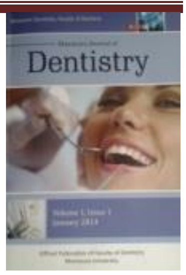

Experimental evaluation of pharmaceutical and prepared compounds as corrosion inhibitors for Copper nickel titanium orthodontic arch wire

Noha Ahmed Abou Mossalam * Essam El Saeid Al-Wakeel Abd El-Aziz El-Sayed Fouda *** Reham Mohamed Abdallah ******

** Dentist, Ministry of health, Mansoura, Egypt.*
*** Professor of Dental Biomaterials, Faculty of Dentistry, Mansoura University, Mansoura, Egypt.*
**** Professor of Physical Chemistry, Faculty of Science, Mansoura University, Mansoura, Egypt.*
***** Associate Professor, Dental Biomaterials Department, Faculty of Dentistry Mansoura University, Mansoura, Egypt.*

Abstract:

Purpose: Evaluation of pharmaceutical compounds (Ciprofloxacin, Clotrimazole, Chitosan) and prepared plant extracts (Clove, Thyme) as corrosion inhibitors for Cu Ni Ti orthodontic arch wire, in acidulated phosphate fluoride solution (APF) (0.5 % NaF + 0.17 % H_3Po_4) adjusted to pH of 3.5. simulating commercial fluoride containing products.
Materials and Methods: For corrosion testing, eighty specimens (10 mm in length) were investigated by pontiodynamic method (five specimens for 0.5% NaF (control group) and five specimens for different corrosion inhibitors). For Surface roughness and Scanning electron microscope examination, a representative samples from each group were investigated. ANOVA and Tukey tests were used to compare between groups at significant level ($p \leq 0.05$).
Results: Significant differences were found in means of corrosion resistance (I_{corr}), between different corrosion inhibitors (ciprofloxacin, clotrimazole, chitosan, clove, thyme) and control group.
Conclusion: The corrosion rate was significantly decreased by adding different corrosion inhibitors, indicating the formation of protective layer on the wire surface.
Keywords: Orthodontic arch wire; Corrosion; Corrosion inhibitor; Surface roughness.

Introduction

The oral cavity is considered as an aggressive environment to orthodontic appliances causing biodegradation of metals as a result of its thermal, ionic, microbiologic, and enzymatic activates. [1] Different alloys as stainless steel (SS), Cobalt-Chromium-Nickel and Titanium containing alloys; Nickel- Titanium (NiTi), Nickel-Titanium-Copper (CuNiTi) and Titanium Molybdenum alloy (TMA), are commonly used in orthodontic treatment. For corrosion resistance, all these alloys depend on the strong protective action of an oxide passive layer. That oxide passive protective film is severely affected by both chemical and mechanical disruption. [2]
Titanium containing wires exhibited good corrosion resistance compared with SS wire, due to the presence of oxide film which provides two actions: First, increasing the integrity of the surface oxide film by preventing the corrosion of the bulk metal. Second, creating a chemical and physical effective barriers that prevent the Ni ion oxidation. It had been concluded that the TiO_2 protective layer on the surface of NiTi wires is much stronger and protective to corrosion than the Cr_2O_3 layer of stainless steel wires.[3] A proved experimental results reveled that SS wires (typically containing 8% Ni) have higher Ni ion release more than NiTi and Cu NiTi arch wires (which have around 50% Ni).[4] Fluoride containing products are commonly used at home. The passive layer of the metal oxide surface can be deteriorated by the action of fluoride ions, as a result of decrease in the corrosion resistance of the alloy and hence its biocompatibility that was caused by hydrogen absorption.[5]

