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Nickel and chromium ion release from stainless steel bracket on immersion various types of mouthwashes

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Abstract. The stainless steel bracket is widely used in orthodontics because of its mechanical properties, strength, and good biocompatibility. However, under certain conditions, it can be susceptible to corrosion. Studies have reported that the release of nickel and chromium ions because of corrosion can cause allergic reactions in some individuals and are mutagenic. The condition of the oral environment can lead to corrosion, and one factor that can alter the oral environment is mouthwash. The aim of this study was to measure the nickel and chromium ions released from stainless steel brackets when immersed in mouthwash and aquadest. The objects consisted of four groups of 17 maxillary premolar brackets with .022 slots. Each group was immersed in a different mouthwash and aquadest and incubated at 37 °C for 30 days. After 30 days of immersion, the released ions were measured using the ICP-MS (Inductively Coupled Plasma-Mass Spectrometer). For statistical analysis, both the Kruskal-Wallis and Mann-Whitney tests were used. The results showed differences among the four groups in the nickel ions released ($p < 0.05$) and the chromium ions released ($p < 0.5$). In conclusion, the ions released as a result of mouthwash immersion have a small value that is below the limit of daily intake recommended by the World Health Organization.

1. Introduction

In orthodontics, malocclusion can be treated using either removable or fixed appliances. The fixed orthodontic appliance is composed of a molar band, wire, and bracket. The bracket is an important element of the appliance because it determines the style of braces and will be in the oral environment for long periods of time. One of the commonly used metals in orthodontic brackets is stainless steel [1,2]. The world of dentistry began using stainless steel in 1919 and became widely used as a bracket material in the 1930s. Stainless steel is widely used in orthodontics because of its good mechanical properties, strength, good biocompatibility, can be forged relatively cheaply, and has good corrosion resistance. The most widely used type in the orthodontic field is the austenitic type of stainless steel, which is 18-8 containing 18-20% chromium and 8-10% nickel. The combination of chromium and nickel increases bracket resistance to corrosion [1-3]. However, stainless steel also has a deficiency, which is that certain conditions in the oral cavity such as changes in temperature, saliva, or plaque, and in pH due to the influence of food and beverages, and the use of toothpaste and mouthwash containing fluoride and chloride may cause corrosion [4].

Corrosion is a process of losing some element from metals. Signs of corrosion include subtle physical changes in metals such as color change and rough surface, and chemical changes resulting from the release of metal ions, known as corrosion products, in the surrounding solution [3,4]. The corrosion products released by stainless steel brackets are nickel, manganese, iron, chromium, and cuprum. Among these corrosion products, the release of nickel and chromium ions is most often studied because of their negative effects, which include allergies, dermatitis, gingivitis, and enamel staining, and they have been found to be mutagenic, carcinogenic, cytotoxic, and can cause DNA damage [5]. The oral environment is highly conducive to corrosion and can produce ion release because of the constantly wet mouth environment, constant temperature, and pH changes in the mouth. Changes in mouth pH may be influenced by mouth rinses containing fluoride and chloride, which causes the oral environment to become acidic and triggers the corrosion process that results in the release of ions [3,4].

The use of mouthwashes containing fluoride, chloride, or essential oils is sometimes recommended by orthodontists as adjunctive therapy to reduce the risk of caries and plaque formation and to overcome periodontal abnormalities such as gingivitis. Some studies mention that mouthwash has a good antimicrobial effect in orthodontic patients [6,7]. However, there is little research on the relationship between mouth rinses and stainless steel metal corrosion [8]. Therefore, the author was interested in conducting research on the effects of mouthwash on stainless steel brackets, as measured by the amount of nickel and chromium ions released when immersed in various types of mouthwash. Knowing the number of ions released could assist the practitioner in determining the appropriate mouthwash prescription, which could be beneficial to the patient.

