

Comparative Evaluation of Fluoride-releasing Properties in Nano-formulated and Conventional Glass Ionomer Cements: An In-vitro Study

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ABSTRACT

Introduction: Numerous efforts have been made to enhance the properties of Glass Ionomer Cements (GICs) using nanotechnology. One of the most advantageous properties of GICs is their ability to release fluoride.

Aim: To compare and evaluate the fluoride release in nano-formulated and conventional GICs.

Materials and Methods: This in-vitro study conducted at the Department of Pedodontics, Saveetha Dental College and Hospitals, Saveetha Institute of Medical and Technical Science, Saveetha University, Chennai, Tamil Nadu, India, assessed the influence of Chitosan-Titanium-Zirconia-Hydroxyapatite (Ch-Ti-Zr-HA) nanoparticles on the fluoride-releasing ability of GICs. A Ch-Ti-Zr-HA nano formulation was synthesised using a single-step, green-mediated process and was incorporated into GICs at concentrations of 3%, 5% and 10% (Groups I, II and III), with conventional GIC serving as the control (Group IV). Specimens from each group (n=30) were immersed in 10 mL of deionised water in sealed polyethylene vials. Fluoride release was measured using a fluoride Ion-Selective Electrode (ISE) in

combination with Total Ionic Strength Adjuster Buffer (TISAB). Measurements were taken at 24 hours, on the third, seventh, 14th and 28th days, using an ion analyser (Orion Star™ A214 pH/ISE Meter). Statistical analysis was performed using One-way Analysis of Variance (ANOVA), followed by Tukey's post-hoc test to determine significant differences between the groups.

Results: The nano-formulated GICs demonstrated higher fluoride release compared to conventional GICs at all time points. All samples initially showed high fluoride release, which gradually decreased over time. The total fluoride release increased from day 1 to day 28 across all concentrations of the nano-formulated GICs. Among these, the 10% concentration released a significantly greater amount of fluoride at every time point: 170.03±0.512 on day 1, 164.83±0.427 on day 3, 155.10±0.275 on day 7, 126.20±0.309 on day 14 and 76.16±0.107 on day 28, compared to the other groups (p-value <0.05).

Conclusion: In all the experimental groups, the addition of the nano formulation to the GICs had an accelerating effect on their fluoride-releasing property.

Keywords: Dental materials, Nanotechnology, Phytomedicine, Restorative dentistry

INTRODUCTION

The GIC is a self-adhesive restorative material that chemically combines fluoro-aluminosilicate glass powder with polyacrylic acid liquid. It has a wide range of applications in both adult and paediatric dentistry and is known for its strong anti-cariogenic properties. Fluoride, a key component, is an effective anti-cariogenic agent that helps reduce the risk of dental caries. Fluoride works by inhibiting the formation of the pellicle, suppressing microbial growth and metabolism and enhancing the remineralisation of tooth enamel [1]. The release of fluoride is a crucial factor in the efficacy of GICs, as it aids in preventing secondary caries and promoting the remineralisation of tooth structure. While conventional GICs are well-regarded for their ability to release fluoride over time, supporting oral health and reducing cavities, they have limitations in terms of fluoride release rates and long-term durability [2,3]. Over the years, manufacturers have modified the composition of GICs to improve their properties [4]. The development of nano-formulated GICs represents a significant step forward in dental material technology. By incorporating nanotechnology, these advanced formulations are designed to enhance fluoride release over an extended period, improve mechanical properties and increase the overall durability of the material [5]. Nano-sized particles are thought to provide better integration with the tooth structure and enable more controlled fluoride release, potentially overcoming some of the limitations seen with conventional GICs [6]. As a result, nano-formulated GICs

have emerged as a new category of materials, offering enhanced features, particularly in terms of fluoride release, compared to traditional GICs.

Plants have been used for medicinal purposes for centuries, a practice that persisted until the rise of modern chemistry in the 16th century. Phytomedicine, which involves the use of plant extracts and compounds, is considered to be minimally toxic [7]. To mitigate potential risks, green-mediated nanoparticles have been synthesised. Understanding the differences between these materials is essential for optimising restorative treatments and improving patient outcomes in clinical settings [8]. Recent studies have shown that incorporating nanoceramics, such as Hydroxyapatite (HA) and Zirconia (ZrO₂), synthesised using various soft chemistry methods to produce nanoscale particles, can enhance the properties of GIC [9,10]. More recently, combinations of nano-sized zirconia (ZrO₂) and HA-ZrO₂ have been explored to further strengthen GIC [11]. Zirconium and its oxide are known for their dimensional stability and toughness, comparable to stainless steel, making them useful for reinforcing brittle HA bio-glasses in biomedical applications [12]. Recent studies on HA-SiO₂-ZrO₂-enhanced GIC and Ch-Ti-Zr-HA-modified GIC have shown promising improvements in hardness [13] and color stability [14], though fluoride release remains a topic of concern. This large-scale comparative analysis aimed to evaluate the fluoride release capacity of green-mediated nano-formulated GICs in comparison to conventional GICs. The null hypothesis for the present study is that the nano-formulated GICs would not

have a significant impact on fluoride release when compared to conventional GICs.