For corrosion prevention, isolation of the metal from corrosive media, is the primary strategy. The addition of a corrosion inhibitor is an effective method in achieving this goal. Corrosion inhibitor is a material added in a small amount to a solution, strongly increase the corrosion resistance of a metal exposed to that aggressive media. Corrosion inhibitor can be classified into two main types ; those increasing the formation of an effective protective oxide layer through an oxidizing effect and those selectively adsorbed on the metal surface resulting in corrosion inhibition and creating an effective barrier that prevents access of the corrosive media to the metal surface.[6] The presence of functional groups containing hetero-atoms (N,O,S etc), that can donate their lone pairs of electrons to metal surface. The selection of certain drugs to be used as corrosion inhibitors is relying on these facts: (a) the chemical structure of drug containing nitrogen, oxygen and sulphur as active sites, (b) drugs are proved to be friendly with the environment and involved in different biological reactions and (c) drugs can be produced easily and purified.[7]

In this study, five different corrosion inhibitors were investigated; ciprofloxacin, clotrimazole, chitosan, thyme and clove.

II. Materials and Methods

Rectangular Cu NiTi orthodontic arch wires with cross-sections of 0.019 x 0.025 inch were used in this study. The chemical composition of the wire is shown in Table 1.

Table 1: Types, composition and manufacturers of the orthodontic arch wires used in the study.

Wire	Composition (wt %)	Batch no.	Manufacturer
CuNiTi	49.1 % Ni, 45.7 % Ti, 0.2 % Cr, 5 % Cu	09A200A	Ormco Glendora, California

1. Corrosion testing

Eighty specimens (10 mm in length) were investigated by electrochemical pontiodynamic polarization method (five specimens for 0.5% NaF as a control group). Five inhibitor (ciprofloxacin, clotrimazole, chitosan, clove, thyme) was tested in three different concentrations (100 – 200 – 300 ppm). Electrochemical investigations were performed in conventional three-electrode electrochemical cell with a capacity of 100 ml. Saturated calomel electrode (SCE) and a platinum foil were used as reference and counter electrodes, respectively**.** The working electrode was in the form of 10 mm of the arch wire under investigation. A constant volume of the test solution (100 ml) was prepared in the glass cell. The potentiodynamic current-potential curves were recorded by changing the electrode potential automatically from -0.5 to +0.5 V with scan rate of $1 mVs^{-1}$ using an electrochemical measurement system. This included Gamry framework system based on the ESA400, and a personal computer with DC105, software. Echem analyst 5.58 software was used for plotting, graphing and fitting data. Prior to each run, the working electrode (sample) was cut and a new one was used after being abraded by different grades of emery papers, and washed by distilled water.

2. Surface roughness testing (AFM)

One representative specimen from each group was investigated by Atomic Force Microscope (nanosurf Flex AFM system Switzerland), The specimens were randomly divided into six groups, one representative specimen for each group, control group and five experimental corrosion inhibitor groups: ciprofloxacin- clotrimazole - chitosan- clove - thyme, after being immersed in different testing solution for one week using the highest concentration (300 ppm).

3. Scanning electron microscopy

Surface morphological changes were evaluated by Scanning electron microscope (JSM-6510LV, JEOL, USA) with magnification power of 5000. The specimen were coated using gold sputtering before imaging. The specimens were randomly divided into six groups, one representative specimen for each group, control group and five experimental corrosion inhibitor groups: ciprofloxacin- clotrimazole- chitosan- clove and thyme, after being immersed in different testing solution for one week using the highest concentration (300 ppm). Means and standard deviations of corrosion rate (tested by Potentiodynamic polarization) were calculated for each group. The data were analyzed using One-way followed by Tukey post-hoc test for determining significance differences among and within different groups ($p < 0.05$).

III. Results

A. Corrosion (Potentiodynamic polarization method)

Means and standard deviations of the I_{corr} (corrosion current density), that is directly proportional to the corrosion rate, for the investigated Cu NiTi wire in control and different corrosion inhibitor groups are shown in Table 2. The highest mean value of I_{corr} was found for control group (NaF) ($463.12 \times 10^{-4} \pm 29.9510^{-4} \mu A\ cm^{-2}$) and the lowest mean value was found for ciprofloxacin (300ppm) ($108.78 \times 10^{-4} \pm 13.72 \times 10^{-4} \mu A\ cm^{-2}$).

