained from a Milli-Q system (Barnstead Nanopure Diamond, Thermo Fisher Scientific Inc., Dubuque, IA, USA) was used in all the experimental procedures.

2.2. Synthesis of [Zn–Al]-LDH

[Zn–Al]-LDH with M\textsuperscript{2+}/(M\textsuperscript{2+}+M\textsuperscript{3+}) molar ratio (\(x\)) of 0.25 was synthesized by the co-precipitation method, with pH control. The synthesis was carried out in an all-glass reactor (capacity of 300 mL) attached to a water circulating system in order to accurately control the temperature at 25.0 °C (±0.5 °C). In a typical reaction, a mixed chloride solution (0.5 mol L\textsuperscript{−1}) containing Zn\textsuperscript{2+} and Al\textsuperscript{3+} cations was gradually injected at a rate of 0.5 mL min\textsuperscript{−1} into the reactor containing sodium hydroxide solution (1.0 mol L\textsuperscript{−1}), under vigorous stirring. At the same time, a solution of Na\textsubscript{2}CO\textsubscript{3} (2 mol L\textsuperscript{−1}) was injected at a rate of 0.025 mL min\textsuperscript{−1} for pH control. Once injection was complete, stirring was kept for a further hour, for precipitate aging. Subsequently, the mixture was centrifuged at 11,200 \(\times\) g for 10 min to remove the excess of NaCl and chloride ions. The precipitate was then purified using three washing-centrifugation cycles with 1:1 water-ethanol solution and was resuspended in water for storage in a freezer. Finally, the material was lyophilized under a vacuum of 1.33 × 10\textsuperscript{−4} bar (Supermodulyo Freeze Dryer, Thermo Fisher Scientific Inc., Kansas City, MO, USA), yielding a white powder.

2.3. Phosphate adsorption by structural reconstruction

Phosphate was loaded into the as-synthesized [Zn–Al]-LDH by means of structural reconstruction. Thermal treatment provides important physicochemical properties to LDH: (i) a “memory effect” of the hydroxide lattice, which allows different anionic species to be incorporated into the LDH interlamellar space, (ii) higher surface area, which increases adsorption of anions, and (iii) elimination of the interlayer carbonate (CO\textsubscript{3}\textsuperscript{2−}), which strongly hinders anion exchange processes in LDH [30]. The synthesis product was calcined for 4 h at two different temperatures: 300 °C ([Zn–Al]\textsubscript{300}) and 600 °C ([Zn–Al]\textsubscript{600}). Portions of 500 mg of the calcined samples were added to 250 mL of KH\textsubscript{2}PO\textsubscript{4} solution, previously equilibrated at 75 °C and adjusted to pH 7.0 using 0.1 M NaOH. The mixture was kept under vigorous stirring for 24 h, followed by centrifugation at 11,200 \(\times\) g for 10 min. The supernatant was used for quantification of the phosphate content at equilibrium, and the precipitate was lyophilized prior to solid-state characterizations. Different molar ratios of PO\textsubscript{4}\textsuperscript{3−} were studied by varying the PO\textsubscript{4}\textsuperscript{3−} concentration from 0.83 mM (1.0:125 Al\textsuperscript{3+}/PO\textsubscript{4}\textsuperscript{3−} molar ratio) to 33.10 mM (1:5 Al\textsuperscript{3+}/PO\textsubscript{4}\textsuperscript{3−} molar ratio).

The concentration of phosphorus was determined according to a procedure reported elsewhere [31]: 5 mL of supernatant was mixed with 2 mL of ascorbic acid solution (0.4 M), 0.2 mL of citric acid solution (0.03 M), and 2 mL of a reagent consisting of sulfurous acid solution (4.7 M), 5.5 mL ammonium molybdate (0.08 M), and 0.6 mL of antimony and potassium tartrate (0.05 M). This mixture was then allowed to react for 15 min in a water bath at 50 °C, forming a phosphoantimonylmolybdenum blue complex. The concentration of the product was determined by UV–vis spectrophotometry, using a PerkinElmer Lambda spectrophotometer operated at a wavelength of 880 nm. All the quantifications were done twice.
2.4. Characterizations

Powder X-ray diffraction (PXRD) measurements were performed using a Shimadzu XRD 6000 diffractometer, with Ni-filtered Cu Kα radiation (λ = 1.5405 Å). The diffractograms were acquired in the 2θ range 3–80°, at a scan speed of 2° min⁻¹. Fourier transform infrared (FTIR) analyses were performed using a Bruker spectrometer, with spectral resolution of 2 cm⁻¹. Scanning electron microscopy (SEM) analyses employed a JEOL microscope operated at 15 kV. Thermal degradation studies were performed using a TGA Q500 thermogravimetric analyzer (TA Instruments, New Castle, DE), under a flow of nitrogen at 60 mL min⁻¹, with heating at 10 °C min⁻¹ from 25 to 800 °C.