MATERIALS AND METHODS

The present in-vitro study was conducted at the Department of Pedodontics, Saveetha Dental College and Hospitals, Saveetha Institute of Medical and Technical Science, Saveetha University, Chennai, Tamil Nadu, India. The study aimed to assess the fluoride-releasing properties of nano-formulated and conventional GICs. It was conducted over a period of one month, in May 2024. Ethical approval for the study was granted by the Institutional Review Board (IRB) under letter number (SRB/SDC/UG-1994/24/PEDO/331).

Inclusion and Exclusion criteria: The inclusion criteria for the study required the use of high-quality GIC samples, both conventional and nano-modified, in disk shape with uniform dimensions of 5 mm in diameter and 2 mm in thickness. The specimens were free from any visible defects such as cracks or porosities. The exclusion criteria included samples that displayed irregularities such as cracks, voids, or other defects during specimen preparation, or any contamination that could affect fluoride release. Additionally, any samples not adhering to the standard mixing procedures were excluded from the study to ensure consistency in the results.

Sample size calculation: Sample size estimation was performed using the GPower sample power calculator, which determined that a minimum of 30 samples per group would be required to achieve a 95% confidence interval and sufficient statistical power. This sample size was chosen to ensure robust data collection and to minimise the risk of statistical errors. Each group included three different concentrations of nano-modified GIC (3%, 5% and 10%), along with a control group of conventional GIC, ensuring that the study's findings would be statistically significant.

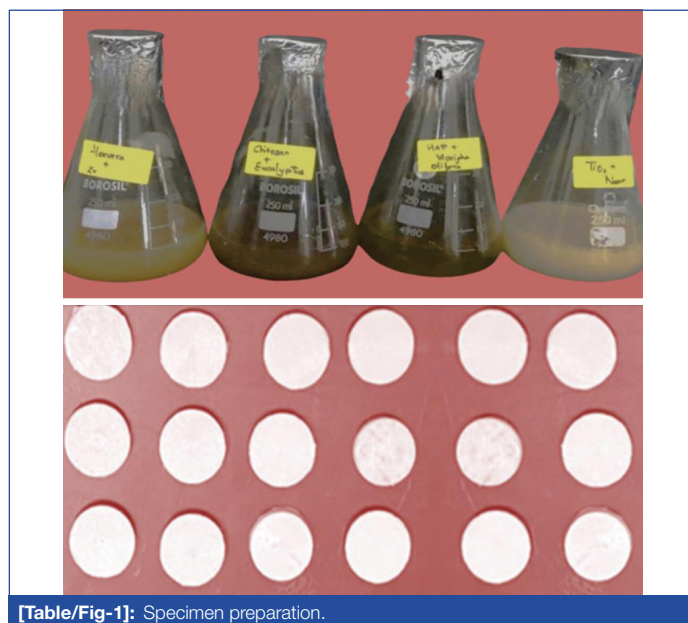
Study Procedure

Preparations of nanoparticles: To produce plant-derived nanoparticles, 50 mL of 1 g of eucalyptus was blended with 50 mL of 0.5 g of chitosan (dissolved in 0.5 g of glacial acetic acid and 49 mL of water) to yield chitosan nanoparticles [14]. For titanium oxide nanoparticles, 50 mL of 1 g of neem extract was mixed with 50 mL of 50 mM TiO_2 [15]. To make zirconium oxide nanoparticles, 50 mL of Aloe vera was combined with 50 mL of 20 mM zirconium oxide and heated overnight at 340-350°C [16]. A solution containing 50 mL of 1 g of *Moringa oleifera* was stirred with 50 mL of 0.1 g of hydroxyapatite (from eggshells) and orthophosphoric acid was added to maintain a 1.67 Ca/P ratio. Following centrifugation, the precipitate was subjected to calcination at 900°C to generate hydroxyapatite nanoparticles [14,17]. Using the one-pot synthesis method described by Rehman IA et al., the four solutions (Chitosan, Titanium, Zirconium and Hydroxyapatite) were combined, stirred at 80°C for 30 minutes, then treated with 1.08 mL of ethanol and refluxed for 90 minutes [18]. The mixture was then heated at 80°C for an additional 30 minutes to remove the ethanol, lyophilised at -92°C for 48 hours and powdered to obtain stable nanocomposites with preserved biochemical properties.

Preparation of Nano-modified GIC: The final nanocomposite solutions (Chitosan, Titanium, Zirconium and Hydroxyapatite) were incorporated into the powder component of GIC at concentrations of 3%, 5% and 10%, based on the methodology outlined in a previous study by Valanezhad A et al., categorised as Group I, Group II and Group III, respectively, with Group IV serving as the control (conventional GIC) [19]. The powder components were then mixed with a polyacrylic acid-based liquid to form the restorative cement.

Specimen preparation and Parameters studied: For each group, 30 disc-shaped samples were prepared. Nanocomposite (Chitosan, Titanium, Zirconia, Hydroxyapatite) was added to glass ionomer powder at concentrations of 3%, 5% and 10%. The mixture was

blended with the GIC liquid component (GC Corporation) using a plastic spatula until smooth. The paste was then placed in a metal mold with a diameter of 5 mm and a thickness of 2 mm. After setting, the samples were checked for porosity or cracks, finished, polished and stored at 37°C [Table/Fig-1].



