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Physicochemical characteristics and discolouration potentials of Pulpine mineral® and Pulpine NE®

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Abstract

Aim: To compare the physicochemical properties (solubility, pH, radiopacity and crown discoloration) of Pulpine mineral (PMIN) and Pulpine NE (PNE) with the conventional material, mineral trioxide aggregate (MTA).

Methodology: Specimens of the tested materials were prepared according to the manufacturer's instructions using split Teflon ring molds. Solubility was evaluated by the percentage of material mass loss over 24 h and one week. The alkalinity was measured after each evaluation period using a pH meter. Other specimens were digitally radiographed on a size 2 sensor plate along with an aluminum step wedge to analyze the radiopacity by the Image J software. Finally, crown discoloration was assessed after applying the tested materials in the pulp chamber of sound human premolars using spectrophotometer. All data were statistically analyzed.

Results: Compared to MTA, both materials had significantly higher solubility and lower radiopacity ($P<0.05$). The alkalinity of PMIN was higher than that of MTA and PNE. Unlike PMIN, PNE and MTA caused crown discoloration.

Conclusions: PMIN exhibits promising results related to high alkalinity and adequate color stability but it needs modifications for radiopacity and solubility.

Keywords: Crown discoloration; MTA; Pulpine NE; Pulpine Mineral; Radiopacity; Solubility.

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INTRODUCTION

Vital pulp therapy (VPT) is indicated whenever the exposed pulp shows signs of reversible pulpitis [1]. It is mostly dependent on correct diagnosis and proper selection of an optimum capping material with adequate physicochemical and biological properties to stimulate dentinogenesis. [2]. Because of its outstanding biocompatibility and capacity to build dentin bridge with minimal inflammation, MTA is the gold standard material applied for VPT [2]. Unfortunately, it showed poor handling characteristics, long setting time and crown discoloration [3].

Hofmann dental manufacture (Hofmann Dental Manufaktur, HDM, Berlin, Germany) lately released Pulpine Mineral (PMIN) and Pulpine NE (PNE) materials as alternatives to MTA in direct and indirect pulp capping [4,5]. Both used Propolis (PS) as the principal constituent in their liquid which is a natural product that has been identified as a valuable material as it contains high levels of flavonoids, aromatic acids, and esters, providing antibacterial and anti-inflammatory activities [6, 7]. The powder in PMIN composes 70% hydroxyapatite (HAP) implanted in a calcium hydroxide [4, 5]. HAP is a calcium phosphate biomaterial that was previously employed as a pulp capping material due to its biocompatibility and osteoconductivity [8]. On the other hand, the powder of PNE contains zinc compounds, and calcium compounds [4, 5], the latter combines with the tissue's carbon dioxide to produce calcite crystals, so

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commencing the calcification process [9].

The physicochemical features of VPT materials are highly critical to their therapeutic relevance [10]. These features include solubility, alkalinity, and radiopacity, for example. The decrease in solubility is critical for long-term sealing capabilities of any dental cement [11], and the solubility in distilled water shouldn't be greater than 3% according to American National Standard/American Dental Association (ANSI/ADA 2000) Specification No. 57 [12]. Adequate radiopacity is another significant physical property of dental materials, as it aids in the differentiation of cements and surrounding tissues and improves the radiographic examination of root fillings [13]. Endodontic sealing materials must have a radiopacity of at least 3 mm of aluminium, according to American National Standard/American Dental Association (ANSI/ADA 2000) Specification No. 57 [12].

Furthermore, the long-term pH maintenance is mandatory to create an apatite-like layer on the surface of the capping materials when it contacts the phosphate-containing fluids[14], thus alkalinity is another important chemical property that guaranteed dental tissue healing and remineralization.

Crown discoloration, on the other hand, is a serious clinical issue that has been documented as an undesirable consequence related to the application of various medications in the pulp chamber [15]. Thus, the purpose of this study was to compare the new Hoffmann's PMIN and PNE to MTA in terms of solubility, alkalinity, radiopacity, and crown discoloration.

MATERIALS AND METHODS

Ethical approval

The research proposal was approved by the ethical committee at Faculty of Dentistry; Ain shams University, Egypt (END 16-18D/7-2017).

