Smear Layer Removing Ability of Root Canal Irrigation Solutions: A Review

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ABSTRACT

Aim: The purpose of this review is to address the smear layer removing ability of root different canal irrigants including ethylenediaminetetraacetic acid (EDTA), a mixture of tetracycline, acid and detergent (MTAD), tetraclean, citric acid, Q-Mix, maleic acid, and smear clear.

Background: Smear layer is a layer which is produced during instrumentation. It contains both organic and inorganic materials. It may also contain bacteria and their byproduct considering the root canal situation. This layer may prevent the penetration of the healing material introduced to the canal to the interior of the dentinal tubules. In addition, it can affect the adaptation of sealing materials to the root canal walls.

Review results: The smear layer removal ability of MTAD is superior and faster than EDTA. Tetraclean is similarly composed of an acid, an antibiotic, and a detergent. The presence of doxycycline is believed to help the smear layer removal ability of these irrigants. Antibiotics such as tetracycline had similar smear layer removal ability as even citric acid. EDTA is an amino acid with a chelating ability that sequestrates metal ions. Some believed EDTA smear layer removing ability is better than MTAD, tetraclean, SmearClear, and 20% citric acid which is controversial in case of comparison between MTAD and EDTA. Phosphoric acid is efficient enough to be comparable to EDTA in removing the smear layer. Maleic acid is an organic compound with acid etching smear layer removal. Its ability seems to be similar or even better than EDTA. Citric acid as another organic acid is believed to be used as smear removing agent. HEBP is another chelating agent that can be used in combination with NaOCl; however, HEBP is a weak decalcifying agent compared to EDTA and hence cannot be applied as a mere final rinse. QMiX is a combination of CHX, EDTA, and detergent and should be used at final rinse. It is believed that QMiX is as efficient as EDTA. Smear clear is a 17% EDTA solution including an anionic and cationic (cetrimide) surfactant. The ability of QMiX is similar to EDTA.

Conclusion: There are different canal irrigation solutions with various smear layer removal ability that some should be used as a mere final rinse and some should not.

Clinical significance: The usage of canal irrigation solutions depends on the clinical situation and preference of the dentists. This study provides a good guide for clinician of the field.

Keywords: Citric acid, Ethylenediaminetetraacetic acid, Irrigation, Maleic acid, Mixture of tetracycline, acid and detergent, Smear layer.

INTRODUCTION

Apart from recent products, chelators and acids were the only decalcifying solutions used in endodontics, mostly EDTA and citric acid. However, several combinations containing characteristics thought helpful for treatment have been produced nowadays. Among these features are...
decreased surface tension and significant antimicrobial activity. The bases of these recent products are mainly composed of EDTA or citric acid.\textsuperscript{1}

A smear layer is produced during the instrumentation process. Although the exact components of this layer have not been determined yet, it is believed to contain thin particles of organic elements and inorganic materials such as odontoblastic processes, pulp tissue debris, blood cells, bacteria, etc.\textsuperscript{2}

At the first stages of the intervention, the organic part of the smear layer is higher due to the presence of vital pulp tissue. The smear layer may be found both on the canal wall and into some dental tubules. None of the instrumentation techniques could erase the canal debris totally. Both mechanical and manual shaping produced smear layer and debris.\textsuperscript{3-6}

According to Ahlquist et al.,\textsuperscript{7} rotary techniques produced more debris than manual techniques. On the other hand, in another experiment, the Quantec rotary system managed to result in cleaner canal walls than conventional manual instrumentation.\textsuperscript{5}

An evaluation was performed on the occurrence of bacterial colonization in the dentinal tubules during root canal instrumentation that showed areas without the smear layer are free of Streptococcus sanguis colonization in 88% of the cases.\textsuperscript{9}

To achieve fast disinfection with intracanal medicaments, smear layer should be removed and dental tubules should have their patency.\textsuperscript{10,11} Furthermore, removal of the smear layer\textsuperscript{12,13} can result in better adaptation of the obturation materials to the canal walls more.