The results of post-hoc tukey test (Table.2) showed that there was significant difference in corrosion resistance (I_{corr}) between all the investigated corrosion inhibitor groups and the control one. For ciprofloxacin, clotrimazole, chitosan and thyme, there was a significant difference between all concentrations (100, 200 and 300 ppm). For clove group, there was no significant difference between concentrations 100 ppm and 200 ppm.

Table 2: Means, standard deviations of I_{corr} x 10^{-4} ($\mu A\ cm^{-2}$) of the CuNiTi wires in different media with different concentrations.

			Concentrations			
			Control	100 ppm	200 ppm	300 ppm
Cu Ni Ti	Ciprofloxacin	Mean	463.12 ^{a}	317.95 ^{b}	246.08 ^{c}	108.78 ^{d}
		±SD	29.95	25.73	40.03	13.72
	Clotrimazole	Mean	463.12 ^{a}	341.95 ^{b}	257.46 ^{c}	146.48 ^{d}
		±SD	29.95	32.62	32.36	22.75
	Chitosan	Mean	463.12 ^{a}	338.54 ^{b}	236.64 ^{c}	134.02 ^{d}
		±SD	29.95	35.05	31.99	24.07
	Clove	Mean	463.12 ^{a}	311.57 ^{b}	272.34 ^{b}	121.51 ^{c}
		±SD	29.95	33.34	23.85	10.84
	Thyem	Mean	463.12 ^{a}	361.52 ^{b}	251.19 ^{c}	137.73 ^{d}
		±SD	29.95	39.76	31.33	16.82

Means with different superscript letters are significantly different at $P \leq 0.05$

B. Surface roughness testing (AFM)

The surfaces of investigated arch wires were characterized by utilizing an atomic force microscope (AFM) that can give a three-dimensional image of surface topography **(Fig.1)**. The highest mean value of average surface roughness (S_a) was found for control group (83.98nm). The values of average surface roughness (S_a) were decreased to be (70.733nm- 787.69nm-61.284nm- 77.175nm-72.284nm) for Ciprofloxacin, Coltrimazol, Chitosan, Clove and Thyme groups, respectively.

C. Scanning electron microscop

Scanning electron micrographs of CuNiTi arch wire after immersion in the testing solutions are showen in **Fig.2**. SEM images proved that the surface morphology for tested arch wire in APF solution (control) with an apparent greater surface roughness and more complicated surface textures, arch wires exhibited scratches, pits and surface defects that may be resulted from the drawing of arch wire or electropolishing stapes during the manufacturing process. These surface defects became more accentuated and obvious after immersion in the APF solutions. On the other hand, SEM images of wire specimens in different corrosion inhibitor groups showed homogeneous protective coating on the metal surface**(Fig. 2 (b, c, d, e, f))**.