Materials

Table 1 shows the composition, manufacturers, and batch number of all tested materials.

Solubility

The solubility test was carried out in accordance with previous studies [16-18].

For all tested materials, six specimens were prepared with split Teflon ring molds (1.5±0.1 mm height and 7.75±0.1 mm internal diameter). Specimens were left to set for three times longer than the manufacturer's recommended (i.e. 15 min for MTA, 30 min for PMIN, and 45 min for PNE). To determine the net weight of each specimen with mold (W0), a high precision scale with 1 X10-4 g accuracy (Precision electrical weighing balance, Sartorius MAX 220 g, Germany) was used. The specimens were immersed in 60 mL deionized water then stored in an incubator for 24 hours and one week (at 37o C and 95% relative humidity). After that, the specimens were partially dried using absorbent papers then placed in a silica-containing desiccator for 24 hours. Specimens with molds were then reweighed (W1). The specimens were unmolded, and the weight of the molds was reported in order to obtain the exact weight of the specimens without molds (W2). For each specimen, the percentage of solubility was computed as follows:

% Wight loss = (W0-W2) -(W1-W2)/(W0-W2) X100.

Measurement of the pH

The pH was measured according to Bernardi et al [17]. In brief, newly mixed samples (n=6) were made in the same Teflon mold. In addition; 2 split Teflon mold without materials were utilized, to act as a base line of measurement, then placed in 60 mL of distilled water and incubated for 24 hours, and 7 days. After each interval, the pH was measured using a pH meter (Orion 3 Star; Thermo Scientific, Singapore).

Radiopacity

Following Oliveira et al. [18], two specimens for each material were prepared using the same Teflon mold, stored at 37°C and 100% humidity for 48h then digitally radiographed on a size 2 sensor plate (FONA, Sri Viag, Galilei, Italy) along with an aluminum step wedge (Artinis CD Dent 1.0, Netherlands) (1 to 5 mm thickness), using A VARIO-2200 X-ray machine operating at 70 kV, 3.5 mA, 0.2 exposure time and focus sensor distance of 30 cm. Image J software (National Institutes of Health, Bethesda, MD) was used to analyse the images. The radiopacity was calculated using a radiographic

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density tool and a region of interest (ROI).

Crown discoloration

Forty single rooted mandibular sound premolars (free of restorations and cracks, extracted for orthodontic or periodontal issues) were collected. The specimens (n=10) were then randomly assigned to four groups: three experimental groups (MTA, PMIN, and PNE) and a control group (without filling). The teeth were sectioned horizontally 2 mm apical to the cement enamel junction then accessed apically. Chemo-mechanical preparation was made with H files from (30-80) and 10 mL of 2.5% sodium hypochlorite (NaOCl) and finally flushed with 5 mL saline solution (19). Materials were prepared according to the manufacturers' instructions and placed into the pulp chamber, then sealed with resin modified glass ionomer cement (Riva Light Cure, SDI Limited, Australia). All specimens were immersed in test tubes containing 10 mL deionized water at room temperature and under light condition. Color was evaluated by VITA Easy Shade spectrophotometer (Easyshade Advance 4.0, VITA Zahanfabrik, Germany) at 3 time points: L0, a0, b0: baseline (after preparation but before insertion of the materials), L1, a1, b1: (immediately after insertion of the filling material), L2, a2, b2: (after 6 weeks of storage). Changes in the Commission Internationale de l'eclairage (CIE L*a*b*) were represented for each experimental group and the corresponding ΔE values were calculated using the following formula:

$\Delta E = [(\Delta L)\ 2+(\Delta a)2+(\Delta b)2]1/2$ as mentioned by Chen et al. [20].

Statistical analysis

The Statistical Package for the Social Sciences was used for the statistical analysis (SPSS 25, IBM, USA). The normal distribution of data was assessed using Kolmogorov-Smirnov and Shapiro-Wilk tests. Parametric data were accomplished using ANOVA test to compare different groups, followed by a Tukey's Post Hoc test to determine the significant one. A dependent t-test was applied for intragroup comparisons. The significance level was set at $P < 0.05$.