Reports have been proposed that the removal of smear layer during apicectomy can fail retrograde filling of the glass-ionomer.\textsuperscript{14} An investigation suggested that root canal sealer infiltration into dentinal tubules, whose smear layer was removed, was irrelevant to higher bond strengths.\textsuperscript{15} Kokkas et al.\textsuperscript{16} revealed that after smear layer degradation, sealers infiltrate at varying depths. The smear layer existence may facilitate some sealers bonding to the root canal walls. Nevertheless, Gettleman et al.\textsuperscript{17} reported no adhesive strength changes in the presence or absence of smear layer with Sealapex and Sealant sealers.

In this part, different irrigating solutions are to be reviewed and discussed.

**Mixture of Tetracycline, Acid and Detergent**

BioPure (Dentsply, OK, USA, Tulsa Dental, Tulsa), also known as MTAD, was presented by Torabinejad et al. in 2003. It consists of, 4.25% citric acid, 3% doxycycline, and a detergent (0.5% Polysorbate 80).\textsuperscript{18}

Torabinejad et al.\textsuperscript{19} for the first time, proposed MTAD as an effective solution for smear layer removal with minimal changes in the dentinal tubules structure, especially in case of canals irrigation with NaOCl, the subsequent rinse with MTAD. Another investigation by Torabinejad reported that although, as an intracanal irrigant, MTAD could eliminate most of the smear layer, remnants of the organic parts of the smear layer may scatter on the canal walls.\textsuperscript{10}

The smear layer removing the ability of MTAD would be empowered when intracanal irrigation was conducted by diluted NaOCl before final rinse with MTAD. However, another investigation proposed that MTAD is unable to eliminate the smear layer.\textsuperscript{19} Tay et al.\textsuperscript{20} found that both EDTA and MTAD can create a demineralized collagen zone of matrices around the dentinal tubules and in eroded dentin, and acidic Bio Pure MTAD was more aggressive than EDTA mildly. Hydrophilic adhesive or sealers may hybridize the demineralized dentin zones. However, the outcome of hydrophobic sealers compaction against air-dried, hydrolytic degradation of incompletely infiltrated matrices, and collapsed collagen matrices remain unresolved. In an ultrastructural study, the same mentioned researcher demonstrated that the resulted demineralized dentin matrix by MTAD was thicker than EDTA. De-Deus et al.\textsuperscript{21} showed that the demineralization kinetics prompted by MTAD was significantly quicker than those prompted by a 17% EDTA.

**Tetraclean**

Tetraclean (Ogna Laboratori Farmaceutici, Muggiò (Mi), Italy), similar to MTAD, is a combination of an acid, an antibiotic, and a detergent. However, there are differences with MTAD such as the type of detergent (polypropylene glycol) and the concentration of the antibiotic, doxycycline (50 mg/mL).\textsuperscript{22} In a comparison made by Giardino et al.\textsuperscript{23} between the surface tension of 17% EDTA, 5.25% NaOCl, MTAD, Cetrexidin, Smear clear, and Tetraclean. EDTA and NaOCl showed the top-rated surface tensions, while Tetraclean and Cetrexidin had the lowest rates.

**Smear Layer Removing Ability**

Poggio et al.\textsuperscript{24} Tetraclean treatment cause higher Ca\textsuperscript{2+} release which is an evidence of significantly higher demineralizing capability than other tested irrigants. Tetracyclines, as bacteriostatic antibiotics that cover a variety of the bacteria, are comprised of tetracycline-HCl, demeclocycline, monocyline, and doxycycline.\textsuperscript{18} This property may be an advantage as they do not lyse the bacterial cell wall and do not produce antigens like endotoxins.\textsuperscript{26}

