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Nanoparticle-Modified *Cassia Fistula* Sawdust-Based G-Filters for Fluoride Removal from Drinking Water

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ABSTRACT

G-filter is a common household ceramic water filter manufactured from kaolinite sawdust. Kaolinite and sawdust wet mixtures are press-formed to produce the frustum shape; air-dried and sintered to manufacture the G-filter. The sawdust used is a mixture of dissimilar wood waste readily available at carpentry workshops. In this article, Cassia fistula pods sawdust is used instead of the sawdust mixture. This new filter is named Cassia Fistula Modified (CFM) G-filter. Thermogravimetric and SEM analysis were performed to characterize and compare the CFM and regular G-filter variants. The CFM G-filter has a double modal mass reduction compared to the G-filter manufactured with sawdust as raw material. Comparative flow analysis revealed a ten-fold increase in filtration rate in CFM-based G-filters compared to regular G-filters. Therefore, CFM-modified G-filters can become a potential solution for fluoride removal from drinking water sources. The CFM greenware mixture is modified with ferric chloride and alumina nanoparticles to produce a Novel Clay Ceramic (NVC) water filter. The control experiments for NVC water filters were conducted on a G-filter modified in similar manner with $FeCl_3$ and Al_2O_3 nanoparticles. Ion-selective elective test for NVC filter achieved ~33% and ~53.33% fluoride removal in the first and the second run, respectively. Similarly, ion chromatography revealed 37.66% and 46.97% fluoride removal in the first run and the second run, respectively. The regular G-filter did not showcase any specific removal whatsoever compared to the NVC. The implication of this work is the use of local plant materials as point-of-use solutions for drinking water problems.

Keywords: *Cassia fistula*; G-filter; Clay; Drinking water; Fluoride removal.

1. INTRODUCTION

Pottery was performed for ages in several households in India. Usually in India, clay ceramic vessels are used for cooking, pickling, water storage, storage of milk products, and many more (Kaurwar *et al.* 2017). In the recent times, water filtration using clay pottery is an added use that functionalizes the porous clay ceramics (Venugopal, 2019). In India, such frustum shaped water filters worked on gravity for their operation and were termed as G-filters.

G-filters were first manufactured, installed and used in potter households in Banad village, Jodhpur, Rajasthan (Gupta *et al.* 2018). Use of equal volumes of local salty clay and sawdust became an easy method to transform pots into a filtering media named G-filter by baking a press-formed wet composite from these materials (Satankar, 2019). They were good in bacterial contaminant removal (especially E. coli) from water making it potable (Satankar *et al.* 2019).

Pollutants such as arsenic which contaminate water were successfully removed following use of additives in the manufacturing raw materials used (Nighojkar *et al.* 2019). The dissolution of fluoride from rocky terrains of western Rajasthan is the cause of the high quantities of fluoride in water. Fluoride levels in water across Rajasthan are higher than prescribed BIS and WHO standards. Fluoride removal with regular G-filter was very negligible in experiments conducted in Hingola Kalan village, Pali, Rajasthan, India. The presence of an ayurvedic plant material, Aragvadh (Cassia fistula (CF) Linn) in the region with pods exhibiting anti-fungal and anti-microbial properties paved a way to engineer the G-filter material (Hazra *et al.* 2022). Pore scale studies were initiated considering G-filter microstructure, which is responsible for decontamination of water. Pore scale modeling enabled the calculation of the theoretical lifetime of G-filters to be approximately two years (Hazra *et al.* 2022). G-filters are used for the same duration (around 4-6 months) as any regular clay pots are used for water storage in Rajasthan, India. Potters were able to get a new market for local water cleansing using self-manufactured G-filters. Recently, the local people started using more of G-filters with clay filtrate containers instead of clay pots in Rajasthan since they served operational functions such as filtration, cooling and storage. Yet, G-filters have a low filtration rate of around 125-2.25 L/h. The flow character of CF-engineered G-filter ceramics is investigated and nanosized materials have been developed for efficient fluoride removal due to their large specific area and high mass transfer efficiency (Bhaumik *et al.* 2011; Kumar *et al.* 2011)]. High electronegativity of fluoride ions allows multi-valent metal ions, such as Al(III) and Fe(III) to bind strongly to it (Kumar *et al.* 2009; Zhao *et al.* 2010). The low cost of Al- and Fe-based materials enables this as a viable option to use them to engineer CF pods. Since they are distributed in the wild and cultivated across India, CF pod organic materials can be possibly manufactured anywhere in India. This article elaborates the influence of CF and its nano-engineered variants to enable G-filter to have a better flow rate and fluoride removal capabilities.

2. MATERIALS AND METHODS

Ripe *Cassia fistula* pods were collected and dried in the open air under sunlight for one week. Weight stabilization of the dried CF pods over time indicates the degree of dryness. Once thoroughly dried, the CF pods were manually crushed to achieve a particle size 300 µm (Fig. 1).