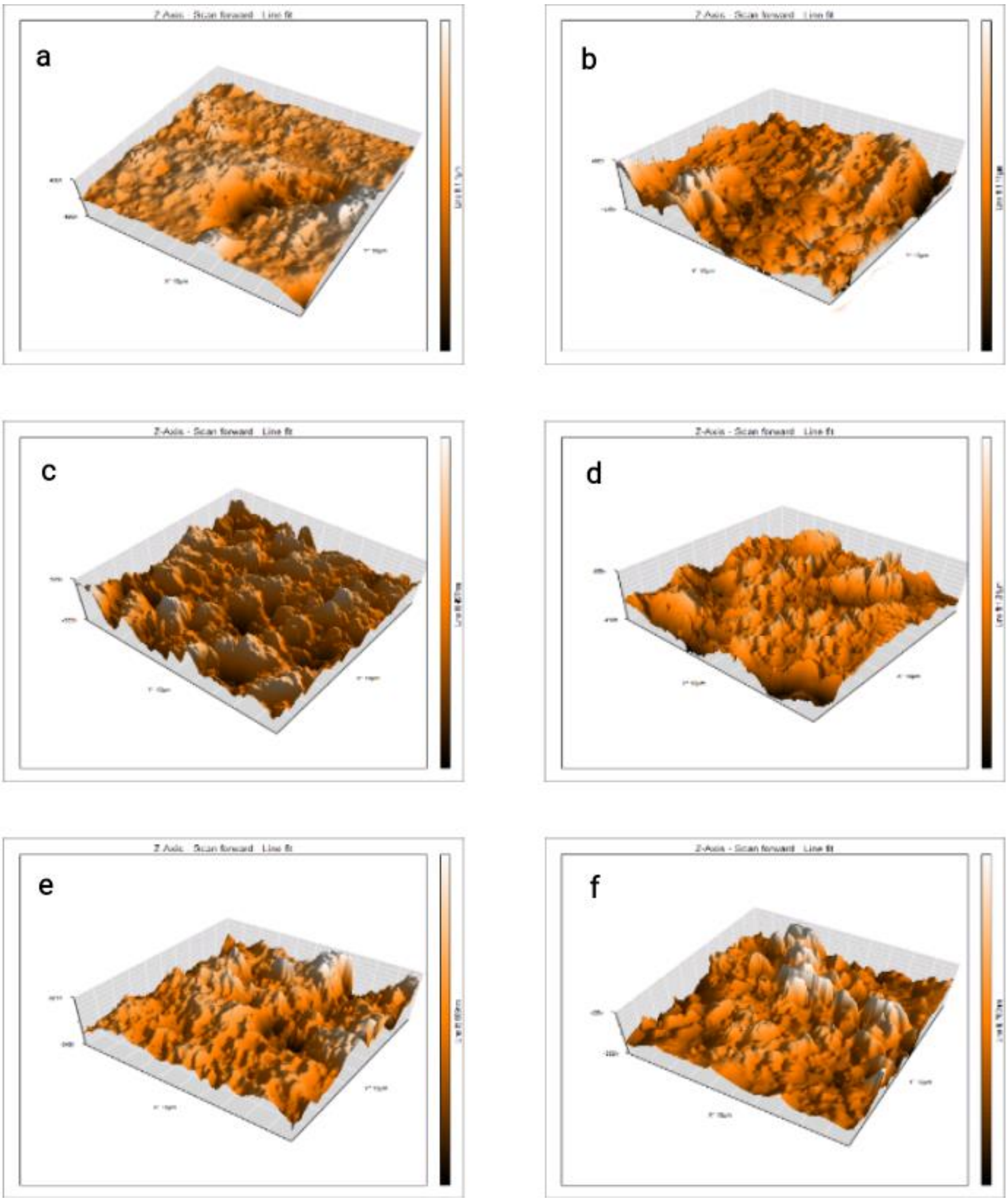

Fig. 1: AFM images of Cu NiTi arch wires after immersion in the testing solutions. a- Control b- Cipro c-Clotrmazol d-Chitosan e-Clove f- Thyme