2.5. Incorporation of the LDH materials in dental resin and evaluation of phosphate release

The calcined materials ([Zn–Al]₀,300 and [Zn–Al]₀,600) loaded with 33.1 mM PO₄³⁻ were incorporated in commercial dental resin (Fill Magic, Coltene) at ratios of 2.5 and 4% (m/m). After complete and homogeneous incorporation of the samples, the composites were submitted to UV radiation (40.3 W m⁻²) for 10 min for photo-curing. Artificial saliva with adapted composition from Ken-ichiro [32], containing KHCO₃ (15.01 g L⁻¹), NaCl (5.85 g L⁻¹), MgCl₂ (0.14 g L⁻¹), citric acid (0.002 g L⁻¹), CaCl₂ (0.16 g L⁻¹), and sodium carboxymethylcellulose (5 g L⁻¹) was used as release media for the dental resin. Resin specimens (2.8 cm × 1.5 cm × 0.225 cm) were placed in contact with 50 mL of artificial saliva under constant stirring (150 rpm) at 28 °C. The concentration of phosphate was analyzed by the same method (at section "Phosphate adsorption by structural reconstruction") after incubation for 0, 6, 14, 20, 27, 34, 41 and 58 days.

3. Results and discussion

3.1. Synthesis of [Zn–Al]-LDH

[Zn–Al]-LDH was synthesized by the co-precipitation method with pH control. Fig. 1 shows a scanning electron micrograph of the pristine LDH. The as-synthesized material presented an irregular nanostructure and layers without the presence of hexagonal structures, as well as some stacked nanoparticle flakes [33]. The PXRD patterns of the as-synthesized [Zn–Al]-LDH presented sharp and intense peak lines, with rhombohedral 3R symmetry, as expected for LDH material (JCPDS: 48-1023) [34]. The d-spacing calculated using Bragg’s law was 0.78 nm, in agreement with the presence of chloride ions in the interlayer space (Fig. 2). The pristine [Zn–Al]-LDH was calcined at 300 °C (Fig. 2A1) and 600 °C (Fig. 2B3). At 300 °C, the typical LDH structure was replaced by the metal oxide phase corresponding to ZnO (JCPDS: 36-1451). When the sample was exposed to pure water, the original LDH structure was restored, confirming installation of the so-called “memory effect”, despite the presence of some residual ZnO phase from the calcination step. On the other hand, calcination at 600 °C resulted in formation of not only ZnO, but also a spinel phase (ZnAl₂O₄) (JCPDS: 05-0669), and when placed in contact with water, the sample was not reconstructed. In other words, the calcination temperature was so high that layers of LDH could not be restored. According to Cavani et al. [30], structural reconstruction is only possible when the heating does not cause modification of the crystal morphology or exfoliation of the layered structure. The lamellar microstructure was retained after thermal decomposition of LDH for 300 °C.

![Fig. 2 – PXRD patterns of pristine [Zn–Al]-LDH (A-0 and B-0); the material calcined at 300 °C ([Zn–Al]₀,300) (A-1); the material calcined at 600 °C ([Zn–Al]₀,600) (B-3); [Zn–Al]₀,300 reconstructed in water (A-2); and [Zn–Al]₀,600 reconstructed in water (B-4). ⊗: ZnAl₂O₄; O: ZnO.](image)
However, the calcination at 600 ºC lead to the formation of spinel phase, a very stable phase, causing microstructural changes that not allowed the installation of the memory effect.

### 3.2. Phosphate interaction with [Zn–Al]-LDH

Although the memory effect was not observed for [Zn–Al]c≤600, the interactions with phosphate were investigated for [Zn–Al]-LDH calcined at both temperatures. The crystalline structures of the samples were assessed by PXRD (Fig. 3). At lower phosphate concentrations, [Zn–Al]c≤300 keep the basic LDH crystalline structure and ZnO phase after the thermal treatment. In this case, the interaction of phosphate with [Zn–Al]-LDH was probably due to electrostatic attraction between the external layers of the LDH and the negative ions of PO₄³⁻ [34]. When PO₄³⁻ concentration was increased, the LDH phase disappeared and was replaced by ZnO and Zn(OH)₂ (JCPDS: 74-0094) phases. At 33.10 mM, crystalline zinc-phosphate phases were identified. In this case, ZnO was the precursor material for phosphate interaction and the presence of OH⁻ groups was identified (Fig. 4A). The PO₄³⁻ ions could exchange with OH⁻ groups and complex with Zn²⁺ on the surface by outer-sphere complexation or electrostatic attraction [35], allowing the formation of zinc-phosphate compounds.

