EFFECT OF CALCIUM CHLORIDE ON THE PH VALUES OF SEVERAL FORMULATIONS OF CALCIUM HYDROXIDE MIXED WITH CHLORHEXIDINE DIGLUCONATE

ABSTRACT

PURPOSE: This study evaluated the effect of the addition of 5% calcium chlorite (CaCl2) on pH values in calcium hydroxide pastes (CH), with or without 2% chlorhexidine digluconate (CHX) used as vehicle, in several periods analysis. MATERIAL AND METHODS: Polyethylene tubes were filled with CH mixed with water (G1), 2% CHX solution (G2) or gel (G3), or CHX solution or gel with 5% CaCl2 (G4 and G5, respectively). All tubes were individually immersed in distilled water. After 12, 24 hours, 7, 14 and 28 days, pH value was evaluated directly in water which the tubes were stored. Data were submitted to ANOVA and Tukey tests (α=0.05). RESULTS: In 24 hs and 14 days, pH values were similar to all groups. In 12 hs, the G1 presented lower pH value than other groups except to G4 (p < 0.05), and G4 presented lower pH value than G5 (p < 0.05). In 7 days, G1 presented lower pH value than G4 and G5 (p < 0.05). In 28 days, G1 and G5 presented lower pH values than G2 and G4 (p < 0.05) and among other groups there are no statistical differences (p > 0.05). CONCLUSIONS: The pH values increased in long-term analysis to all CH pastes. The association of 5% calcium chloride with 2% CHX solution as vehicle of CH paste provided a pH value increase in relation to CH mixed with distilled water. The CHX gel interfered negatively on pH value in comparison to CHX solution when mixed with CaCl2.

KEYWORDS

Calcium. Chlorhexidine. Hydrogen. pH.
INTRODUCTION

Calcium hydroxide (CH) is recommended as intracanal dressing, because of its adequate biologic properties. To endodontic clinical use, several vehicles have been proposed to mixed with CH, which provide different effects on concentration of hydrogen ions (pH) and calcium release values.

The efficacy of CH paste as an intracanal medication is due to its ionic effect based on chemical dissociation into calcium and hydroxyl ions in aqueous solution, which promotes alkalization of the medium. The high concentration of hydrogen ions (pH) induces hard tissue formation through mineralization and is also responsible for its bactericidal effect.

The chlorhexidine digluconate (CHX) is a molecule positively ion charged that interacts with phospholipids and lipopolysaccharides on the cell membrane of bacteria and has a wide use as endodontic irrigation solution. Currently have been suggested that CHX could be mixed with CH to improve antimicrobial efficacy against CH-resistant microorganisms.

On the other hand, the combination of CHX and NaOCl has been advocated to enhance their antimicrobial properties. However, when NaOCl is mixed with CHX is produced an orange-brown precipitate that stains the walls of the pulp chamber and contains parachloroaniline (PCA). A possible alternative is the addition of calcium chloride (CaCl₂) to the CHX, because the presence of chlorine could provide a synergistic effect of CHX, without that occur the discoloration of the dental structure.

CaCl₂ at various concentrations have been added to MTA sealer to reduce its setting. The addition of 10% CaCl₂ to MTA produces reduction of the initial setting time of cements by 50% and by 35.5% to 68.5% in the final setting time. Despite these considerations, there are no investigations about the effects of addition of CaCl₂ to CHX when used as vehicle in calcium hydroxide pastes, mainly on its physical and chemical properties.

The objective this study was to evaluate the effect of the addition of 5% CaCl₂ solution on pH values of the calcium hydroxide mixed 2% chlorhexide digluconate paste, in solution or gel forms, in the periods of 12 and 24 h, 7, 14 and 28 days. The null hypothesis was that there were no statistically differences among different groups, independently of the period analyzed.