2. Materials and Methods

This research was an experimental laboratory study. The materials used were stainless steel maxillary premolar brackets with .022 slots, with an MBT prescription of 3M brand Gemini type. The focus of this research was the solution resulting from the immersion of the stainless steel brackets in several types of mouthwash and Aquadest for 30 days. Mouthwashes used in this study were separated into four groups: Group A (Minosep 0.2%), Group B (Listerine), Group C (Pepsodent), and Group D (Aquadest). A total of 68 brackets were used in the study, divided into 4 groups of 17 brackets each. Each bracket was placed in a test tube, which was then capped and stored in an incubator at 37 °C for 30 days. After 30 days of immersion, the brackets were removed from the test tubes with non-metallic tweezers. The tweezers used were different for each solution to prevent concentration mixing. The test tubes were then centrifuged for approximately one minute to avoid deposits concentrating at the bottom of the tubes. The amount of nickel and chromium ions released was measured in each solution using ICP-MS. For this study, the minimum amount of nickel value considered significant was 0.150 ppb, and the value of chromium considered significant was0.167 ppb. The value obtained below this minimum threshold was0.The ANOVA test was performed when the distribution of data was normal. The Kruskal-Wallis test was performed when the data distribution is not normal. If the resulting data in this analysis was significant, then a post-hoc analysis was done to identify the significant group.

3. Results and Discussion

3.1 Results

After the data was obtained, the Kolmogorov Smirnov test for data normality was performed. The Kolmogorov-Smirnov test results for the assessment of nickel ions showed a distribution of normal data ($p > 0.05$) in group B with $p = 0.177$. The Kolmogorov-Smirnov test results for the assessment of chromium ions assessment showed a distribution of abnormal data ($p < 0.05$) in groups A, B, and C. The normality data test showed the distribution of normal and abnormal data in all groups; therefore, the data distribution was not normal. Because of the abnormal distribution of data, the non-parametric Kruskal-Wallis statistical test was used. In Table 1, the results for nickel and chromium ions released show a significance value of $p = 0.000$ and $p = 0.001$, $p < 0.05$. Thus, there was a difference among mouthwash Groups A, B, C, and Aquadest wash Group D in the amount of nickel and chromium ions released after soaking stainless steel brackets for 30 days.

Table 1. Kruskal-Wallis test results of nickel and chromium ions released from stainless steel brackets after 30-day immersion in Mouthwash Groups A, B, C, and Aquadest wash D

Ions	Groups	Mean ± SD	p-value
Nickel Ion	Group A	0 ± 0	0.000*
	Group B	22.63 ± 4.50	
	Group C	2.53 ± 1.33	
	Group D	0 ± 0	
Chromium Ion	Group A	2.91 ±5.27	0.001*
	Group B	7.15 ± 8.97	
	Group C	5.87 ± 7.41	
	Group D	0 ± 0	

In the Kruskal-Wallis test, the release of nickel ions was greatest in Group B (Listerine) compared with the other groups; whereas, the lowest release of nickel ions was produced in Group A (Minosep) and in Group D (Aquadest).The release of chromium ions had the highest value in Group B (Listerine) compared with other groups; whereas the lowest release of chromium ions was produced in Group D (Aquadest). Thus, Group B (Listerine) provided the highest value of nickel and chromium ions released, and Group D (Aquadest) provided the lowest value of nickel and chromium ions released. After the Kruskal-Wallis test, a post hoc Mann-Whitney test was performed to discover which groups had significant differences. In this test, the comparison was made between two sample groups. Table 2 show the results of the Mann-Whitney post hoc test on the release of nickel ions. Almost all group combinations showed significant differences, except between Groups A and D, which were not significantly different.