[Table/Fig-1]: Specimen preparation.

A total of 10 mL of deionised water was poured into test tubes and the nanoformulated specimens (3%, 5% and 10%) as well as the unmodified specimen (control group) were immersed. The deionised water in each test tube was replaced after the 1st, 3rd, 7th, 14th and 28th days. Equal volumes of Total Ionic Strength Adjustment Buffer (TISAB III) were added to maintain the solution at a pH of 5.0, providing an ionic background and facilitating the decomplexation of fluoride.

A fluoride Ion-Selective Electrode (ISE) (Orion Star™ A214 pH/ISE Meter) was employed to measure the release of fluoride after the 1st, 3rd, 7th, 14th and 28th days [Table/Fig-2]. Analysis was carried out using a pre-calibrated ion analyser (calibrated to 0.20, 1.00, 2.00, 10.00, 20.00 and 100 ppm F containing a standard fluoride ion solution). The analysis was performed on the specified days after buffering the 10 mL test solutions with 1 mL of TISAB III (Total Ionic Strength Adjustment Buffer, Orion, MA, USA).



[Table/Fig-2]: Assessment of fluoride release using ion selective electrode analyser.

Time-dependent variations in the fluoride release concentration were assessed. At each interval (1st, 3rd, 7th, 14th and 28th days),

data on the total amount of fluoride (ppm) released were recorded and tabulated.

STATISTICAL ANALYSIS

Data were tabulated and analysed using Statistical Package for Social Sciences (SPSS) software version 22.0 (IBM Corp.). Statistical analysis was performed using Analysis of Variance (ANOVA) followed by Tukey's Honestly Significant Difference (HSD) post-hoc test, with significance set at p-value <0.05.

RESULTS

The fluoride ion release profiles for all groups were monitored over a 28-day period, with measurements taken at five specific intervals. The fluoride release was quantified in parts per million (ppm). A comparison of the data revealed that the nano-formulated GIC released significantly higher amounts of fluoride compared to the conventional GIC (control group) (p-value <0.05) [Table/Fig-3]. The highest fluoride release occurred on the first day for all groups, followed by a gradual decline in fluoride levels over the 28-day period [Table/Fig-4]. Among the various concentrations tested, the

Groups	Days (Mean±SD) ppm				
	Day 1	Day 3	Day 7	Day 14	Day 28
3%	129.04±0.146	94.28±0.194	78.16±0.149	68.15±0.151	44.18±0.183
5%	153.96±1.015	126.10±0.109	98.430±0.408	70.36±0.512	54.75±1.172
10%	170.03±0.512	164.83±0.427	155.10±0.275	126.20±0.309	76.16±0.107
Control	117.11±0.098	48.13±0.073	40.18±0.164	31.15±0.204	24.05±0.151
p-value amongst groups	0.001*	0.001*	0.001*	0.001*	0.001*

[Table/Fig-3]: Overall comparison of fluoride release for nano-formulated GIC and conventional GIC.

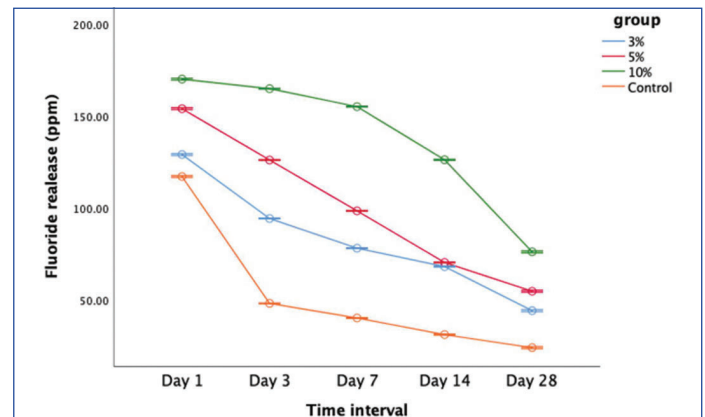
*statistically significant value of p<0.05; SD: Standard deviation; p-value was derived from One-way ANOVA test

Groups	Time interval (day)	Mean±SD	Std. Error	95% CI		p-value
				Lower bound	Upper bound	
3%	Day 1	129.045±0.146	0.059	128.891	129.198	0.001*
	Day 3	94.283±0.194	0.079	94.079	94.487	
	Day 7	78.161±0.149	0.061	78.004	78.318	
	Day 14	68.150±0.151	0.061	67.990	68.309	
	Day 28	44.183±0.183	0.074	43.990	44.375	
5%	Day 1	153.966±1.015	0.414	152.901	155.032	0.001*
	Day 3	126.100±0.109	0.044	125.985	126.215	
	Day 7	98.433±0.408	0.166	98.004	98.861	
	Day 14	70.366±0.512	0.209	69.828	70.904	
	Day 28	54.750±1.172	0.478	53.519	55.980	
10%	Day 1	170.033±0.512	0.209	169.495	170.571	0.001*
	Day 3	164.833±0.427	0.174	164.384	165.281	
	Day 7	155.100±0.275	0.112	154.810	155.389	
	Day 14	126.200±0.309	0.126	125.874	126.525	
	Day 28	76.166±0.107	0.044	76.053	76.279	
Control	Day 1	117.116±0.098	0.040	117.013	117.219	0.001*
	Day 3	48.135±0.073	0.030	48.057	48.212	
	Day 7	40.186±0.164	0.066	40.014	40.358	
	Day 14	31.151±0.204	0.083	30.937	31.366	
	Day 28	24.051±0.151	0.061	23.893	24.210	

[Table/Fig-4]: Comparison of fluoride releasing capacity within the group-based on time interval.