In a similar way, when [Zn–Al]-LDH calcined at 600 ºC was exposed to solutions containing different concentrations of phosphate, the predominant crystalline phases were the spinel component (ZnAl₂O₄) and ZnO. At a phosphate concentration of 33.10 mM, the Zn₃(PO₄)₂ phase (JCPDS: 29-1390) was dominant. However, even at lower starting PO₄³⁻ concentrations, the phosphate interaction with the materials was evidenced by FTIR (Fig. 4B) and phosphate quantification analyses (Table 1). According to Lv et al. [36], phosphate causes dissolution of ZnO particles. Since ZnO was present with phosphate, a mixture of crystalline and amorphous phases of ZnO and zinc phosphate was obtained. Phosphate

![Fig. 3 - Powder X-ray diffraction (PXRD) patterns for phosphate adsorption by structural reconstruction on (A) [Zn–Al]c≤300 and (B) [Zn–Al]c≤600. (O): pristine [Zn–Al]-LDH; (1): 0.83 mM PO₄³⁻; (2): 3.31 mM PO₄³⁻; (3): 16.55 mM PO₄³⁻; (4): 33.10 mM PO₄³⁻. (A): ZnO; (B): ZnPO₄; (C): ZnAl₂O₄; (C): Zn₃(PO₄)₂.](image)

![Table 1 - Phosphate concentrations after interaction with [Zn–Al]-LDH calcined at 300 ºC and 600 ºC.](table)

![Fig. 4 - FTIR spectra for phosphate adsorption on (A) [Zn–Al]c≤300 and (B) [Zn–Al]c≤600. (O): pristine [Zn–Al]-LDH; (1): 0.83 mM PO₄³⁻; (2): 3.31 mM PO₄³⁻; (3): 16.55 mM PO₄³⁻; (4): 33.10 mM PO₄³⁻.](image)
Fig. 5 – Thermogravimetric (TG) and differential thermogravimetric (DTG) curves for samples [Zn–Al]_{c300} and [Zn–Al]_{c600} loaded with PO_4^{3−} by structural reconstruction using different initial PO_4^{3−} concentrations: (A) 0.83 mM - [Zn–Al]_{c600}; (B) 3.31 mM - [Zn–Al]_{c600}; (C) 16.55 mM - [Zn–Al]_{c600}; (D) 33.10 mM - [Zn–Al]_{c600}; (E) 0.83 mM - [Zn–Al]_{c300}; (F) 3.31 mM - [Zn–Al]_{c300}; (G) 16.55 mM - [Zn–Al]_{c300}; (H) 33.10 mM - [Zn–Al]_{c300}. 
can react by adsorption and precipitation on solid phase surfaces, leading to a complex mixture of components and structural transformation of ZnO to zinc phosphate. In addition, the formation of amorphous zinc phosphate phases can occur due to complexation between dissolved PO$_4^{3-}$ and Zn$^{2+}$.

These results can be compared to our previous findings for other LDH structures, showing that at higher PO$_4^{3-}$ concentrations Ca-Al-based LDH converted to hydroxyapatite, and Mg-Al-based LDH converted to boehmite [23,37].

Fig. 4A shows the FTIR spectra for the samples, where the interaction with phosphate was confirmed by the presence of the band at 1040 cm$^{-1}$ attributed to the $\nu_3$ (P-O) stretching vibration mode [38]. This was an important indication of the phosphate interaction with [Zn–Al]$_{c300}$, even though the XRD analysis did not reveal any crystalline phosphate phases. Furthermore, the phosphate contents of the samples (Table 1) increased at higher initial phosphate concentrations. Regardless of the mechanism of interaction of phosphate with calcined [Zn–Al]-LDH, at high phosphate concentrations [Zn–Al]$_{c600}$ was able to incorporate higher amounts of PO$_4^{3-}$, while better results were obtained for [Zn–Al]$_{c300}$ at low phosphate concentrations (Table 1). These results are in agreement with the study of Cheng et al. [16], who found that material calcined at 300 °C presented better phosphate adsorption at an initial PO$_4^{3-}$ concentration of 20 mg L$^{-1}$, due to the greater specific surface area of the sample.

The thermal stabilities and compositions of [Zn–Al]-LDH calcined at 300 °C and 600 °C and loaded with PO$_4^{3-}$ were investigated using TG/DTG (Fig. 5). The main phases for 0.83-[Zn–Al]$_{c600}$ were zinc oxides (ZnO and ZnAl$_2$O$_4$), resulting in no significant mass loss. Although the XRD patterns for the materials produced with intermediate phosphate concentrations showed the presence of the same zinc oxides, changes were observed in the mass loss profiles. The main mass losses occurred at around 75 °C, 300 °C, 500 °C, and 600 °C, related to the losses of surface water, loosely bound water molecules, and amorphous phosphate compounds leading to the formation of pure ZnO and ZnAl$_2$O$_4$, respectively [39]. At 33.10 mM of phosphate, only two small peaks were present, at 208 °C and 535 °C, attributed to the loss of adsorbed water and phosphate anions, respectively, culminating in oxide formation.