Table 2. The Mann-Whitney post hoc test results of nickel ion release

n	Mean ± SD (μg/l)	p-value		Result
Group A	17	0 ± 0		
Group B	17	22.63 ± 4.50	0.000*	B > A
Group A	17	0 ± 0		
Group C		2.53 ± 1.33	0.000*	C > A
Group A	17	0 ± 0		
Group D	17	0 ± 0	1.000	
Group B	17	22.63 ± 4.50		
Group C	17	2.53 ± 1.33	0.000*	B > C
Group B	17	22.63 ± 4.50		
Group D	17	0 ± 0	0.000*	B > C
Group C	17	2.53 ± 1.33		
Group D	17	0 ± 0	0.000*	B > C

Table 3 shows the results of the Mann-Whitney post hoc test on the release of chromium ions. Significant differences are seen between Groups A and D, with a value of p = 0.008; Groups B and D, with value of p = 0.000; and between Groups C and D ,with a value of p = 0.001.

Table 3. The Mann-Whitney Post Hoc test results of chromium ion release

n	Mean ± SD (µg/l)	p-value		Result
Group A	17	2.91 ± 5.27		
Group B	17	7.15 ± 8.97	0.080	
Group A	17	2.91 ±5.27		
Group C		5.87 ± 7.41	0.233	
Group A	17	2.91 ±5.27		
Group D	17	0 ± 0	0.008*	A>D
Group B	17	7.15 ± 8.97		
Group C	17	5.87 ± 7.41	0.580	
Group B	17	7.15 ± 8.97		
Group D	17	0 ± 0	0.000*	B>D
Group C	17	5.87 ± 7.41		
Group D	17	0 ± 0	0.001*	B>C

* p <0.05, significant difference

To determine the ratio of nickel to chromium ions released in each group, a comparative hypothesis test was conducted using the Mann-Whitney test on two unpaired groups (Table 4). Table 5 shows the discrepancies between nickel and chromium ions released, with a significance value of p = 0.008. The test also disclosed a significance value of p = 0.000 for Group B.

Table 4. Ratio of nickel to chromium ions dislodged from stainless steel brackets after30-day immersion in mouthwash Groups A, B, C, and aquadest

	Nickel	Chromium	p-value
Group A	0 ± 0	2.91 ± 5.27	0.008*
Group B	22.63±4.50	7.15 ± 8.97	0.000*
Group C	2.53±1.33	5.87 ± 7.41	0.742
Group D	0 ± 0	0 ± 0	1.000

3.2 Discussion

These mouthwash products were selected because they are widely marketed in Indonesia and are easily obtained by patients. These mouthwash selections also have active ingredients such as fluoride and chloride, which influence metal corrosion [4]. These products are also representative of each type of mouthwash, which are used for medication and health maintenance. Aquadest was used as the control group. This type of control group was also proposed by Park and Shearer (1983) and Schiff *et al.* (2005), who stated that in order to compare ion releases in different mouthwashes, the researcher should use a basic solution that does not affect the release of ions because the composition of artificial saliva could affect the end result [9,10]. This study also measured the pH of each mouthwash with a pH meter to better determine whether there was any effect on the pH of the mouthwash by the amount of metal ions released from the stainless steel brackets. The study found that Minosep 0.2% has a pH of 5.11; Listerine has a pH of 4.33; Pepsodent has a pH of 4.95; and Aquadest has a pH of 7.37.

This study used stainless steel maxillary premolar brackets with .022 slots, with an MBT prescription of 3M brand Gemini type. The type of stainless steel used in this brand is the SS 17-4. These brackets were chosen because they are widely circulated in Indonesia and the materials are considered to be of good quality. The reason for using the maxillary premolar bracket was so the bracket shape could be made uniform based on the bracket dimensions, thus eliminating any bias on the amount of metal ions are released. The stainless steel brackets were immersed in mouthwash for 30 days. The basis for this time frame rests on the assumption that an individual gargles twice a day, and the active components remain in the mouth for 30 minutes after each gargle. In some previous studies, the immersion time varied, as did the results of the research data. Danaei (2011) stated that the duration of a mouthwash component surviving in the oral cavity was difficult to determine [8]. The same was also found by Schmalz *et al* (2002) and Eliades *et al* (2004), observing that the values obtained in standard intersections vary. This occurs because of the characteristics of the metal sample [11,12].