*statistically significant value of p<0.05; SD: standard deviation; p-value was derived from One-way ANOVA test

10% nano-formulated GIC exhibited the highest fluoride release at all time points throughout the study [Table/Fig-5]. The pair-wise comparison further highlighted that Group III (10%) consistently released significantly more fluoride than the other groups. In contrast, the control group, which used conventional GIC, showed the lowest fluoride release levels across all intervals [Table/Fig-6]. Additionally, statistical analysis demonstrated that all the differences across the groups for each concentration and time point were significant, as



[Table/Fig-5]: Fluoride release of nano-formulated GIC and conventional GIC over time.

Time interval	Pair-wise comparison	MD	SE	95% Confidence Interval		p-value
				Lower bound	Upper bound	
Day 1	3% vs 5%	-24.921	0.332	-25.85	-23.99	0.001*
	3% vs 10%	-40.988	0.332	-41.91	-40.05	0.001*
	3% vs control	11.928	0.332	10.99	12.85	0.001*
	5% vs 10%	-16.066	0.332	-16.99	-15.13	0.001*
	5% vs control	36.850	0.332	35.92	37.77	0.001*
	10% vs control	52.916	0.332	51.98	53.84	0.001*
Day 3	3% vs 5%	-31.816	0.140	-32.21	-31.42	0.001*
	3% vs 10%	-70.550	0.140	-70.94	-70.15	0.001*
	3% vs control	46.1483	0.140	45.75	46.54	0.001*
	5% vs 10%	-38.733	0.140	-39.12	-38.33	0.001*
	5% vs control	77.965	0.140	77.57	78.35	0.001*
	10% vs control	116.698	0.140	116.30	117.09	0.001*
Day 7	3% vs 5%	-20.271	0.155	-20.70	-19.83	0.001*
	3% vs 10%	-76.938	0.155	-77.37	-76.50	0.001*
	3% vs control	37.975	0.155	37.53	38.41	0.001*
	5% vs 10%	-56.666	0.155	-57.10	-56.23	0.001*
	5% vs control	58.246	0.155	57.81	58.68	0.001*
	10% vs control	114.913	0.155	114.47	115.34	0.001*
Day 14	3% vs 5%	-2.216	0.187	-2.74	-1.69	0.001*
	3% vs 10%	-58.050	0.187	-58.57	-57.52	0.001*
	3% vs control	36.998	0.187	36.47	37.52	0.001*
	5% vs 10%	-55.833	0.187	-56.35	-55.30	0.001*
	5% vs control	39.215	0.187	38.68	39.74	0.001*
	10% vs control	95.048	0.187	94.52	95.57	0.001*
Day 28	3% vs 5%	-10.566	0.346	-11.53	-9.59	0.001*
	3% vs 10%	-31.983	0.346	-32.95	-31.01	0.001*
	3% vs control	20.131	0.346	19.16	21.10	0.001*
	5% vs 10%	-21.416	0.346	-22.38	-20.44	0.001*
	5% vs control	30.698	0.346	29.72	31.66	0.001*
	10% vs control	52.115	0.346	51.14	53.08	0.001*

[Table/Fig-6]: Pair-wise comparison of fluoride release among nano-modified groups and control group.

*statistically significant value of p<0.05, MD: Mean difference; SE: Standard error; p-value was derived from multiple comparison Tukey HSD test

indicated by the p-values (0.001*), suggesting that fluoride release varied significantly over time in each group [Table/Fig-7]. These findings suggest that the incorporation of nanocomposites into GIC enhances fluoride release, potentially offering greater long-term therapeutic benefits compared to traditional GIC formulations.

