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PROPOLIS EXTRACT AS ANTI-CORROSIVE AGENT INHIBITS METAL IONIC RELEASE FROM ORTHODONTIC BRACKETS

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ABSTRACT
Background: *A combination of nickel (Ni), chromium (Cr), and iron (Fe) can be found in the stainless steel orthodontic bracket. Ion release takes place as a result of the chemical interaction between metals and the oral environment, which leads to the potential of hypersensitivity during fixed orthodontic treatment. Propolis contains phytochemicals that have the ability to reduce corrosion, making it a potential treatment option.*
Purpose: *to determine the release of Ni, Cr, and Fe in metal brackets in an 8.2% propolis solution*
Method: *Four sets of six brackets were made from 24 brackets. Artificial saliva, sodium fluoride, sterilized distilled water (aquabidest), and 8.2% propolis were applied to these brackets. After incubating at 37°C for seven days, ICP EOS measured the metal ions Ni, Cr, and Fe. The analysis revealed significant differences ($p<0.05$) in ionic release of Ni, Cr, and Fe among groups exposed to sterilized distilled water (aquabidest) and an 8.2% propolis solution. Additionally, the Mann-Whitney test showed substantial Ni ion release differences ($p<0.05$) between 8.2% propolis solution and sterilized distilled water. The 8.2% propolis solution and sodium fluoride solution released Cr ions differently. Fe ion levels differed between propolis solution 8.2%, sodium fluoride solution, sterilized distilled water, and fake saliva.* ***Conclusion:*** *Propolis affects metal bracket ionic release of Ni, Cr, and Fe.*

Keywords : *Cr and Fe, ions of Ni, propolis solution, Stainless steel bracket*
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INTRODUCTION

Orthodontic brackets are defined as components in fixed orthodontic treatments, attached in the dentition where the orthodontic wire as an active component is placed and tied in. Stainless steel is the commonly used metal material in the field of orthodontics, containing 8% Nickel (Ni), 71% Iron (Fe), 18% Chromium (Cr), and 0.2% Carbon (C). Nickel and chromium can induce hypersensitivity reactions in many individuals, not only in the oral cavity but also in other parts of the body. Hypersensitivity reactions are caused by nickel and chromium in 20% of females and 2% of males. [1, 2]

The use of fixed orthodontic appliances may lead to hypersensitivity reactions caused by chemical compounds released from the metal ions within brackets and wires. Chemical or electrochemical processes through metal exposed to natural elements like water and air can result in the dissolution of ions. This may lead to damage or weakening of orthodontic brackets and wires. The release of ions from orthodontic brackets within the oral cavity can have detrimental effects on health, such as hypersensitivity, toxic effects, and carcinogenic effects in the human body. [3]

Hypersensitivity reactions can be identified through intraoral examinations, manifesting as inflammation in the mucosa due to the release of Ni, Cr, and Fe ions associated with ion release from orthodontic materials. Long-term use of dental materials that come into direct contact with the oral cavity, especially metal materials in patients with burning mouth syndrome, was influenced by the pH concentration within saliva.

When in contact with high concentrations of Ni ions over an extended period of time, the metal ions within these materials were released and could result in severe toxic reactions. Symptoms frequently observed on the mucosa and hypersensitivity reactions due to the release of Ni, Cr, and Fe ions could lead to undesirable effects.[4]

Prevention and alternative treatments that can be considered to provide economical, safe anti-corrosion effects include products derived from plants (named as green corrosion inhibitor), such as traditional medicine, one of which is propolis. Propolis is a resinous substance collected by bees from the buds of leaves and the bark of trees. Propolis contains flavonoids, pinocembrin, galangin, and pinobanksin. Propolis has twelve flavonoids, one of which is chrysin. Chrysin is a natural and active component of flavonoids that possesses anti-inflammatory, anti-cancer, anti-allergic, and antioxidant properties.[5] The research conducted by Fouda stated that the anodic inhibition process, caused by adsorption, is a fundamental aspect of the phytochemicals present in propolis extract through oxygen atoms. Oxygen atoms found in flavonoids, phenolic acids, or oxygen atoms in the -OH group of kaempferol can protect the metal surface from ion release processes and form a protective layer to prevent ion release. Previous studies have examined the impact of propolis as a mouthwash on gingivitis in orthodontic appliance users, with a concentration of 8.2% being the most effective concentration in reducing the potential for gingivitis in orthodontic appliance wearers.[6]