Apart from their antimicrobial action, Tetracyclines also have many special properties, such as inhibition from tissue degradation by inhibiting the mammalian
collagenases\textsuperscript{27} and clastic cells\textsuperscript{27-29} It also can enhance collagen and bone formation in inflammatory diseases such as periodontitis because of its ability to block tissue collagenases which elevate in such diseases.\textsuperscript{26}

The smear layer removal is one of the uses of Tetracycline during the instrumentation of canal walls.\textsuperscript{26,30} It is also used for retrograde cavi
ty irrigation in periapical surgical procedures\textsuperscript{31} and as an intracanal medicament.\textsuperscript{32}

Barkhordar et al.\textsuperscript{26} showed the efficiency of doxycycline-HCl to eliminate the smear layer mainly in the concentration of 100 mg/mL. In another investigation, tetracycline and citric acid had the same effect in removing the smear layer.\textsuperscript{30} Another study showed that irrigating the amalgam fillings and retrograde IRM with doxycycline inhibited the dye penetration significantly.\textsuperscript{31}

**Ethylenediaminetetraacetic Acid**

Ethylenediaminetetraacetic acid (EDTA) is an amino acid with the formula of (HO\textsubscript{2}CCH\textsubscript{2})\textsubscript{2}NCH\textsubscript{2}CH\textsubscript{2}N(CH\textsubscript{2}CO\textsubscript{2})H\textsubscript{2} that has a chelating effect and can sequester divalent and trivalent metal ions. The carboxylate and amine groups are responsible for metal binding in EDTA. EDTA construct especially powerful combinations with Cu(II), Mn(II), and Co(III), and Fe(III). EDTA is frequently synthesized using 1, 2-diaminoethane (ethylenediamine), formaldehyde (methanol), water and sodium cyanide. The resulted tetrasi
dium salt, which can be converted into the acidic forms through acidification process.\textsuperscript{33}

EDTA is a polyamino carboxylic acid and a water-soluble, colorless solid. It is frequently used in dissolving limescale. Being chelating agent and hexadentate ligand (such as the ability to sequester metal ions like Ca\textsuperscript{2+} and Fe\textsuperscript{3+}) has made EDTA applicable. The metal ions showed lower reactivity in the solution when binding EDTA. Disodium EDTA and calcium disodium EDTA are among a variety of the produced salts. The first proposed formulation of the EDTA was proposed by Ferdinand Munz in 1935 that was a combination of ethylenediamine and chloroacetic acid.\textsuperscript{34,35} In new formulations EDTA is a combination of ethylenediamine (1,2-diaminothene (ethylenediamine), sodium cyanide and formaldehyde.\textsuperscript{35} The result of EDTA reaction with calcium ions is soluble calcium chelates. EDTA demineralizes dentine with a depth of 20–30 \textmu m in 5 minutes.\textsuperscript{36}

Wu et al.\textsuperscript{37} showed that the 17% EDTA was notably more powerful than 20% citric acid, BioPure MTAD and smear clear in removing the smear layer. According to another study, orthophosphoric acid had higher surgical smear layer removing ability with lesser action time than EDTA.\textsuperscript{38}

Prado et al.\textsuperscript{39} revealed that phosphoric acid was efficient enough to be comparable to EDTA in removing the smear layer. Another study proved the efficacy of EDTA in removing the smear layer.\textsuperscript{40} According to Caron et al.,\textsuperscript{41} the sonic and ultrasonic activation of 17% EDTA/3% NaOCl combination removed the smear layer more efficiently.