MATERIAL AND METHODS

In this study, CH (Biodinâmica, Ibiporã, PR, BR) was manipulated with different vehicles and samples were divided into 5 groups, as follows: Group 1: CH + distilled water alone (DW, control group); Group 2: CH + 2% CHX solution alone (Biodinâmica, Ibiporã, PR, BR); Group 3 CH +
2% CHX gel alone (Biodinâmica, Ibiporã, PR, BR); Group 4: CH + 2% CHX solution (Biodinâmica, Ibiporã, PR, BR) and 5% CaCl₂ solution (Merck, Darmstadt, GER); Group 5: CH + 2% CHX gel (Biodinâmica, Ibiporã, PR, BR) and 5% CaCl₂ solution (Merck, Darmstadt, GER). The CHX/CaCl₂ ratios was determined by volume (50%:50%), and the powder/vehicle ratio was the same for all groups (1g powder to 1 mL vehicle). Fifty polyethylene tubes measuring 10 mm in length and 1.5 mm in internal diameter were filled with the mixtures to be evaluated.

For pH analysis, 10 specimens were prepared from each material studied. Immediately after manipulating the materials, the tubes were filled and weighed to check the standardization of the amount of sealer in each specimen (+ 0.002 g) and placed in polypropylene flasks (Injeplast, São Paulo, SP, BR) containing 10 mL of distilled water. All specimens were kept at 37°C (Farmen, São Paulo, SP, BR).

After 12, 24, 7, 14 and 28 days, the distilled water was assessed for pH values. Previous to the immersion of specimens, the pH of distilled water was verified, attesting pH 6.9. The specimens were maintained in same distilled water during all study.

The pH measurements were conducted with a pH meter (model DM22, Digimed, São Paulo, SP, BR), as described Vivan et al.¹⁷ All data were compared by ANOVA and Tukey test (p = 0.05), in each period analyzed.

RESULTS

The means and standard deviation showed by groups, in several periods, were: In 12 hours period, G1 (11.30 + 01.19), G2 (11.61 + 0.16), G3 (11.60 + 0.13), G4 (11.42 + 0.28) and G5 (11.71 + 0.16); In 24 hours period, G1 (11.57 + 0.27), G2 (11.62 + 0.16), G3 (11.57 + 0.21), G4 (11.41 + 0.12) and G5 (11.48 + 0.18); In 7 days, G1 (11.68 + 0.26), G2 (11.95 + 0.14), G3 (11.88 + 0.33), G4 (12.04 + 0.33) and G5 (11.95 + 0.10); In 14 days, G1 (11.95 + 0.13), G2 (12.06 + 0.10), G3 (12.00 + 0.06), G4 (12.02 + 0.10) and G5 (11.93 + 0.06); In 28 days, G1 (12.12 + 0.13), G2 (12.27 + 0.07), G3 (12.15 + 0.14), G4 (12.26 + 0.09) and G5 (12.11 + 0.01).

In 24 hours and 7 days the pH values were similar among all groups. In 12 hours, the G1 presented lower pH value than other groups except to G4 (p < 0.05) and G4 presented lower pH value than G5 (p < 0.05). In 7 days, G1 presented lower pH value than G4 and G5 (p < 0.05). In 28 days, G1 and G4 presented lower pH values than G2 and G4 (p < 0.05) and there are no statistical differences among other groups (p > 0.05).

The figure 1 shown the pH values obtained by several groups and analysis periods.

DISCUSSION

The null hypothesis was rejected because the pH values of several calcium hydroxide pastes increased after 28 days. Furthermore, there were statistical differences among groups. The addition of 5% CaCl₂ in calcium hydroxide paste increased pH value in relation to CH mixed with distilled water. Additionally, CH mixed with 5% CaCl₂ and 2% CHX gel provided lower pH value than CH mixed with 2% CHX solution with 5% CaCl₂ or 2% CHX alone.
The assessment of pH values with pH meter using the method of immersion of properly standardized polyethylene tubes in distilled water is well established. Once the reading was performed, the tubes were again immersed in same flask containing distilled water, under this condition is possible follow the pH values behavior throughout the experiment.