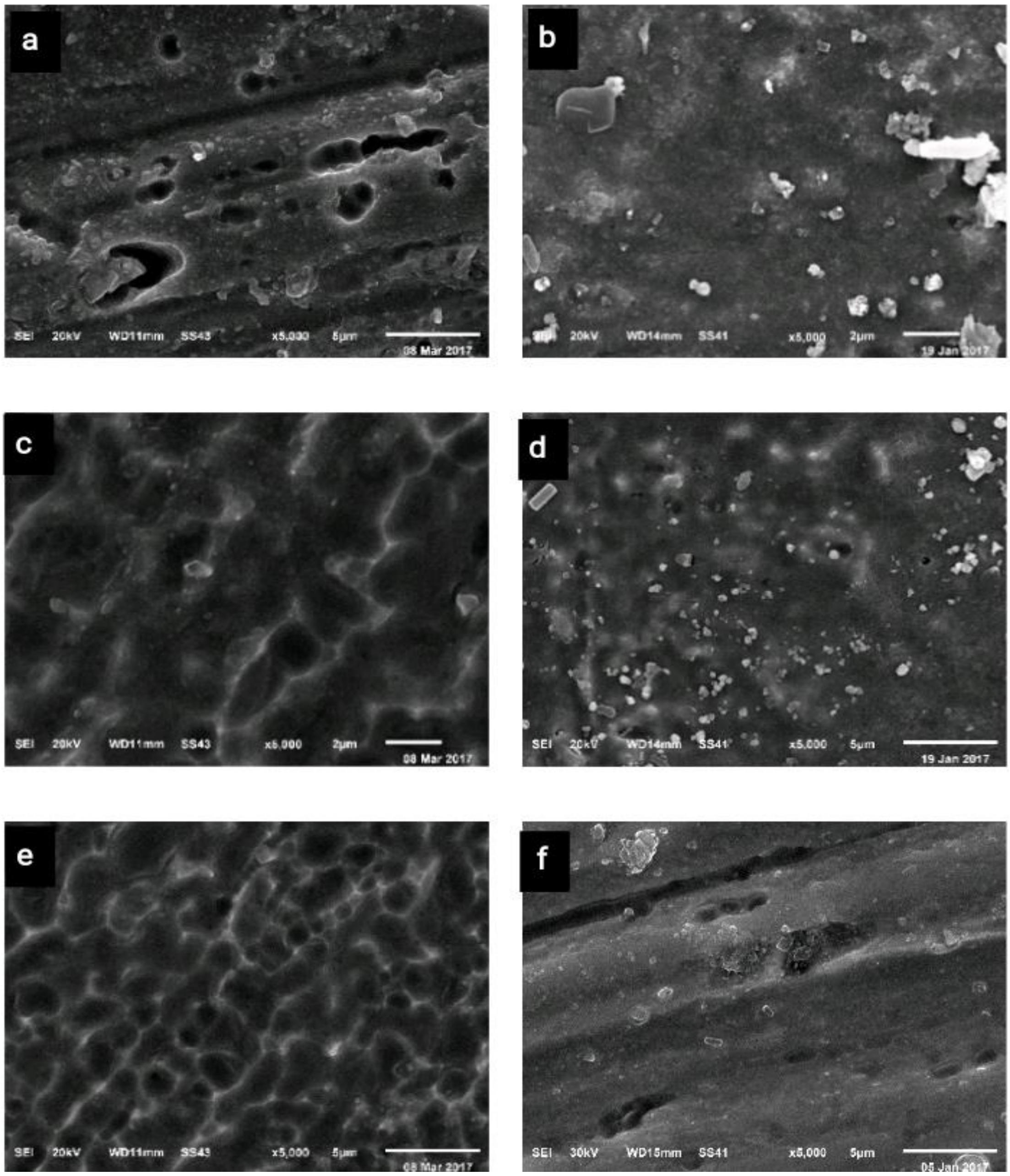

Fig.2: SEM images of Cu NiTi specimens after immersion in the testing solutions. a- Control b- Cipro c-Clotrmazol d-Chitosan e-Clove f- Thyme

IV. Discussion

The oral cavity is an aggressive environment that can enhances corrosion of orthodontic arch wires. Conditions, such as fluctuating temperature, variable (acidic) pH, mechanical stresses, plaque, proteins and oral flora can affect the corrosion processes. Fluoride-containing products is another contributor to acidic oral conditions, these substances have pH rang of 3.5 to 7.0 [8] commercial fluoride gels with more acidic pH were proved to be more potent in increasing the calcium fluoride (CaF2) formation[9].

The passive film of the oxide layer surface of orthodontic arch wires , can be severely affected by fluoride ions decreasing it's corrosion resistance and biocompatibility. Fluoride concentration [10], exposure time, and acidic pH[11].These interrelated factors promote the surface corrosion of orthodontic wires[12].

For corrosion prevention, corrosion inhibitor is added to the corrosive media that reacts with the metal surface forming a protective film on it. Luciane et al indicated that certain proteins in saliva can form a protective film on orthodontic wires on the oral cavity acting as corrosion inhibitor[13]. Effective corrosion inhibitors should contained functional groups (such as -OR, -OH, C=C-, -NR_2, -NH_2 and –SR). The functional groups provide electrons that help the adsorption of the inhibitor on the metal surface [14].