Groups	Pair-wise comparison	MD	SE	95% Confidence interval		p-value
				Lower bound	Upper bound	
3%	Day 1 vs day 3	34.761	0.095	34.479	35.043	0.001*
	Day 1 vs day 7	50.883	0.095	50.601	51.165	0.001*
	Day 1 vs day 14	60.895	0.095	60.613	61.176	0.001*
	Day 1 vs day 28	84.861	0.095	84.579	85.143	0.001*
	Day 3 vs day 7	16.121	0.095	15.839	16.403	0.001*
	Day 3 vs day 14	26.133	0.095	25.851	26.415	0.001*
	Day 3 vs day 28	50.100	0.095	49.818	50.381	0.001*
	Day 7 Vs day 14	10.011	0.095	9.729	10.293	0.001*
	Day 7 vs day28	33.978	0.9595	33.696	34.260	0.001*
	Day 14 vs day 28	23.966	0.095	23.684	24.248	0.001*
5%	Day1 vs day 3	27.866	0.435	26.587	29.146	0.001*
	Day 1 vs day 7	55.533	0.435	54.253	56.812	0.001*
	Day 1 vs day 14	83.600	0.435	82.320	84.879	0.001*
	Day 1 vs day 28	99.216	0.435	97.937	100.496	0.001*
	Day 3 vs day 7	27.666	0.435	26.387	28.946	0.001*
	Day 3 vs day 14	55.733	0.435	54.453	57.012	0.001*
	Day 3 vs day 28	71.350	0.435	70.070	72.629	0.001*
	Day 7 vs day 14	28.066	0.435	26.787	29.346	0.001*
	Day 7 vs day 28	43.683	0.435	42.409	44.962	0.001*
10%	Day 14 vs day 28	15.616	0.435	14.337	16.896	0.001*
	Day1 vs day 3	5.200	0.204	4.598	5.801	0.001*
	Day 1 vs day 7	14.933	0.204	14.332	15.534	0.001*
	Day 1 vs day 14	43.833	0.204	43.232	44.434	0.001*
	Day 1 vs day 28	93.866	0.204	93.265	94.468	0.001*
	Day 3 vs day 7	9.733	0.204	9.132	10.334	0.001*
	Day 3 vs day 14	38.633	0.204	38.032	39.234	0.001*
	Day 3 vs day 28	88.666	0.204	88.065	89.268	0.001*
	Day 7 vs day 14	28.900	0.204	28.298	29.501	0.001*
Control	Day 7 vs day 28	78.933	0.204	78.332	79.534	0.001*
	Day 14 vs day 28	50.033	0.204	49.432	50.634	0.001*
	Day1 vs day3	68.981	0.084	68.734	69.229	0.001*
	Day 1 vs day 7	76.930	0.084	76.682	77.177	0.001*
	Day 1 vs day 14	85.965	0.084	85.717	86.212	0.001*
	Day 1 vs day 28	93.065	0.084	92.817	93.312	0.001*
	Day 3 vs day 7	7.948	0.084	7.700	8.196	0.001*
	Day 3 vs day 14	16.983	0.084	16.735	17.231	0.001*
	Day 3 vs day 28	24.083	0.084	23.835	24.331	0.001*
	Day 7 vs day 14	9.035	0.084	8.787	9.282	0.001*
	Day 7 vs day 28	16.135	0.084	15.887	16.382	0.001*
	Day 14 vs day 28	7.100	0.08433	6.852	7.347	0.001*

[Table/Fig-7]: Pair-wise comparison on time interval of fluoride releasing capacity for each group.

*statistically significant value of $p < 0.05$, MD: Mean difference; SE: Standard error; p-value was derived from multiple comparison Tukey HSD test

DISCUSSION

In recent years, there has been growing interest in the fluoride-releasing properties of dental materials, especially GICs. Nano-formulated GICs have emerged as a promising alternative to traditional GICs, with claims of improved performance due to the integration of nanotechnology [20]. Conventional GICs have

been widely recognised for their ability to release fluoride, which plays a key role in preventing secondary caries and aiding in the remineralisation of tooth structure. These materials gradually release fluoride ions over time, providing ongoing protection. However, the rate and total amount of fluoride release are often constrained by the formulation of the material and the physical properties of the glass particles used in the cement [21].

In contrast, nano-formulated GICs incorporate nanoparticles, typically on the scale of nanometers, to enhance the material's performance [22]. These nanoparticles are thought to increase the surface area available for fluoride release, potentially improving both the rate of release and the duration of its effects. Studies suggest that nano-GICs may offer superior fluoride-releasing capabilities compared to conventional GICs, thanks to the more efficient distribution of fluoride within the material matrix [23,24].

Chitosan nanoparticles, commonly used as drug delivery agents, are favoured for their higher solubility, low toxicity and controlled release properties [25]. Titanium nanoparticles, known for their strength, light weight, excellent corrosion resistance and biocompatibility, make them valuable for various applications [26]. Additionally, the incorporation of zirconia and hydroxyapatite in GICs enhances not only their mechanical properties but also their biological activity [27].

In the present study, nano-formulated GIC demonstrated significantly higher fluoride release compared to conventional GIC, supporting the findings of several previous studies. Nishanthine C et al., reported that the addition of chitosan to the glass ionomer liquid accelerated its fluoride-releasing properties [28], a result that aligns with the findings of this study. Similarly, Patel A et al. observed that chitosan-modified Resin-Modified GIC (RMGIC) released more fluoride than conventional RMGIC after 15 and 30 days [29]. The results of the present study also corroborate the work of Senthil Kumar R et al., who found that nanochitosan-modified GIC exhibited higher fluoride release at one hour, 24 hours and seven days [30]. In accordance with this, Morales-Valenzuela AA et al. demonstrated that the incorporation of TiO_2 nanoparticles enhanced fluoride release in glass ionomers, a finding consistent with our study [26]. Panigrahi A et al. reported that hydroxyapatite-incorporated GIC, like the one tested in the present study, effectively took up and released fluoride, similar to conventional GIC [31]. Additionally, Kukreja R et al. observed that while both conventional GIC and Zirconomer released fluoride, Zirconomer exhibited significantly higher fluoride release at all time intervals [32].