![Figure 1 - pH values shown by several calcium hydroxide pastes formulations, in different analysis periods. G1: CH + distilled water (DW); G2: CH + 2% CHX solution (2% CHX s); G3: CH + 2% CHX gel (2% CHX g); G4: CH + 2% CHX solution and 5% CaCl$_2$ solution (2% CHX s + 5% cc); G5: CH + 2% CHX gel and 5% CaCl$_2$ solution (2% CHX g + 5% cc).](image)

The vehicle mixed with CH interferes in its physical and chemical properties and clinical applications. Additives, such as chlorhexidine and CMPC, are often mixed with CH to be used in infected root canal. The use of CH with CHX is unclear and controversial, but it has been demonstrated that the alkalinity of CH remained unchanged after mixing.

However, it is observed that the use of NaOCl and CHX combined within the root canal produced the greatest percentage reduction of post-irrigant positive cultures due to the formation of chlorhexidine chloride, which increases the ionizing capacity of the CHX molecule. On the other hand, calcium ion participates in the mineralization healing process and the hydroxyl ion promotes an...
alkaline environment in the surrounding tissues.\textsuperscript{2,23}

After 28 days, the addition of CaCl\textsubscript{2} in CH pastes increased pH values but only different of CH mixed with distilled water or CH mixed with CHX gel and CaCl\textsubscript{2}. Therefore gel form only when mixed with CaCl\textsubscript{2} negatively interfered in increase of pH value. There were no significant differences between two formulations of CH mixed with 2\% CHX solution or gel, in accordance to previous studies.\textsuperscript{7,8} As in present study the CaCl\textsubscript{2} was used in solution form, when added to CHX gel, in long-term is possible that solubility this solution in CHX gel is lower than when used associated with CHX solution.

The mean pH of all medications stayed above 12.0 in final period. In similar study, the pH changes provided by 2\% CHX gel, calcium hydroxide and their combination with iodoform and zinc oxide powder were analyzed and showed that the pH values were above 12.0, after 7 days.\textsuperscript{24} In contrast, CH mixed with saline solution provide higher pH values than CH mixed with 2\% CHX.\textsuperscript{25}

Considering the result obtained in present study is important to emphasize that the association of 2\% CHX solution with 5\% CaCl\textsubscript{2} is interesting to increase pH value of calcium hydroxide paste without risk of occurred dental discoloration, as occurs when CHX is combined with sodium hypochlorite.

When CaCl\textsubscript{2} is associated with CHX the following reactions occurs: a) CHX is a base capable of forming salts with a number of organic acids; b) sodium hypochlorite is an oxidizing agent capable of oxidizing the gluconate part of CHX into gluconic acid. The chlor-groups might be added to the guanidine component of the chlorhexidine molecule, thereby forming "chlorhexidine chloride". If this were to happen, it would increase the ionizing capacity of the chlorhexidine molecule and the solution would incline towards an alkaline pH.\textsuperscript{13}

Based in previous researches and substantiated with these results, there is need of new studies with objective to verify the antimicrobial activity and biocompatibility this association in calcium hydroxide pastes with objective to apply clinically.

CONCLUSION

The pH values increased in long-term analysis to all calcium hydroxide paste. The association of 5\% calcium chloride with 2\% chlorhexidine digluconate solution as vehicle of calcium hydroxide paste provided a pH value increase in relation calcium hydroxide mixed with distilled water. When associated with calcium chloride the CHX gel interfered negatively in pH values in comparison to CHX solution.
REFERENCES


16. Bortoluzzi EA, Broon NJ, Bramante CM, Felippe WT, Tanomaru-Filho M, Esberard RM. The influence of calcium chloride on the setting time, solubility, disintegration, and pH of Mineral Trioxide Aggregate...