Table 1: Tested materials and their composition according to the manufacturers

Material	Composition	Manufacturer	Batch no
MTA	-Calcium oxide 55%–60% -Silicon dioxide 17%–20% -Aluminum oxide 2%–4% -Bismuth oxide 18%–22%	Angelus, Londrina, PR, Brazil	41840
Pulpine mineral (PMIN)	- 5g powder containing calcium and hydroxyapatite compounds -10 mL liquid containing ethanol and propolis.	Hoffmann's Germany company	84078 84077
Pulpine NE (PNE)	-10g powder containing calcium and zinc compounds -10 mL liquid containing ethanol and propolis.	Hoffmann's Germany company	8456 8457

Results

Solubility values (percentage of weight loss)

The data are collected in table (2). At 24 hours, the PMIN group had the largest value of solubility (-2.5), followed by PNE (-2.4) while MTA had the least value (-1.2) with no statistically significant difference between PMIN and PNE but a statistically significant difference between MTA and the other groups (P=0.027). At one week, the PMIN group exhibited the largest value (-12.8), followed by the PNE group (3.4), dislikes) x100. while MTA group showed the least mean percentage value (-1.6) with a statistically significant difference between the three groups (P<0.000).

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Table 2: Mean± (SD) values of solubility (percent of weight loss) among the different tested

Times	MTA	PMIN	PNE	P-value
24 hours	-1.2±0.251^{Aa}	-2.5±0.305^{Ab}	-2.4±0.556^{Ab}	0.027*
One week	-1.6±0.200^{Aa}	-12.8±0.200^{Bb}	-3.4±0.556^{Ac}	0.000*
P-value	0.093	0.001*	0.301	

Means with different capital superscript letters in the same column are statistically significant different. Means with different small letters in the same row are statistically significant difference (P<0.05).

Moreover, MTA and PNE groups showed a slight increase in the mean weight percentage loss from 24 h to one week without statistically significant difference (P=0.093, 0.301 respectively) while PMIN group had a high increase in the mean weight percentage loss from 24 h to one week with a significant difference (P<0.001) .

pH values

The results of pH values are collected in table (3). At 24 hours and one week, the greatest pH value was recorded in PMIN group , followed by MTA group, while the least value was recorded in PNE group with no statistically significant difference between the MTA and PMIN groups, but a statistically significant difference was found between the PNE group and other groups (P<0.05). Furthermore, the mean pH value slightly decreased in MTA and PNE groups but increased in PMIN group without statistically significant difference within each group.

Radiopacity values

The values are collected in table (4) and figure (1). The greatest mean radiopacity value was recorded in MTA group (equivalent to 5 Aluminum step-wedge), followed by PNE group (equivalent to 3 Aluminum step-wedge, and the least value was recorded in PMIN (equivalent to less than number one aluminum step-wedge). There was statistically significant difference between different groups (P<0.05).

Table 3: Mean± (SD) values of pH among the different tested materials at different time intervals.

Times	MTA	PMIN	PNE	P-value
24 hours	11.5±0.100^{Aa}	11.6±0.152^{Aa}	8.1±0.208^{Ab}	0.000*
One week	11.2±0.568^{Aa}	11.9±0.100^{Aa}	7.2±0.550^{Ab}	0.000*
P-value	0.547	0.250	0.05	

Means with different capital superscript letters in the same column are statistically significant different. Means with different small letters in the same row are statistically significant difference (P<0.05).

Tooth discoloration values

MTA group showed a slight increase in luminance L*; while other groups showed a slight decrease with a statistically significant difference between them after each evaluation period (P<0.05).

Additionally, all groups showed a decrease in a* and b* values except the control group that showed a slight increase with a statistically significant difference between them after each evaluation period (P<0.05). Still, All groups revealed clinically noticeable discoloration with ΔE > 3.3, however, the control group showed the least change in discoloration (ΔE= 3.9) followed by the PMIN group (ΔE =7.66) and MTA group (ΔE =17.71), while the highest value was recorded in the PNE group (22.14) as shown in table (5) figure (2).

Statistically, there was no significant difference between MTA and PNE groups nor between PMIN and control groups (P>0.05).