After the research was completed, data showed that there was a release of metal ions in Groups A, B, and C and, therefore, that the corrosion process on the stainless steel brackets had occurred. As described by Eliades *et al* (2002) and Eliades *et al* (2004), corrosion is an electrochemical reaction on the metal surface in which the metal produces an ion release. Corrosion can be caused internally and externally. Internal factors that affect corrosion include metal composition and structures. External factors that could affect corrosion include the biological environment, the media of the metal, the pH, and the temperature [13,14]. The results of this study showed that Group B (Listerine) released the highest number of nickel and chromium ions. The average number of nickel ions released was 22.63±4.5 μg/l, and the average chromium ions released was 7.15±8.97 μg/l. Group D (aquadest) released the least nickel and chromium ions. The average release of nickel and chromium ions was 0±0 μg/l. The pH value for Group B was 4.33, and the pH value for Aquadest was 7.37. Group B had the lowest acidity level compared to the other groups, with aquadest having a neutral pH.

Based on the number of metal ions released, most came from Group B, followed by group C (Pepsodent), Group A (Minocep 0.2%), and the least number of metal ions came from Group D (Aquadest). These results reflect the influence of the mouthwash pH factors. The Listerine mouthwash had the lowest pH value when compared to that of Pepsodent and Minosep 0.2%, with a pH of 4.33, and to Group D, with the highest pH value of 7.37. This was in line with previous research, which mentions the effect of the solution pH on the amount of releases of metal ions produced [10,15-18]. In a study conducted by Huang TH, Yen CC and Kao CT (2004), they compared new and recycled brackets immersed in a solution with a pH of 4 and found that more nickel ions were released. As well, more chromium, iron, and manganese ions were released in solutions with a pH 7 or pH 10 [16]. This was in line with Weisman's (1968) study, which stated that acidity created a condition in which the oxide films contained in stainless steel became unstable, resulting in reduced corrosion resistance [19]. In the Huang *et al.* (2004) study, metal brackets immersed in a pH 4 solution released more ions when compared to that of metal brackets immersed in an artificial saliva solution with a pH of 7. In this study, the immersion was carried out for 48 weeks. The results of this study suggest that metal brackets used in orthodontic treatment will corrode under acidic conditions [16].

In a study conducted by Kuhta *et al*. (2009), the pH factor significantly affected ion release; more visible ions were released at pH 3.5 compared to pH 6.75 after a 28-day immersion. This research study can conclude, therefore, that there are some factors that significantly affect the release of metal ions from orthodontic appliances, including metal type, the pH of the immersion solution, and the duration of the immersion process. This study is in line with Huang et al. research hypothesis that low pH reduces metal resistance to corrosion [18]. The presence of fluoride could also contribute to the corrosion process, resulting in the release of metal ions. This is in accordance with the statement of Nakagawa, Matsuya and Udoh (2001) that in a corrosive acid environment, corrosive conditions would be more likely to occur even in low fluoride concentrations.20 Schiff (2005) mentioned that stainless steel brackets immersed in a stannous fluoride mouthwash with a pH of about 4.3 caused corrosion, indicated by the damage to the oxide layer protection seen using SEM and ion release analysis. This shows the effects of solution acidity and fluoride ions on bracket corrosion [10, 20]. Titanium is a good oxide film protector formed on metal surfaces, and the presence of fluoride ions in acidic environments could cause damage to the surface metal. Titanium is said to have higher corrosion resistance than chromium [1].