In the present study, the combination of all four nanoparticles tested at various concentrations resulted in the highest fluoride release on day 1. This rapid release is likely linked to the "burst phenomenon," commonly observed in GICs, where a large amount of fluoride is released during the initial setting period [33]. This burst release is attributed to the setting reaction of GICs [34] and the results of the present study are in agreement with previous studies by Neelakantan P et al., who also reported high fluoride release during the first day. This initial surge in fluoride may have beneficial biological and bactericidal effects immediately after the restoration [35]. Following this initial release, a decline in fluoride release was observed during the first week, which then stabilised after approximately three weeks. This pattern of fluoride release is consistent with findings from other studies, all of which reported a similar trend, with GIC showing the highest fluoride release on the first day, followed by a gradual tapering off and stabilisation over several weeks [36-38].

There was a statistically significant difference in fluoride release among the groups, with the nano-formulated GIC showing the highest fluoride release. This increased fluoride release is likely due to its higher fluoride content and greater water uptake. The most substantial fluoride release occurred in the first week, with the highest rate of release observed within the first 24 hours. In

contrast, conventional GIC released a relatively lower amount of fluoride, ranging from 20 to 50 ppm over the same period.

The fluoride release process is complex and influenced by various intrinsic and environmental factors, including the composition of the organic matrix and fillers, the method of manipulation, solubility, porosity, surface area and pH [39]. For all the samples tested, the fluoride release was highest on the first day, followed by a gradual decline in the subsequent days, stabilising by day 30. Fluoride release from GIC follows two main mechanisms: a rapid short-term release, where fluoride dissolves quickly from the surface and a sustained long-term release, driven by ionic diffusion. After the initial burst, fluoride release slows down, with a sustained release occurring over time. The overall amount of fluoride released in the short term is primarily controlled by diffusion, accompanied by a decreasing concentration gradient [40].

While the anticaries effect of fluoride has been well studied, there is no consensus in the literature on the minimum amount of fluoride release required to effectively prevent secondary caries. In the present study, ISE potentiometer devices were used to ensure that the fluoride analysis methods adhered to universal standards, offering an easily accessible and reliable means of detection.

Overall, the addition of nanofillers to GIC significantly accelerated fluoride release over the 30-day period. Among the different groups tested, the 10% nano-modified GIC consistently released the highest fluoride levels at all time intervals. The enhanced fluoride release from the inorganic matrix was facilitated by reinforced complexes, where polyacrylic acid adsorbed onto the Ch-Ti-Zr-HA nanoparticles, which then attached to the GIC particles. Materials with high fluoride release can be advantageous in preventing secondary caries. However, when comparing fluoride release between nano-formulated and conventional GICs, various factors need to be considered, including testing conditions, the presence of fillers, the type of acid used in the setting reaction and storage conditions.

In conclusion, both nano-formulated and conventional GICs offer distinct advantages in fluoride release, with nano-GICs potentially providing superior performance. Comparative studies like these are essential for optimising material choices in clinical applications, ensuring patients receive the most effective fluoride protection possible.

Limitation(s)

The present study was limited by its in-vitro design and therefore, the fluoride release behaviour observed may not fully replicate the complex conditions found in the oral environment, such as variations in temperature, pH and the presence of saliva. Additionally, the study only assessed fluoride release over a 28-day period, which may not fully capture long-term release patterns. Therefore, future clinical trials should evaluate the long-term fluoride release behaviour.

CONCLUSION(S)

The fluoride estimation results demonstrate that the 10% nano-formulated GIC exhibits a high fluoride release capacity. The present study clearly shows that incorporating nanoparticles enhances the fluoride-releasing properties of glass ionomer cements. Nanoparticles may modify the cement matrix structure, facilitating more efficient fluoride ion diffusion. Overall, the nano-formulated GIC proves to be more effective than conventional GIC. However, further in-vivo studies are required to confirm and validate these findings.