In the present study, rectangular Cu nickel titanium arch wires was used. It had cross-section of 0.019 ×0.025 inches, this was the largest common dimension available, and were chosen to maximize surface area for testing. The purpose of this study is to investigate corrosion inhibitory effect of some pharmaceutical and prepared compounds on Cu NiTi orthodontic arch wires in acidulated phosphate fluoride solution (0.5% NaF), simulating commercial fluoride-containing products.

A. Corrosion

Venith concluded that TiO_2-based passive film formed on titanium metal has better corrosion resistance in acidic artificial saliva than the Cr_2O_3-based passive film on SS[15].

This result was also agree with a previous study which has also found that Cr_2O_3 passive film is less corrosion resistant than TiO_2[16].

In case of Cu NiTi wire, the TiO2 passive film reacts with NaF to form titanium-fluoride complex compound[17].

$TiO2 + NaF \rightarrow Na2\ TiF6$

The corrosion resistance of CuNiTi was found to be inferior to that of NiTi wire. **Pun et al.,** found localized instability of the passive film of CuNiTi wire, with much more susceptibility to pitting corrosion. This may be attributed due to the presence of 6.5 % Cu[18]. Addition of copper (Cu) as a third element can improve some mechanical features of orthodontic nickel titanium arch wires, such as narrowing of stress hysteresis and a more stable stress-strain plateau. However, it was accompanied by an increase in the corrosion rat. **Kassab** revealed a lower corrosion resistance of CuNiTi in physiological medium[19]. Based on the results of corrosion testing, corrosion resistance of Cu NiTi was reduced in 0.5% acidulated phosphate fluoride solution (APF). This was attributed to the presence of fluoride ion and acidic conditions (pH3.5) that enhance break down of the oxide film[20].

By adding different concentrations of corrosion inhibitors the corrosion resistance or the two investigated wires increase indicating the presence of strong effective film on surface the wire.

B. Surface roughness AFM

There is positive correlation between corrosion of arch wires, Surface roughness and ion release in the oral environment[21]. Surface roughness may affect the biocompatibility of orthodontic arch wires[22]. In the current study the surfaces topography of investigated arch wires were characterized by using an atomic force microscope (AFM) which can provide a three-dimensional information of surface morphology[23]. A cleared surface morphology changes (severe corrosion) was evidenced for the control groups (high value of S_a), by adding the different corrosion inhibiters the values of Sa were reduced indicting the presence of strong effective protective film on surface of the metal this was in agreement with the results of Huang who observed sever corrosion on the NiTi arch wires surface immersed in higher fluoride-containing environments[24].

Scanning electron microscope

The Scanning electron microscope image for the investigated wire revealed that 0.5% acidulated phosphate fluoride solution with pH3.5 (control group) is an aggressive solution that make more destruction to the wire surface (oxide layer) . Arch wires exhibited scratches, pits and surface defects that may be resulted from drawing of arch wire or electropolishing procedures accompanied with the manufacturing process. By adding different corrosion inhibitors, it was found that nearly no corrosion products were present on the wire surface. The morphology is quite different such that the image was much more smooth than the control group.

References :

(1) McCann H C. "Inorganic components of salivary secretions," in Art and Science of Dental Caries Research, R. S. Harris, Ed., Academic press, New York, NY, USA,1968; 55-70.

(2) Huang H. Variation in corrosion resistance of nickel–titanium wires from different manufacturers. Angle Orthod 2005; 75: 661-665.

(3) Espinos JP, Fernandez A, Gonzalez-Elipe AR. Oxidation and diffusion processes in nickel-titanium oxide systems. Surf Scien1993; 295: 410-420.

(4) Suarez C , Vilar T, Sevilla P, Gil J. In Vitro Corrosion Behavior of Lingual Orthodontic Arch wires. Intern J Corros 2011; 111:1-9.

(5) Wang J, Li N, Rao G, Han EH, Ke W. Stress corrosion cracking of Ni–Ti in artificial saliva. Dent Mater 2007; 23: 133-137.

(6) Dyab M. New trends for corrosion inhibition of Carbon Steel in Petroleum field Lambert Academic Publishing . 2014; 130-136.