The Kruskal-Wallis test results showed a significant difference in the release of nickel and chromium ions in the three groups of mouthwashes and Aquadest. This was indicated by p-value <0.05. The Mann-Whitney test revealed that most groups had significant differences. The results obtained in this study differ from previous studies because the amount of metal ions produced bychlorhexidine 0.2% mouthwash is not as high as that found in Danaei *et al.* [8]. Of note, this study's results could not be compared directly with previous research because of the composition of the fluoride medium, the type of mouthwash used, and the immersion time. In the study done by Danaei *et al.* (2011), the chlorhexidine mouthwash used was composed of 0.2% chlorhexidine digluconate and 13.65% ethanol. Their research concluded that the corrosive effect of the mouthwash was highly dependent on the chemical structure of the mouthwash. This chemical structure later influenced the metal ion released from the brackets [8]. Another factor in previous research found that the composition and manufacturing process of stainless steel brackets may affect the amount of metal ions released. Von Fraunhofer (1997) discovered that the microstructure of metals is parameters that affect the mechanical and corrosion properties of a metal. The variation in the manufacturing processes and the polishing process after manufacture might affect the corrosive properties of orthodontic appliances [21].

Huang *et al.* (2001) concluded that the combination of bracket manufacturing and bracket composition had an effect on the release of nickel, chromium, iron, and manganese ions [15]. Similarly, the effect of the manufacture process on the amount of metal ions released was also studied by Haddad *et al.* (2009), comparing the amount of nickel and chromium ions released in different brackets. Haddad *et al.* (2009) concluded that the brackets made by different manufacturers provided different corrosion properties as well [22]. The main products released from stainless steel are iron, chromium, and nickel. Of the products released by stainless steel, nickel and chromium are often a major concern because of their potential to induce allergic, toxic, or carcinogenic reactions [23]. In this study, the release of nickel and chromium ions produced by the stainless steel bracket was not very large. The average amount of metal ions produced during immersion for 30 days was still well below the daily intake recommended by WHO. Of notable importance, however, are patients with a history of allergies. Although chromium ions might contribute to existing allergies, nickel ions most often cause allergies in patients. It has been reported that even a small amount of ionic release may contribute to allergic reactions. Low concentrations of soluble metal ions could affect the cells in mucous membranes if there has been direct contact with metals. Nickel ions released from metals can accumulate in cells and have a chemotaxis effect on leukocytes, alter DNA synthesis, and alter enzyme activity. The effects of low concentrations are still unclear, and there is no data on acceptable minimum levels of soluble metal ions [13,14].

When viewed with the results of different tests, the Group A mouthwash delivered significantly more chromium ion releases than nickel ions, with 2.91±5.27 μg/l for chromium ions and 0±0 μg/l for nickel ions. Group B released more nickel ions than chromium ions, with 22.63±4.50 μg/l for nickel ions and 7.15±8.97 μg/l for chromium ions. Mouthwash C also released more chromium ions than nickel ions, with 2.53±1.33 μg/l for chromium ions and 5.87±7.41 μg/l for nickel ions. Based on these results, the Group B mouthwash was released the highest amounts of nickel ions and chromium ions compared with the other groups. In this study, mouthwash in static conditions was controlled by the researchers, but the amount of ions released might be more in clinical conditions, where the corrosion in clinical conditions could be influenced by the consumption of low pH foods and drinks, plaque, saliva in the mouth, and the oxide layer which might be lost by mechanical factors such as brushing the teeth [21, 24]. This study found that the lowest pH mouthwash released the highest nickel and chromium ions, and stainless steel released nickel and chromium ions after corrosion. The problem with stainless steel bracket corrosion is the effect on patients with a history of allergies. In this study, it could be concluded that the number of ion releases resulting from immersion of Minosep 0.2% mouthwash, Listerine, Pepsodent is still within safe limits, and far from the maximum intake described by WHO recommendations. The recommended maximum limit is 200-300 µg for nickel and 50-200µg [11]. Orthodontists should remain cautious when giving instructions on the use of mouthwash to patients with a history of allergies, especially mouthwash with a low acidity level.

4. Conclusion
It can be concluded that the resulting ion release from brackets immersed in mouthwash has a small value that is below the limit of daily intake recommended by WHO.

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