For [Zn–Al]$_{c300}$, the thermal profiles loaded with phosphate concentrations up to 16.55 mM were typical of LDH, with removal of (i) physically adsorbed water at temperatures below 100 °C, (ii) interlayer water up to 200 °C, (iii) hydroxyl groups from the layers as water vapor at around 300 °C, and (iv) anions, with consequent oxide formation, above 400 °C [40]. However, at 33.10 mM of phosphate, the peak related to removal of PO$_4^{3-}$ was no longer observed, indicating thermal stability of the compound formed (Zn$_3$(PO$_4$)$_2$).

3.3. Phosphate release from modified dental resin.

According to Ferracane [3], the development of “smart” materials (which reacts to its environment to release remineralizing ions) is very attractive for dental restorations. The remineralization may be promoted by the slow release of phosphate ions, followed by the precipitation of new phases, like calcium-phosphate mineral.

The kinetics of phosphate release from the dental resins containing PO$_4^{3-}$–loaded [Zn–Al]-LDH$_c$ was evaluated by exposing the materials to artificial saliva. The results (Fig. 6) showed that all the samples could release phosphate, although a substantially higher concentration of phosphate in artificial saliva was obtained using the resin containing 2.5% 33.10-[Zn–Al]$_{c300}$. Even after 58 days, the materials evidence an increased capacity for phosphate release, attesting the potential of these materials to act as slow phosphate release source, specially the system 2.5% 33.10-[Zn–Al]$_{c300}$. Several studies demonstrated the tissue remineralization occurring around 21–30 days [41,42], which demonstrate the potential of 2.5% 33.10-[Zn–Al]$_{c300}$ to be useful at dental reparation.

CPP-ACP (casein phosphopeptide – amorphous calcium phosphate) is one bioactive agent able to release elements that enhance remineralization of enamel and dentin [43]. Zalizniak et al. [44] observed that phosphate ion release in water was not detectable, however at citric acid at the end of two days 17.6 nmol/mm$^2$ of phosphate was released. In contrast, 2.5% 33.10-[Zn–Al]$_{c300}$ showed potential to release phosphate in an extended way, in an artificial saliva medium. Besides that, Srivivasan et al. [45] verified that CPP–ACP and fluoride combination showed higher remineralization potential than only CPP–ACP. That demonstrates the need of supplementary elements, such as Ca and F, to provide full remineralization of enamel, which can be obtained from other sources like dentifrices and chewing gums [24,46]. Caries are caused by the bacterial production of organic acids that dissolve the dental minerals, and it has been found that the mineral formed during remineralization is more resistant to acid than the original dental enamel [47]. Therefore, the dental resin containing 2.5% 33.10-[Zn–Al]$_{c300}$ acted as source of phosphorus, which is an important element for mineralization and the avoidance of future dental problems.

Restoratives materials that release Ca, PO$_4$, or F ions are relatively weak and cannot be used in large stress-bearing restorations [48]. Supporting Table 1 (Supporting Information) summarizes the results for the three-point flexural test applied to these four nanocomposites and the pris-
tine dental resin. The values for the resin containing 2.5% 33.10-[Zn–Al]_{c=300} were similar to those for the pristine resin, while decreased for the other materials, mainly because high inorganic loadings in brittle polymers are expected to have negative impacts on their mechanical characteristics, due to the heterogeneous distribution of the particles at the polymer matrix [49,50]. In this sense, 2.5% 33.10-[Zn–Al]_{c=300} was able to release phosphate and keep the mechanical properties of dental resin, indicating the potential of LDH to act as matrices for remineralization ions without losses at the mechanical properties.

4. Conclusions

The phosphate adsorption by [Zn–Al]-LDH was evaluated by the reconstruction method at 300 °C and 600 °C. The samples calcinated at 600 °C suffered change at the microstructure and the memory effect was not observed. Therefore, the interaction with phosphate was mainly with the external surface of the materials. However, the reconstruction was effective for the samples calcinated at 300 °C and the interaction with phosphate leads to the formation of new crystalline phases. The incorporation of these materials at dental resin and evaluation of the phosphate release showed that the sample 2.5% 33.10-[Zn–Al]_{c=300} was able to release significant amounts of phosphate into an artificial saliva medium, indicating that modified dental resin could assist in dental remineralization and provide protection against dental problems.

Conflicts of interest

The authors declare no conflicts of interest.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jmrt.2018.10.001.

References

[20] Aliakbahi E, Ghasemi E, Mahdavian M, Ramezanizadeh B, Farashi S. Fabrication and characterization of PO43-