(7) Eddy N O, Stoyanov S R, Ebenso E E Fluoroquinolones as Corrosion Inhibitors for Mild Steel in Acidic Medium; Experimental and Theoretical Studies Int. J. Electrochem. Sci.2010; 5: 1127 - 1150.

(8) Toumelin- Chemla F, Rouelle F, Burdairon G. Corrosive properties of fluoride-containing odontologic gels against titanium. J Dent 1996; 24: 109-115.

(9) Muguruma T, Iijima M, Brantley WA, Yuasa T, Kyung H-M, Mizoguchi I. Effects of sodium fluoride mouth rinses on the torsional properties of miniscrew implants. Am J Orthod Dentofacial Orthop 2011;139: 588-593.

(10) Lee TH, Huang TK, Lin SY, Chen LK, Chou MY, Huang HH. Corrosion resistance of different nickel–titanium arch wires in acidic fluoride-containing artificial saliva. Angle Orthod 2010; 80: 547-553.

(11) Yokoyama K, Ogawa T, Asaoka K, Sakai J, Nagumo M. Degradation of tensile strength of Ni-Ti super elastic alloy due to hydrogen absorption in methanol solution containing hydrochloric acid. Mat Sci Eng 2003; 360: 153-159.

(12) Walker MP, White RJ, Kula KS. Effect of fluoride prophylactic agents on the mechanical properties of nickel-titanium-based orthodontic wires. Am J Orthod Dentofacial Orthop. 2005; 127: 662-669.

(13) Luciane Macedo de Menezes and Cátia Cardoso Abdo Quintão The Release of Ions from Metallic Orthodontic Appliances. semin Orthod 2010;16:282-292.

(14) Agrawal Y. K, J. D. Talati, M. D. Shah, M. N. Desai and N. K. Shah, Corros. Sci. 2003;46: 633- 642.

(15) Venith Jojee Pulikkottil , S Chidambaram,1 P. U. Bejoy, P. K. Femin, Parson Paul, Mohamed Rishad. Corrosion resistance of stainless steel, nickel-titanium, titanium molybdenum alloy, and ion-implanted titanium molybdenum alloy archwires in acidic fluoride-containing artificial saliva: An in vitro study. J Pharm Bioallied Sci. 2016; 8: 96-99

(16) Lin MC, Lin SC, Lee TH, Huang HH. Surface analysis and corrosion resistance of different stainless steel orthodontic brackets in artificial saliva. Angle Orthod. 2006;76:322–329

(17) Huang HH, Lee H, Huang TK, Lin SY, Chen LK, Chou MY. Corrosion resistance of different nickel – Titanium archwires in acidic fluoride containing artificial saliva. Angle Orthod. 2010;80:547-53.

(18) Pun DK, Berzins DW. Corrosion behavior of shape memory, superelastic, and non superelastic nickel–titanium-based orthodontic wires at various temperatures. Biomate J 2008; 24: 221-227.

(19) Kassab, E., Neelakantan, L., Frotscher, M., Swaminathan, S., Maaß, B., Rohwerder, M., Jockenhoevel, S., Gomes, J., Eggeler, G. Effect of ternary element addition on the corrosion behaviour of NiTi shape memory alloys. Mate Corr. 2014; 65: 18-22.

(20) Eliades T, Athanasiou AE. In vivo aging of orthodontic alloys: implications for corrosion potential, nickel release, and biocompatibility. Angle Orthod 2002; 72: 222-237.

(21) Hemand S, Puri BR. Text Book of Inorganic Chemistry. Trivandrum: New Jyothi Publication; 2007.

(22) Neeraj Kumar Guptaa, P.G. Joshia, Vandana Srivastavaa, M.A. Quraishia Chitosan: A macromolecule as green corrosion inhibitor for mild steelin sulfamic acid useful for sugar industry. International Journal of Biological Macromolecules. 2017;64:1-8.

(23) Rapiejko C, Fouvry S, Grosgogeat B, Wendler B. A representative fretting wear investigation of orthodontic arch wire/bracket contacts. J Dent Res 2009; 266: 850-858.