REFERENCES

- [1] Wiegand A, Buchalla W, Attin T. Review on fluoride-releasing restorative materials fluoride release and uptake characteristics, antibacterial activity and influence on caries formation. *Dent Mater*. 2007;23(3):343-62.
- [2] El-Adl ET, Ebaya MM, Habib EE, Zaghloul NM. Comparative measurement of short-term fluoride release and inhibition of caries around restoration by ion releasing restorative materials: An in-vitro study. *Sci Rep*. 2025;15(1):1600.
- [3] Ganesh S, Paulraj J, Maiti S, Shanmugam R. Surface roughness and wettability of green-mediated titanium, zirconium, and hydroxyapatite nanocomposite-based glass ionomer cement under toothbrushing simulation: An in-vitro study. *Int J Prosthodont Restor Dent*. 2024;14(1):30-38.
- [4] Frencken JE. Atraumatic restorative treatment and minimal intervention dentistry. *Br Dent J*. 2017;223(3):183-89.
- [5] Rix D, Foley TF, Banting D, Mamandras A. A comparison of fluoride release by resin-modified GIC and polyacid-modified composite resin. *Am J Orthod Dentofacial Orthop*. 2001;120(4):398-405.
- [6] Shashirekha G, Jena A, Mohapatra S. Nanotechnology in dentistry: Clinical applications, benefits, and hazards. *Compend Contin Educ Dent*. 2017;38(5):e1-e4.
- [7] Sherief DI, Fathi MS, Abou El Fadl RK. Antimicrobial properties, compressive strength and fluoride release capacity of essential oil-modified glass ionomer cements-an in-vitro study. *Clin Oral Investig*. 2021;25(4):1879-88.
- [8] Jingarwar MM, Pathak A, Bajwa NK, Sidhu HS. Quantitative assessment of fluoride release and recharge ability of different restorative materials in different media: An in-vitro study. *J Clin Diagn Res*. 2014;8(12):ZC31-ZC34.
- [9] Shiekh RA, Rahman Ab I, Masudi SM, Luddin N. Modification of glass ionomer cement by incorporating hydroxyapatite-silica nano-powder composite: Sol-gel synthesis and characterization. *Ceram Int*. 2014;40:3165-70.
- [10] Aldhuwayhi SD, Sajjad A, Bakar WZW, et al. Evaluation of fracture toughness, color stability, and sorption solubility of a fabricated novel glass ionomer nano zirconia-silica-hydroxyapatite hybrid composite material. *Int J Polym Sci*. 2021;01-08. Doi:10.1155/2021/6626712.
- [11] Rajabzadeh G, Salehi S, Nemati A, Tavakoli R, Hashji MS. Enhancing glass ionomer cement features by using the HA/VSZ nanocomposite: A feed forward neural network modelling. *J Mech Behav Biomed Mater*. 2014;29:317-27.
- [12] Silva VV, Lameiras FS, Lobato ZI. Biological reactivity of zirconia-hydroxyapatite Composites. *J Biomed Mater Res*. 2002;63:583-90.
- [13] Ab Rahman IA, Ghazali NAM, Bakar WZW, Masudi SM. Modification of glass ionomer cement by incorporating nanozirconia-hydroxyapatite-silica nano-powder composite by the one-pot technique for hardness and aesthetics improvement. *Ceram Int*. 2017;43:13247-53.
- [14] Dhivya Sri E, Paulraj J, Maiti S, Shanmugam R. Comparative analysis of colour stability and its impact on artificial aging: An in-vitro study of bioactive Chitosan, Titanium, Zirconia, and hydroxyapatite nanoparticle-reinforced glass ionomer cement compared with conventional glass ionomer cement. *Cureus*. 2024;16(2):e54517. Doi: 10.7759/cureus.54517.
- [15] Ravi B, Paulraj J, Maiti S, Shanmugam R. Assessing the influence of thermocycling on compressive strength, flexural strength, and microhardness in green-mediated nanocomposite-enhanced glass ionomer cement compared to traditional glass ionomer cement. *Cureus*. 2024;16(3):e56078. Doi: 10.7759/cureus.56078.
- [16] Jain K, Paulraj J, Maiti S, Shanmugam R. Green synthesis and investigation of antimicrobial activity and compressive resilience of glass ionomer cement modified with zirconia nanoparticles: An in-vitro study. *Cureus*. 2024;16(6):e62837. Doi: 10.7759/cureus.62837.
- [17] Ilancheran P, Paulraj J, Maiti S, Shanmugam R. Green synthesis, characterization, and evaluation of the antimicrobial properties and compressive strength of hydroxyapatite nanoparticle-incorporated glass ionomer cement. *Cureus*. 2024;16(4):e58562. Doi: 10.7759/cureus.58562.
- [18] Rahman IA, Masudi SM, Luddin N, Shiekh RA. One-pot synthesis of hydroxyapatite-silica nanopowder composite for hardness enhancement of Glass Ionomer Cement (GIC). *Bull Mater Sci*. 2014;37:213-19.
- [19] Valanezhad A, Odatsu T, Udoh K, Shiraiishi T, Sawase T, Watanabe I. Modification of resin modified glass ionomer cement by addition of bioactive glass nanoparticles. *J Mater Sci: Mater Med*. 2016;27:01-03.
- [20] Crystal YO, Rabie S, Janal MN, Cerezal G, Hu B, Bromage TG. Effects of LED curing light on silver diamine fluoride penetration into dentin. *J Clin Pediatr Dent*. 2023;47(6):44-50.
- [21] May E, Donly KJ. Fluoride release and re-release from a bioactive restorative material. *Am J Dent*. 2017;30(6):305-08.
- [22] Melo MA, Orrego S, Weir MD, Xu HH, Arola DD. Designing multiagent dental materials for enhanced resistance to biofilm damage at the bonded interface. *ACS Appl Mater Interfaces*. 2016;8(18):11779-87.
- [23] Hasan AMHR, Sidhu SK, Nicholson JW. Fluoride release and uptake in enhanced bioactivity glass ionomer cement (glass carbomer) compared with conventional and resin-modified glass ionomer cements. *J Appl Oral Sci*. 2019;27:e20180230.
- [24] Najeeb S, Khurshid Z, Zafar MS, Khan AS, Zohaib S, Martí JMN, et al. Modifications in glass ionomer cements: Nano-sized fillers and bioactive nanoceramics. *International Journal of Molecular Sciences*. 2016;17(7):1134.
- [25] Wang JJ, Zeng ZW, Xiao RZ, Xie T, Zhou GL, Zhan XR, et al. Recent advances of chitosan nanoparticles as drug carriers. *Int J Nanomedicine*. 2011;6:765-74.
- [26] Morales-Valenzuela AA, Scougall-Vilchis RJ, Lara-Carrillo E, Garcia-Contreras R, Hegazy-Hassan W, Toral-Rizo VH, et al. Enhancement of fluoride release in glass ionomer cements modified with titanium dioxide nanoparticles. *Medicine (Baltimore)*. 2022;101(44):e31434.
- [27] Gu YW, Yap AU, Cheang P, Khor KA. Effects of incorporation of HA/ZrO₂ into glass ionomer cement (GIC). *Biomaterials*. 2005;26(7):713-20.
- [28] Nishanthine C, Miglani R, R I, Poorni S, Srinivasan MR, Robaian A, et al. Evaluation of fluoride release in chitosan-modified glass ionomer cements. *Int Dent J*. 2022;72(6):785-91.
- [29] Patel A, Dhupar JKMS, Jajoo SS, Shah P, Chaudhary S. Evaluation of adhesive bond strength, and the sustained release of fluoride by chitosan-infused resin-modified glass ionomer cement: An in-vitro study. *Int J Clin Pediatr Dent*. 2021;14(2):254-57.