Another study which used a scanning electron microscope (SEM) showed that using NaOCl gel along with EDTA is as efficient as NaOCl solution in removing the smear layer in three parts of the root canal walls.\textsuperscript{42} In another SEM study, Mello et al.\textsuperscript{43} indicated that the rinsing process with 5 mL of EDTA continuously for 3 minutes can remove the smear layer from root canal walls effectively. Another study showed that EndoActivator could not enhance the smear layer ability of NaOCl/EDTA.\textsuperscript{44}

Two studies proved the efficacy of EDTA in removing the smear layer.\textsuperscript{45,46} Atomic absorption spectroscopy and SEM results,\textsuperscript{47} indicated that 15% EDTA was the optimum concentration of calcium ions compared to the other chelating agents and the most effective smear layer removing ability. A study presented that a 1-minute ultrasonic activation of EDTA causes effective smear layer and debris removal of the canal apex.\textsuperscript{48}

Saito et al.\textsuperscript{49} showed that an increase in irrigation time with 17% EDTA from 30 seconds to 1 minute make smear layer removal more efficient after root canal instrumentation. According to another study, application of a combination of EDTA and NaOCl irrigants, for 1, 3 and 5 minutes showed similar smear removing in the canal walls of straight roots.\textsuperscript{50} Sen et al.\textsuperscript{51} showed no significant difference between different concentrations of EDTA (15%, 10%, 5%, and 1%) in the smear layer removal ability.

Perez and Rouqueyrol-Pourcel\textsuperscript{52} showed similar smear layer removing the ability for one minute 15% EDTA irrigation and three minutes irrigation with 8% EDTA during root canal provision.

Another study revealed that 3-minute irrigation with EDTA compared to 15 minutes had statistically significantly better results. Furthermore, there were no significant differences for the 3-time intervals of irrigation with EDTA-T.\textsuperscript{53}

Adiguzel et al.\textsuperscript{54} indicated that the Self-adjusting File operation with continuously irrigating with EDTA resulted in root canal walls that were free of smear layer in 85%, 60%, and 50% and of debris in 95%, 90%, and 85% of the coronal, middle, and apical thirds of the root canals, respectively.

**Maleic Acid**

Maleic acid (C\textsubscript{4}H\textsubscript{4}O\textsubscript{4}) is a dicarboxylic organic acid that is the trans-isomer of butenedioic acid and cis-isomer of fumaric acid. It is mainly the precursor of fumaric acid.
and compared to its parent maleic anhydride has more uses.\textsuperscript{35}

Maleic acid possesses smear layer removal ability as an acid etchant in restorative dentistry.\textsuperscript{56} Prabhu et al.\textsuperscript{56} got to the result that, using maleic acid at the concentrations than 7%, damaged the intertubular dentin. Ballal et al.\textsuperscript{57} reported that 7% of maleic acid was a more powerful smear layer removing irrigant than 17% EDTA in the third part of the root canal apex. Ballal et al.\textsuperscript{58} demonstrated that maleic acid had a similar effect to EDTA in reducing the microhardness of root dentin but enhanced the surface roughness significantly more than EDTA. Furthermore, maleic acid eradicates \textit{E. faecalis} biofilms when used at a concentration of 0.88% after 30 seconds and 0.11% after 2 minutes of contact time. It can eradicate the biofilms at 30 seconds, 1 minute and two minutes in combination with 0.2% cetrimide.\textsuperscript{59}

Final irrigation by 7% maleic acid can improve the post-obturation apical seal in comparison with 17% EDTA and has minimal tissue-dissolution capacity in comparison with NaOCl.\textsuperscript{60,61}

Ballal et al.\textsuperscript{62} indicated maleic acid's demineralization of the root dentine by energy dispersive spectrometer, with the highest calcium and phosphorus extracted during the first 5 minutes, in comparison with EDTA.