However, there were significant differences between MTA and both PMIN and control groups (P<0.05).

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Also, there were significant differences between the PNE and both PMIN and control groups (P<0.05).

radiopacity, and crown discoloration of PMIN, and PNE to MTA.

The results revealed that none of the evaluated materials had optimal

Table 4: Mean± (SD), minimum, maximum and median values of radiopacity among the different tested materials.

Groups	Mean±SD	Minimum	Maximum	Median	P-value
MTA	165.18±2.40[a]	163.72	167.95	163.86	0.000*
PMIN	38.47±1.90 [b]	36.38	40.09	38.94	0.000*
PNE	124.64±1.44[c]	123.30	126.16	124.46	0.000*

Means with different superscript letters in the same column are statistically significant different (P<0.05).

Discussion

Because the selection of an acceptable capping material with adequate physicochemical qualities is required to stimulate dentinogenesis in VPT procedures, this study compared the solubility, pH,

attributes in this investigation. Although PMIN showed promising results related to high alkalinity and adequate color stability but it needs modifications for radiopacity and solubility.

Table 5: ΔL,Δa,Δb and Mean±(SD) of ΔE among the different tested materials

Groups	ΔL	Δa	Δb	ΔE (mean±SD)	P-value
MTA	2.0250	-6.9250	-16.1250	**17.713±3.646[a]**	0.000*
PMIN	-4.6000	-3.7000	-3.7750	**7.6615±2.216[b]**	0.000*
PNE	-2.9250	-8.6250	-20.1500	**22.142±2.111[a]**	0.000*
Control	-3.30	-1.05	1.7	**3.9695±0.159[b]**	0.000*

Means with different superscript letters in the same column are statistically significant different (P<0.05)

In the current study, split Teflon molds with smaller dimensions than ANSI/ADA Standards 57 were used to support the materials during the experiment, notably with PMIN, which became crumble when stressed during mold removal, resulting in cracks and disintegration of the samples.

The solubility of MTA recorded here was 1.6% in one week that is like the results of previous studies [17,21]. This low value could be explained by leaching calcium and hydroxide ions at the initial setting [22]. Conversely, after one week, PMIN showed an increase in solubility (12.8%) which exceeds the ANSI/ADA recommendation. This can be attributed to its chemical composition that includes PS which in an aqueous solution creates phenoxide ions and raised the solubility as found by Ganapathi MR et al [23]. Additionally, Hesperidin, which is the most important flavonoids present in PS, increased the solubility in distilled water after 28 days [24].

On the other hand, PNE showed lower solubility in comparison to PMIN which slightly exceeds the maximum recommendation. This could be explained by the addition of zinc compound in its powder as this resulted in a lower solubility [25].

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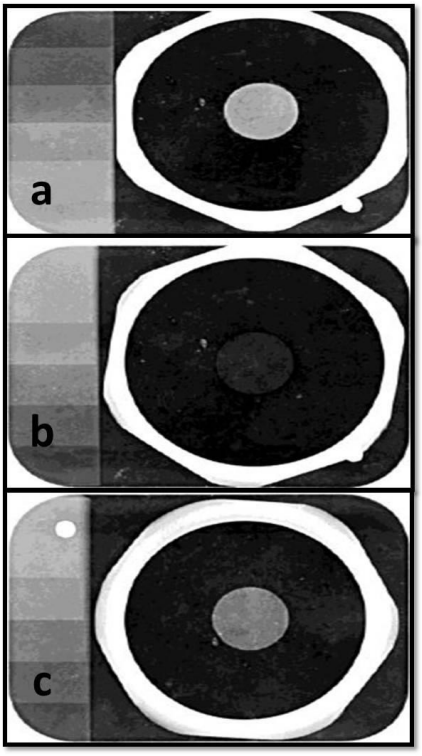
Figure 1: The different radiopacity of the MTA (a), PMIN (b) and PNE (c) inside the split Teflon mold along with aluminum step wedge.