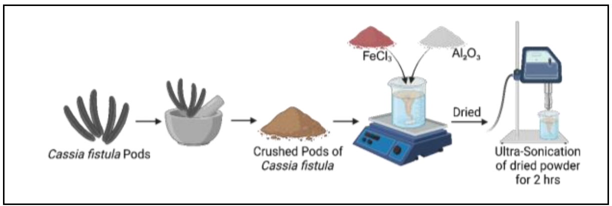

Fig. 1: Laboratory process for CFM G-filter base material from Cassia Fistula pods

Table 1. Volume percent of components in the CFM, NVC and regular G-filter greenware variants

Composite Samples	Cassia fistula dust	Fe Cl$_3$	Al$_2$O$_3$	Saw dust	Kaolin clay
CFM G-filter	90 mL	-	-	-	90 mL
NVC G-filter	30 mL	30 mL	30 mL	-	90 mL
Regular G-filter	-	-	-	90 mL	90 mL

Ferric chloride ($FeCl_3$) and alumina (Al_2O_3), 30 mL each were added to equal amount of CF pods powder in 250 mL water. The water was then stirred at room temperature for 12 hours to ensure thorough blending. Subsequently, the heterogenous mixture underwent evaporation (by heating) at 60 °C using the co-precipitation method until complete dryness was achieved. The dried mixture was then ultrasonicated for 2 hours to obtain Cassia fistula-modified (CFM) nanoparticles. To remove residual moisture and ensure optimal stability and performance in subsequent filtration processes, the CFM nanoparticles were dried again. Table 1 shows the composition of the regular G-filter, CFM and NVC G-filters.

The plant-based organic materials, CF pods and heterogenous sawdust were analyzed using differential thermal analysis (DTA) to ascertain the physical and chemical transformations that occur in them when subjected to heat treatment. The DTA curves for these plant materials indicate the absorbed or evolved heat energies corresponding to the transformation at different temperatures. The area of the peak relates to the quantity of reactive materials present in the CF pod and the sawdust samples. The powdered plant material samples were analyzed using the Simultaneous thermal analyzer [STA 6000® Perkin Elmer] at IIT Jodhpur, CASE facility. The heating was performed at a constant rate of 10 °C/min, with the plant material samples (10-15 mg) transitioning from ambient conditions to 900 °C under a nitrogen atmosphere at a flow rate of 40 mL/min (Mitchell *et al.* 1965). The analyzer was designed to compute the individual weight loss of each sample as it undergoes heating.

The manufacturing of the G-filter has been elaborated by (Duhan *et al.* 2023). The CFM G-filter was fabricated, incorporating equal volume of locally sourced Cassia fistula pods with equal volume of locally available kaolin clay (Duhan *et al.* 2023). The NVC G-filters were prepared by appending these CFM nanoparticle-modified CF pods into an equal volume of kaolin clay. Green composites manufactured from the above mixtures contained water equivalent to 70% by volume of the total volume of mixture in use. A similar manufacturing process was followed for the regular G-filter, scaled-down version (250 mL) and other G-filter variants used in the study.

Fig. 2: 250-mL G-filter press developed in-house

The press with a 5000-kg hydraulic jack (TUV-GS 350 MPa) (Fig. 2) was developed and manufactured by Y&Co, Jodhpur. This was used for making the 250-mL G-filter greenware samples from green composites. Weight stabilization of the 250-mL frustum shaped green composites took three to four days time in ambient conditions (30 °C in Jodhpur, Rajasthan) (Fig. 3).

Fig. 3: Frustum shaped 250 mL G-filter greenware

The greenware samples were dried in a device, Thermotech PID-91Se, Muffle Furnace [Globe-Tex Industries, UP, India] at 100 °C for an hour in order to ensure complete moisture removal. They were further heat treated in the same device in a two-step process (Plappally *et al.* 2011). The rate of heating was 50 °C/hour. After the device crossed 200 °C, the heating rate was increased to 100 °C/hour. Further, the samples were heated to 450 °C for 3 hours to ensure complete combustion of organic content. Finally, samples were heated at sustained temperatures for 5 hours as elaborated in Table 2. Ceramic 250-mL G-filters were thus produced (Fig. 4) and left to cool to room temperature.

Table 2. Baking temperature of the 250 mL G-filter greenware variants

Type of G-filter	Sintering Temperature
CFM G-filter	550 °C
NVC G-filter	550 °C
Regular G-filter	750 °C

Fig. 4: Baked 250-mL G-Filters

The analysis of microstructure and surface inspection of new G-filter ceramics were performed using a scanning electron microscope [SEM-Carl Zeiss model EVO 18, IIT Jodhpur]. Elemental composition analysis was carried out for these ceramics using energy-dispersive X-ray spectroscopy [EDS-Oxford Instruments model 51-ADDD-0048, IIT Jodhpur] (Gupta *et al.* 2023). Porosity was measured using SEM and was compared with porosity measured by water absorption. The process included measuring the amount of water absorbed by G-filter samples (1 cm × 1 cm × 1 cm) after being submerged in boiling water (100°C) for 2 hours (Gupta *et al.* 2018).