\section*{Citric Acid}

Citric acid is an organic weak acid, and a white crystalline powder when at room temperature. There are two forms of citric acid available, monohydrous and anhydrous (water-free). The monohydrous form crystallizes from cold water, whereas the anhydrous forms when citric acid is crystallized in cold water. In the temperatures above 78°C, the two forms are convertible to each other.\textsuperscript{63}

It can be used as an irrigation agent in the root canal to remove the smear layer.\textsuperscript{64} Concentrations ranging from 1 to 50% have been used.\textsuperscript{65} According to a study, among the concentrations, 10% of citric acid was more efficient in the smear layer removal from apical root-end cavities than ultrasound.\textsuperscript{66} Another study made a comparison between the antibacterial and chelating features of citric acid and EDTA. The solubility of dentine–resin combined powder was higher in 0.5, 1, and 2M citric acid concentrations than in a 0.5M EDTA solution. Citric acid solution possessed antibacterial effects for all 12 root canal bacteria.\textsuperscript{67}

However, Liolios et al.\textsuperscript{68} reported better ability in removing the smear layer by commercial EDTA preparations than 50% citric acid. and two other studies reported either minor or no difference in smear layer removal with 15% EDTA and citric acid.\textsuperscript{69,70} In a recent study, Machado-Silveiro et al.\textsuperscript{71} measured the demineralization capability of 10%, sodium citrate, 1% and 10% citric acid, and 17% EDTA during immersions of 5, 10, and 15 minutes on root canal dentin which showed the 10% citric acid as the best efficient agent among the others. Takeda et al.\textsuperscript{72} conducted an \textit{ex vivo} study on the smear layer removal ability of two kinds of laser and three endodontic irrigants in the apical and middle thirds of root canals. Six percent phosphoric acid, 17% EDTA, and 6% citric acid did not have the ability to remove the smear layer thoroughly from the root canal system. Furthermore, these solutions cause tubular opening through demineralization of the intertubular dentine tubular, which in turn caused them to enlarge. According to a study, citric acid solutions removed the smear layer after 60 s of application, cleaning the dentin tubules, but also widening and demineralizing inter- and peritubular dentin.\textsuperscript{73}

\section*{Tannic Acid}

Bitter\textsuperscript{74} reported that 25% of tannic acid had the efficiency to remove the smear layer. The results of another study were contrary to these findings and demonstrated that tannic acid increased the collagen cross-linking within the underlying dentin matrix and the smear layer, thus increasing organic connections to the tubules.\textsuperscript{75}

Takahashi et al.\textsuperscript{76} performed a study using scanning electron microscopy and explained that an application of 2% tannic acid for 60 seconds or 5% tannic acid for 15, 30, or 60 seconds efficiently removed the smear layer and left the dentinal tubules occluded. Duration of 15 seconds treatment with 40% phosphoric acid exposed many dentinal tubules and opened their orifices.

\section*{Polyacrylic Acid}

Polyacrylic acid (Fuji II liquid and Durelon liquid) at 40% concentration was reported as a very effective smear layer removing agent. In order to achieve the patency, the acid exposure duration should be lower than 30 seconds according to the studies guide.\textsuperscript{77}

\section*{Derivatives of Oxine (8-hydroxyquinoline)}

Dequalinium compounds have been used against bacterial and fungal infections widely. Bis-dequalinium-acetate (BDA) has been shown to have the ability of removing the smear layer throughout the canal, even in the apical third.\textsuperscript{78,79} The low surface tension of the BDA helps its penetration into spaces that instruments cannot have access.\textsuperscript{78}

According to a study, 5.25% NaOCl and Salvizol (a commercial brand of 0.5% BDA) had comparable efficiencies in removing organic debris; however, only Salvizol was able to open dentinal tubules.\textsuperscript{80} In comparison
with REDTA, another study declared that Salvizol was less effective at opening dentinal tubules.81

HEBP
1-bisphosphonate, 1-hydroxylidene-1or etidronic acid (HEBP) is a chelator that is usable in combination with sodium hypochlorite (NaOCl) keeping its proteolytic or antimicrobial properties intact.82 However, the decalciying property of HEBP is weak compared to EDTA, and thus its use as an only final rinse is limited. Therefore, a mixture of HEBP and NaCl is recommended for a complete root canal irrigation. As this solution has a tendency toward NaOCl production in sodium hypochlorite–hypochlorous acid equilibrium, it has better tissue dissolution capacity than hypochlorous acid83 and it has lower cytotoxicity.84 In addition, NaOCl and HEBP mixture has been proposed to optimize the bonding by Resilon/Epiphany root fillings.85