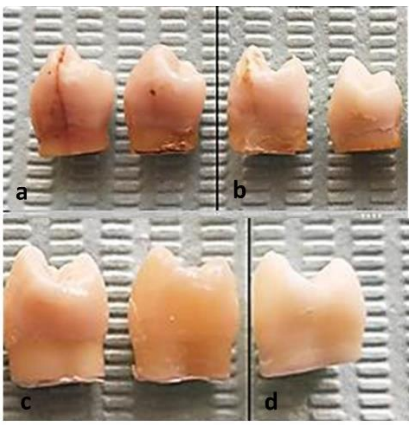


Alkalinity of the environment plays a crucial role in the process of hard tissue formation and is usually assessed by the pH meter [26]. In the present study, MTA revealed a significant increase in pH value after 24h and slight decrease after one week and this agrees with the results of previous research [3]. On the contrary, another study demonstrated a lower pH after one week [27] which could be attributed to the difference in the preparation and evaluation methods used. On the other hand, PNE group showed pH of 8.1 after 24 h and reached 7.2 after one week, this is totally related to the chemical properties of propolis, as the flavonoids present in propolis are acidic [24].

On contrary, PMIN group showed high pH value (11.6) at 24h that increased to 11.9 after one week and properly, this could be explained by the addition of HAP to its powder which are responsible for releasing hydroxyl ions that elevates the pH value.

The radiopacity was also evaluated as it is an important feature that should be considered when evaluating material for VPT. Radiopacity of the capping materials facilitate the observation of gaps or material deficiency in dental radiographs [28]. This was done in accordance with ANSI/ADA specification #57 which suggested that endodontic material should develop radiopacity correspondent to at least 3 mm Aluminum steps [29]. In the present study, three different regions were evaluated (ROI) within the same material to balance out the effect of localized irregularities not observed by the naked eye or air bubbles incorporated [29].

Figure 2: The different tooth discoloration of the PNE (a), PMIN (b), MTA (c) and control groups (d) after 6 weeks immersed in deionized water and under light



MTA demonstrated greater radiopacity values than PNE and PMIN among studied materials due to the presence of bismuth oxide in its component, which possesses appropriate radiopacity features [28] and this was like earlier studies [30,31]. PMIN group had the lowest radiopacity value which was lower than the no.1 Aluminium step wedge, thus, further research involving the addition of radiopacifiers to PMIN is highly advised. PNE group demonstrated the minimum Aluminium thickness suggested by ANSI/ADA specification n.57 (3mm), this is because Zn compound is present in its powder [32].

The spectrophotometric and CIE L*a*b* systems were chosen to evaluate the color change (ΔE) because they can detect minute variations in color and have several advantages such as repeatability, objectivity, and sensitivity [33]. The current results showed that PNE had the most discoloration, followed by MTA, and the PMIN group had the least. The presence of PS and ethanol in PNE liquid may explain this discoloration [34] while adding HAP to PMIN may explain the little change in tooth color as it is used for whitening purposes [35].

This is a preliminary study that analyzed PMIN and PNE materials' physicochemical qualities; more research on more physical, mechanical, and biological features of both products is required to emphasize the overall characteristics of these innovative materials.

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CONCLUSION

Compared to MTA, both PMIN and PNE had significantly higher solubility and lower radiopacity. PMIN showed significant color stability, while PNE didn't. The alkalinity of PMIN was higher than that of MTA while that of PNE wasn't.

Clinical Relevance

PMIN showed promising results related to high alkalinity and adequate color stability but it needs modifications for radiopacity and solubility.

Conflict of Interest

The authors declare that they have no conflict of interest.

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Not applicable

REFERENCES

1. Mesenchymal stem cells promote hard-tissue repair after direct pulp capping. Obeid M, Saber Sel D, Ismael Ael D, Hassanien E. J Endod. 2013 May;39(5):626-31. PMID: 23611380.

2. Outcome of pulpotomy in permanent teeth with irreversible pulpitis: a systematic review and meta-analysis. Ather A, Patel B, Gelfond JAL, Ruparel NB. Sci Rep. 2022 Nov 16;12(1):19664. PMID: 36385132.

3. Physicochemical Properties of a Bioceramic Repair Material - BioMTA. Coaguila-Llerena H, Ochoa-Rodriguez VM, Castro-Núñez GM, Faria G, Guerreiro-Tanomaru JM, Tanomaru-Filho M. Braz Dent J. 2020 Sep-Oct;31(5):511-515. PMID: 33146335.