METHODS

The type of research used in this study was laboratory experimentation with a randomized Post-Test Only Control Group Design. This research had obtained ethical approval from the Research Ethics Commission of the Faculty of Dentistry, Universitas Islam Sultan Agung of Semarang No 044/B.1-KEPK/SA-FKG/V/2016. The study involved conducting experiments on the release of metal ions (Ni, Cr, and Fe) in stainless steel metal brackets. The research groups consisted of four major groups, namely stainless steel metal brackets immersed in artificial saliva, 0.2% sodium fluoride, aquadest, and propolis solution. Propolis solution was designed and produced in the Pharmaceutical laboratory of Universitas Islam Sultan Agung.

The brackets were immersed in various solution for 28 days in a closed container and were placed inside an incubator with a temperature of 37°C.

The Ni, Cr, and Fe content in stainless steel metal brackets was measured using ICP-OES Perlun Elmer Optima 8300®.

This research used simple random sampling, with each group containing 6 samples of stainless steel metal brackets. The total number of samples used was 24 first premolar lower jaw brackets, selected using the Federer formula. The analysis of the research results involved calculating the amount of released and inhibited metal ions (Ni, Cr, and Fe) in the metal brackets using a Ratio scale. Data normality was tested using the Shapiro-Wilk test (since the sample size was less than 50). Homogeneity was assessed using the Levene's test, and the data were analyzed using non-parametric tests, specifically the Kruskal-Wallis test, followed by the Mann-Whitney test to determine differences between groups.

RESULTS

This study was conducted to determine the differences in the release of metal ions from stainless steel brackets that were immersed in artificial saliva, sodium fluoride, aquadest, and an 8.2% propolis solution. The measurement results using ICP-OES Perlun Elmer Optima 8300® yielded the following results: (Table1)

Table 1. The average measurement of metal ions release

Groups	Metal ions	After (mg/L)
Propolis 8,2%	Ni	0.0005±0.00033
	Cr	0.0019±0.0026
	Fe	0.014±0.0225
Sodium flouride	Ni	0.0013±0.00141
	Cr	0.0055±0.00486
	Fe	0.0695±0.06924
Aquadest	Ni	0.0131±0.00185
	Cr	0.0869±0.09662
	Fe	0.0773±0.06692
Artificial Saliva	Ni	0.0017±0.00097
	Cr	0.0088±0.01024
	Fe	0.0281±0.01024

Based on the research results that have been conducted, it was shown that there were changes in the release of metal ions (Ni, Cr, and Fe).

After immersion in artificial saliva, sodium fluoride, aquadest, and an 8.2% propolis solution, the highest and lowest metal ion (Ni, Cr, and Fe) release results were observed in the sterile distilled water (aquades) and 8.2% propolis solution groups. Subsequently, a Shapiro-Wilk test was conducted. (Tabel 2)

Tabel 2 Normality test using the Shapiro-Wilk test

Metal ions	Solution	Statistic	Df	Sig
Ni	Propolis	0.876	6	0.252*
	Sodium flouride	0.750	6	0.020
	Sterile Aquabides	0.932	6	0.524*
	Artificial Saliva	0.844	6	0.142*
CR	Propolis	0.627	6	0.001
	Sodium flouride	0.898	6	0.326*
	Sterile Aquabides	0.661	6	0.002
	Artificial Saliva	0.778	6	0.037*
Fe	Propolis	0.582	6	0.000
	Sodium flouride	0.756	6	0.023*
	Sterile Aquabides	0.897	6	0.375*
	Artificial Saliva	0.721	6	0.010

(*) = (p>0.05)

Table 3 Homogeneity test using Levene's test

	Levene's statistic	df1	df2	Sig
Ni	6.082	3	20	.021
Cr	5.133	3	20	.000
Fe	6.716	3	20	.009

From the normality test results using the Shapiro-Wilk method, p-values greater than 0.05 were obtained for all four groups. Therefore, it can be concluded that some groups had a normal distribution, as indicated by the Ni ion in the 8.2% propolis solution, aquadest, and artificial saliva groups (p>0.05), the Cr ion in the sodium fluoride and artificial saliva groups (p>0.05), and the Fe ion in the sodium fluoride and artificial saliva groups (p>0.05). However, some data did not have a normal distribution, such as the Cr ion in the 8.2% propolis solution and aquadest groups (p<0.05), and the Fe ion in the 8.2% propolis solution group (p<0.05).