[30]

Senthil Kumar R, Ravikumar N, Kavitha S, Mahalaxmi S, Jayasree R, Sampath Kumar TS, et al. Nanochitosan modified glass ionomer cement with enhanced mechanical properties and fluoride release. *Int J Biol Macromol*. 2017;104:1860-65.

[31]

Panigrahi A, Sudeep S, Sharma S, Mohanty S. Comparative evaluation of fluoride recharge ability of conventional and hydroxyapatite modified glass ionomer cement with daily low fluoride exposure- an in-vitro study. *J Clin Diagn Res*. 2016;10(2):ZC53-ZC55.

[32]

Kukreja R, Singla S, Bhadoria N, Pawar P, Gupta K, Khandelwal D, et al. An in-vitro study to compare the release of fluoride from glass ionomer cement (Fuji IX) and Zirconomer. *Int J Clin Pediatr Dent*. 2022;15(1):35-37.

[33]

Bansal R, Bansal T. A comparative evaluation of the amount of fluoride release and re-release after recharging from aesthetic restorative materials: An in-vitro study. *J Clin Diagn Res*. 2015;9(8):ZC11-ZC14.

[34]

Crisp S, Lewis BG, Wilson AD. Glass ionomer cements: Chemistry of erosion. *J Dent Res*. 1976;55(6):1032-41.

[35]

Neelakantan P, John S, Anand S, Sureshbabu N, Subbarao C. Fluoride release from a new glass-ionomer cement. *Oper Dent*. 2011;36(1):80-85. Doi: 10.2341/10-219-LR.

[36]

Exterkate RA, Damen JJ, Ten Cate JM. Effect of fluoride-releasing filling materials on underlying dentinal lesions in-vitro. *Caries Res*. 2005;39(6):509-13.

[37]

Sivarajan M, Rakshagan V, Govindaraju L. Choice of restorative material by dentists for Class I caries in second mandibular primary molar in 3-6 year children visiting a university dental hospital: A retrospective study. *Journal of Advances in Medicine and Medical Research*. 2024;36(1):105-14.

[38]

Ganesh SB, Rani SI. Knowledge and awareness of fluoride releasing dental materials. *International Journal Of Psychosocial Rehabilitation*, 2020;24(1):7409-19.

[39]

Al Ibrahim NS, Tahmassebi JF, Toumba KJ. In-vitro and in-vivo assessment of newly developed slow-release fluoride glass device. *Eur Arch Paediatr Dent*. 2010;11(3):131-35.

[40]

Yip HK, S RJ. Fluoride release from a polyacid-modified resin composite and 3 resin-modified glass-ionomer materials. *Quintessence Int*. 2000;31(4):261-66.

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PLAGIARISM CHECKING METHODS: [Jain H et al.]

- Plagiarism X-checker: Nov 22, 2024
- Manual Googling: Feb 07, 2025
- iThenticate Software: Mar 01, 2025 (23%)

ETYMOLOGY: Author Origin

EMENDATIONS: 7

AUTHOR DECLARATION:

- Financial or Other Competing Interests: None
- Was Ethics Committee Approval obtained for this study? Yes
- Was informed consent obtained from the subjects involved in the study? No
- For any images presented appropriate consent has been obtained from the subjects. NA

Date of Submission: Nov 19, 2024

Date of Peer Review: Dec 18, 2024

Date of Acceptance: Mar 03, 2025

Date of Publishing: Apr 01, 2025