4. https://hoffmann-dental.com/produkte/?lang=en.

5. Histopathological and immunohistochemical profiles of pulp tissues in immature dogs' teeth to two recently introduced pulpotomy materials. Mohamed M, Hashem AAR, Obeid MF, Abu-Seida A. Clin Oral Investig. 2023 Jun;27(6):3095-3103. PMID: 36781475.

6. Evaluation of antibacterial activity of propolis on regenerative potential of necrotic immature permanent teeth in dogs. El-Tayeb MM, Abu-Seida AM, El Ashry SH, El-Hady SA. BMC Oral Health. 2019 Aug 6;19(1):174. PMID: 31387578.

7. Biological evaluation of hesperidin for direct pulp capping in dogs' teeth. Abo El-Mal EO, Abu-Seida AM, El Ashry SH. Int J Exp Pathol. 2021 Feb;102(1):32-44. PMID: 33405328.

8. Hydroxyapatite applied as direct pulp capping medicine substitutes for osteodentin. Hayashi Y, Imai M, Yanagiguchi K, Viloria IL, Ikeda T. J Endod. 1999 Apr;25(4):225-9. PMID: 10425944.

9. Evaluation of the tissue reaction to fast endodontic cement (CER) and Angelus MTA. Gomes-Filho JE, Rodrigues G, Watanabe S, Estrada Bernabé PF, Lodi CS, Gomes AC, Faria MD, Domingos Dos Santos A, Silos Moraes JC. J Endod. 2009 Oct;35(10):1377-80. PMID: 19801233.

10. Physiochemical properties of experimental nano-hybrid MTA. Akhavan Zanjani V, Tabari K, Sheikh-Al-Eslamian SM, Abrandabadi AN. J Med Life. 2017 Jul-Sep;10(3):182-187. PMID: 29075348.

11. Marginal adaptation, solubility and biocompatibility of TheraCal LC compared with MTA-angelus and biodentine as a furcation perforation repair material. Alazrag MA, Abu-Seida AM, El-Batouty KM, El Ashry SH. BMC Oral Health. 2020 Oct 29;20(1):298. PMID: 33121465.

12. ANSI/ADA (2000) Specification no 57 Endodontic sealing material. Chicago, USA: ADA Publishing.

13. Densitometric measurement of radiopacity of Gutta-percha cones and root dentin. Katz A, Kaffe I, Littner M, Tagger M, Tamse A. J Endod. 1990 May;16(5):211-3. PMID: 2074412.

14. Bioceramic materials in endodontics. Endodontic topics. Wang Z. 2015;32:3-0.

15. A Review of Tooth Discoloration after Regenerative Endodontic Therapy. Kahler B, Rossi-Fedele G. J Endod. 2016;42(4):563-569. PMID: 26852148.

16. Solubility and dimensional change after setting of root canal sealers: a proposal for smaller dimensions of test samples. Carvalho-Junior JR, Correr-Sobrinho L, Correr AB, Sinhoreti MA, Consani S, Sousa-Neto MD. J Endod. 2007;33(9):1110-1116. PMID: 17931945.

17. Effects of the addition of nanoparticulate calcium carbonate on setting time, dimensional change, compressive strength,

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Vol 12 No 1 (2024) DOI 10.5195/d3000.2024.533

solubility and pH of MTA. Bernardi A, Bortoluzzi EA, Felippe WT, Felippe MC, Wan WS, Teixeira CS. Int Endod J. 2017;50(1):97-105. PMID: 26659859.

18. A laboratory evaluation of cell viability, radiopacity and tooth discoloration induced by regenerative endodontic materials. Oliveira LV, da Silva GR, Souza GL, Magalhães TEA, Barbosa GLR, Turrioni AP. Int Endod J. 2020; 53:1140-1152. PMID: 32299123.

19. Color stability of teeth restored with biodentine: A 6-month in vitro study. Vallés M, Roig M, Duran-Sindreu F, Martínez S, Mercadé M. J Endod. 2015; 41:1157-1160. PMID: 25937179.