Due to calcium hypochlorite adaptation of HEBP, it is used in pool water disinfection as Ca(OCl)2 tablets are used in swimming pools. The HEBP prevents stain formation from inorganic compounds at the water line. It also prevents the accumulation of dentin debris in the root canal during instrumentation.86

QMIX
QMIX is one of the recently introduced mixtures for irrigating the root canal. It was recommended to be used at the end of instrumentation after NaOCl irrigation. It contains CHX, EDTA, and a detergent, coming as a ready-to-use clear solution. As mentioned above, QMIX usage is limited to the final rinse. Although no precipitate has been described in QMIX and NaOCl mixture, saline rinse for NaOCl should be conducted whenever sodium hypochlorite is used throughout the cleaning and shaping processes to prevent the PCA formation.87-89

Stojicic et al.87 performed a study using scanning electron microscopy and resulted that Q-Mix removed the smear layer similar to the EDTA. Another study represented that QMiX had similar smear layer removing ability as 17% EDTA after the application of 5.25% NaOCl as the initial rinse.88

SmearClear
SmearClear (Orange, Sybron Endo, CA) is a product introduced for removing the smear layer. It is a 17% EDTA solution including an anionic and cationic (cetrimide) surfactant. There were no significant differences shown between 17% EDTA, SmearClear, and 10% citric acid regarding their smear layer removal ability.90

Da Silva et al.91 represented that SmearClear ability to remove the smear layer from the root canals of permanent teeth was similar to 14.3% EDTA. Another study got to the result that there was no significant difference between SmearClear and EDTA in the process of removing the smear layer from the root canals of primary teeth.92 On the other hand, Wu et al.93 indicated that 17% EDTA was more efficient than that of SmearClear, whilst another study demonstrated that the efficacy of SmearClear on E. faecalis biofilms was significantly less than 1% and 6% NaOCl.94

Authors Perspective
The smear layer removal ability of MTAD is superior and faster than EDTA. Tetraclean is similarly composed of an acid, an antibiotic, and a detergent. The presence of doxycycline is believed to help the smear layer removal ability of these irrigants. Antibiotics such as tetracycline had similar smear layer removal ability as even citric acid. EDTA is an amino acid with a chelating ability that sequestrates metal ions. Some believed EDTA smear layer removing ability is better than MTAD, tetraclean, SmearClear, and 20% citric acid which is controversial in case of comparison between MTAD and EDTA. Phosphoric acid is efficient enough to be comparable to EDTA in removing the smear layer. Maleic acid is an organic compound with acid etching smear layer removal. Its ability seems to be similar or even better than EDTA. Citric acid as another organic acid is believed to be used as smear removing agent. HEBP is another chelating agent that can be used in combination with NaOCl; however, HEBP is a weak decalciying agent compared to EDTA and hence cannot be applied as a mere final rinse. QMIX is a combination of CHX, EDTA, and detergent and should be used at final rinse. It is believed that QMiX is as efficient as EDTA. SmearClear is a 17% EDTA solution including an anionic and cationic (cetrimide) surfactant. The ability of QMiX is similar to EDTA.

CONCLUSION
Different canal irrigation agents with different clinical significance and usage have been proposed. These ranges from combinatory solutions to organic acids and even some of the antibiotics such as doxycycline. MTAD, EDTA, QMiX, SmearClear seems to have a similar smear layer removing abilities. However, many believe EDTA is more effective than MTAD. Contrary, some proposed that MTAD is more efficient than EDTA. QMiX and SmearClear should be used at final rinse. Still, controversies remained in this topic.

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