Regarding the homogeneity test using Levene's test (Table 3), data variance that was not homogeneous was obtained (p<0.05), with p-values for Ni ion (0.021), Cr ion (0.000), and Fe ion (0.009) being less than 0.05. Therefore, to determine whether there were differences in the release of metal ions, a non-parametric test, namely the Kruskal-Wallis test, was conducted.

Table 4 The *Kruskal-Wallis* Test Result

	Ni	Cr	Fe
Chi-Square	16.603	15.5	11.443
Df	3	3	3
AsympSig.	0.001	0.001	0.01

The Kruskal-Wallis test (Table 4) yielded p-values of 0.001 for Ni ion, 0.001 for Cr ion, and 0.010 for Fe ion (p<0.05). Therefore, it can be concluded that there were differences in the release of Ni, Cr, and Fe ions in the 8.2% propolis solution, sodium fluoride, sterile distilled water (aquades), and artificial saliva.

Table 5 The Mann-Whitney Test Results

		Sodium flouride	Sterile Aquabides	Artificial Saliva
Propolis 8.2%	Ni	0.589	0.002*	0.002*
	Cr	0.065	0.002*	0.065
	Fe	0.026*	0.009*	0.041*
Sodium flouride	Ni		0.002*	0.240
	Cr		0.002*	0.818
	Fe		0.082	0.132
Aquadest	Ni			0.002*
	Cr			0.004*
	Fe			0.026*
* = Statistical significance (p<0.05)				

The Mann-Whitney test results (Table 5) revealed significant differences in Ni ion levels among the four groups (p<0.05). Therefore, it can be concluded that there were differences in the release of Ni ions between the 8.2% propolis solution and sterile distilled water (aquadest), the 8.2% propolis solution and artificial saliva, sodium fluoride and aquadest, and aquadest and artificial saliva. However, in the comparisons between the 8.2% propolis solution and aquadest and between sodium fluoride and artificial saliva, the Ni ion levels were relatively similar (p>0.05).

There were significant differences in Cr ion levels among the four groups ($p<0.05$). Therefore, it can be concluded that there were differences in the release of Cr ions between the 8.2% propolis solution and aquadest, sodium fluoride and aquadest, and aquadest and artificial saliva. However, in the comparisons between the 8.2% propolis solution and sodium fluoride and between sodium fluoride and artificial saliva, the Cr ion levels were relatively similar ($p<0.05$).

There were significant differences in Fe ion levels among the three groups ($p<0.05$). Therefore, it can be concluded that there were differences in the release of Fe ions between the 8.2% propolis solution and sodium fluoride, the 8.2% propolis solution and aquadest, and sodium fluoride and aquadest. However, in the comparisons between the 8.2% propolis solution and artificial saliva, sodium fluoride and artificial saliva, and aquadest and artificial saliva, the Fe ion levels were relatively similar ($p<0.05$).

DISCUSSION

The average results of testing the release of Ni, Cr, and Fe ions in the 8.2% propolis solution group, sodium fluoride, sterile aquabides, and artificial saliva were shown (Table 1). The highest release of Ni, Cr, and Fe ions was found in the immersion of sterile aquadest, while the lowest release was observed in the 8.2% propolis solution group. Nickel (Ni) in orthodontic brackets serves to enhance the strength and durability of the metal against ion release. When an excess of nickel components is present, it can lead to ion release from the brackets. The researchers found that the amount of Ni ions released was very low in all four research groups. They speculated that the relatively small amount of Ni content in the brackets had only a minor influence on the release of Ni ions.[7, 8]