20. Spectrophotometric Analysis of Coronal Tooth Discoloration Induced by Tricalcium Silicate Cements in the Presence of Blood. Chen SJ, Karabucak B, Steffen JJ, Yu YH, Kohli MR. J Endod. 2020;46(12):1913–9. PMID : 32949559.

21. Solubility of Root-end-Filling Materials: A Comparative Study. Poggio C, Lombardini M, Alessandro C, Simonetta R. J Endod. 2007;33(9):1094–7. PMID: 17931941.

22. Changes in the surface of four calcium silicate-containing endodontic materials and an epoxy resin-based sealer after a solubility test. Borges RP, Sousa-Neto MD, Versiani MA, Rached-Júnior FA, De-Deus G, Miranda CES. Int Endod J. 2012; 45:419-428. PMID: 22150403.

23. Nucleophilic effects on the deprotonation of phenol radical cations. Chem Phys Lett. 2001; 337:335-340.

24. A comparative study of the physicochemical properties of hesperidin, MTA-Angelus and calcium hydroxide as pulp capping materials. Abo El-Mal EO, Abu-Seida AM, El Ashry SH. Saudi Dent J. 2019; 31: 219-227. PMID: 30983832.

25. Antimicrobial Activity and pH of Calcium Hydroxide and Zinc Oxide Nanoparticles Intracanal Medication and Association with Chlorhexidine. Aguiar AS, Guerreiro-Tanomaru JM, Faria G, Leonardo RT, Tanomaru-Filho M. J Contemp Dent Pract. 2015; 16:624-629. PMID: 26423497.

26. Physical evaluation of a new pulp capping material developed from Portland cement. Negm A, Hassanien E, Abu-Seida AM, Nagy M. J Clin Exper Dent. 2016; 8, e278–e283. PMID: 27398178.

27. Influence of powder-to-water ratio on radiopacity, setting time, pH, calcium ion release and micro-CT volumetric solubility of white mineral trioxide aggregate. Cavenago BC, Pereira TC, Duarte MAH. Int Endod J. 2014; 47:120-126. PMID: 23647286.

28. Radiopacity of Portland cement associated with different radiopacifying agents. Húngaro Duarte MA, de Oliveira El Kadre GD ar, Vivan RR, Guerreiro Tanomaru JM, Filho MT, de Moraes IG. J Endod. 2009; 35:737-740. PMID: 19410095.

29. Radiopacity of root filling materials using digital radiography. Carvalho-Junior JR, Correr-Sobrinho L, Correr AB, Sinhoreti MAC, Consani S, Sousa-Neto MD. Int Endod J. 2007; 40 :514-520. PMID: 17511790.

30. Mineral trioxide aggregate enriched with iron disulfide nanostructures: an evaluation of their physical and biological properties. Argueta-Figueroa L, Delgado-García JJ, García-Contreras R. Eur J Oral Sci. 2018; 126:234-243. PMID: 29442393.

31. Comparison of the physical and mechanical properties of MTA and portland cement. Islam I, Kheng Chng H, Jin Yap AU. J Endod. 2006; 32:193-197. PMID: 16500224.

32. Effect of zirconium oxide and zinc oxide nanoparticles on physicochemical properties and antibiofilm activity of a calcium silicate-based material. Guerreiro-Tanomaru JM, Trindade-Junior A, Costa BC. Sci World J. 2014: Article ID 975213. PMID: 25431798.

33. Color stability of white mineral trioxide aggregate. Vallés M, Mercadé M, Duran-Sindreu F, Bourdelande JL, Roig M. Clin Oral Investig. 2013; 17:1155-1159. PMID: 22814761.

34. Does Modification of Amalgomer with Propolis Alter Its Physicomechanical Properties? An In Vitro Study. Abdallah Abdallah RM, Abdelghany AM, Aref NS. Int J Biomater. 2020;2020:3180879. PMID: 32454828.

35. Whitening effect and morphological evaluation of hydroxyapatite materials. Dabanoglu A, Wood C, García-Godoy F, Kunzelmann KH. Am J Dent. 2009; 22:23-29. PMID: 19281109.