Chromium (Cr) in orthodontic brackets, comprising 18-20% of the material, is essential for increasing the resistance to ion release. Cr ions on the metal's surface react with oxygen to form chromium oxide, which is resistant to oxidation. This study found that the release of Cr ions was the highest among Ni and Fe ions. The researchers hypothesized that Cr ions have passive surface oxide properties with self-repairing capabilities. Thus, if damage occurs to the metal's surface, it can quickly form a protective layer, making it resistant to ion release. This might explain why manufacturers potentially add an excessive amount of Cr components that do not conform to AISI standards, resulting in a relatively high release of Cr ions after conducting the research.[9]

The research revealed that the second-highest release of ions was for Fe ions after Cr ions. This is due to the fact that the production of stainless steel brackets contains a substantial 71% of iron, the largest component among the materials used (Oh, 2005). The researchers speculated that the relatively high release of Fe ions occurred because the brackets' material had a significant iron content, leading to a large release of Fe ions compared to Ni ions.[10]

Research by Palombo stated that propolis contains several minerals such as Mg, Ca, I, K, Na, Cu, Zn, Mn, Fe, and some vitamins B1, B2, B6, C, and E. The research findings on Ni ion content in the 8.2% propolis solution were relatively minimal compared to the Fe ions. This is because the propolis solution already contains Fe ions, and the addition of iron components in the bracket's composition slightly increased the Fe ion levels in the 8.2% propolis solution. However, the released Fe ions were not significantly higher than in the other research groups.[11]

Other metal ions present in propolis were also released, including Mg, Ca, I, K, Na, Cu, Zn, and Mn. According to Franz's research, the percentage of iron ions present in 100% propolis is 5%. The researchers speculated that different concentrations of propolis solutions might affect the levels of metal ions present. A higher concentration of propolis solution likely results in higher concentrations of contained ions.[12]

The research results indicated that the 8.2% propolis solution had the lowest release of Ni, Cr, and Fe ions compared to the control groups. This is because the propolis solution's components can form a coating agent, minimizing ion release compared to the control materials in this study. Fouda and Bard's research suggested that the adsorption process mechanisms in propolis extract involve phytochemical components with oxygen atoms or oxygen ring structures present in -OH groups in flavonoids and phenolic acids. These heteroatoms provide active sites for adsorption processes that form a coating agent on the metal's surface, protecting it from ion release.[13]

The research results showed that aquabides had the highest release of metal ions (Ni, Cr, and Fe) compared to the other groups. The highest levels were recorded for Cr ions (0.087 mg/L), followed by Fe ions (0.077 mg/L), and Ni ions (0.013 mg/L). Aquabides steril is water that has been purified from various minerals, making it pure and free from other contaminants. It is tightly sealed, with no expected contamination from microorganisms.

The researchers speculated that during the distillation of aquadest in glass containers, not all mineral content was filtered out. Therefore, when immersion was performed, the water's content of aquadest combined with the metal bracket's content (Ni, Cr, and Fe), resulting in a very high ion release.[14]

Orthodontic treatment over an extended period puts brackets in direct contact with the oral cavity, mediated by saliva. According to Gajapurada et al.'s research in 2016, the amount of Ni and Cr ions released after soaking for 45 days in artificial saliva was greater and higher. The research found that the release of ions soaked in artificial saliva showed an increase in Fe ions (0.0281 mg/L) and Cr ions (0.0088 mg/L). The researchers speculated that most of the mixed materials used in orthodontic equipment contain varying components of Ni, Cr, and Fe, and the type, brand, and weight of brackets also have differing components. Research by Siwy stated that there were differences in the release of Ni and Cr ions in several bracket brands soaked in artificial saliva for 30 days. The study showed that the highest release of Cr (0.027 ppm) and Ni (1.176 ppm) occurred in the GX brand (China).[15, 16] The highest and lowest metal ion (Ni, Cr, and Fe) releases in metal brackets were observed in the aquadest and 8.2% propolis solution groups. The release of Ni, Cr, and Fe in metal brackets immersed in an 8.2% propolis solution showed the lowest metal ion release compared to the other control materials. Therefore, the 8.2% propolis solution can be considered an alternative for inhibiting the corrosive rate which can be applied daily during orthodontic treatment

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