Flow rate was measured by timing a 100-mL flow through the 250-mL ceramic filter in a fully filled condition. Fluoride contaminated water samples with 15 ppm concentration of fluoride were prepared and passed through the 250-mL G-filter.

For fluoride determination, 50 to 100 mL of the sample was transferred into a 150 mL plastic beaker, followed by the addition of total ionic strength adjustment buffer (TISAB, 115368 Millipore, Merck, KGaA, Darmstadt, Germany). The electrode slope using the ion meter was fixed, rinsed and dried. It was immersed into the sample for thorough stirring and steady readings on the meter were recorded. The meter was recalibrated at intervals of 1 or 2 hours as needed. Consistency in the sample, standard temperatures and adjustment of ionic strength with TISAB were maintained. To verify the results, a standard of known concentration was introduced into the sample solution and the original sample concentration was determined based on the change in electrode potential before and after addition. In order to ascertain fluoride removal, the fluoride concentrations prior to filtration and after filtration were measured using a Benchtop pH/ISE Meter (Thermo Scientific Orion Star A214 Benchtop pH/ISE Meter, IIT Jodhpur) as well as Ion Chromatography (881 compact IC pro-Anion, IIT Jodhpur).

3. RESULTS AND DISCUSSION

The greenware (Fig. 3) and ceramics (Fig. 4) varied in their weights as shown in Fig. 5. The CFM embedded G-filters were heavier than the regular sawdust-based G-filters. Regular G-filter lost more weight than those with CF pods and those embedded with nanoparticles. This loss in weight is due to the oxidation of the organic materials present in the greenware. The oxidation of organic materials was evaluated using thermogravimetric analysis. The derivative thermo-gravimetric (DTG) curves for the organic materials is illustrated in Fig. 6 and Fig. 7. The black curve is TGA which represents weight loss at each temperature and the blue curve represents DTG which confirms a change of phase during the material loss transformation. Both TGA curves in Fig. 6 and Fig. 7 show a steep dip till 100 °C denoting water loss from the sawdust and CF pod sample, respectively, thus suggesting desorption as well as reduction. The first derivative curves (Fig. 6 and Fig. 7) portray relative mass of carbonaceous material combusted or evaporated. This corresponds to an endothermic mass loss around 380 °C in a single step for sawdust (Fig. 5). Also, two endothermic peaks of sample mass change at around 200 °C and 350 °C are noticed (Fig.6).

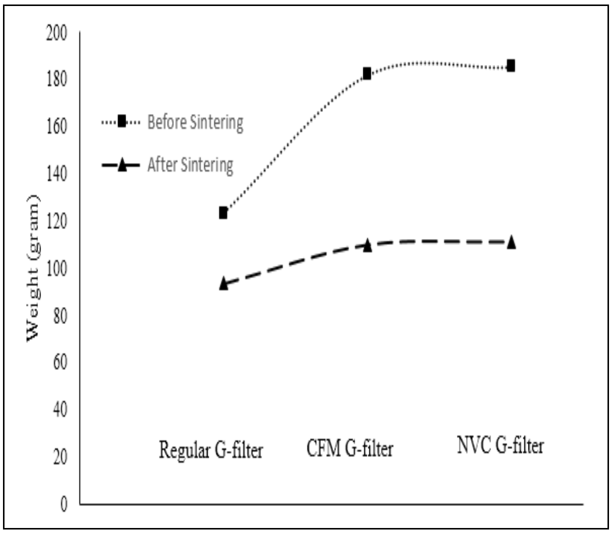

Fig. 5: Occurrence of weight loss during the transformation from greenware to ceramic

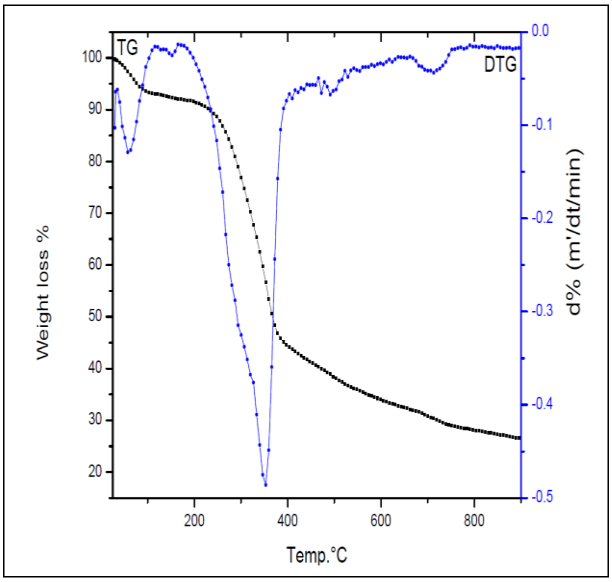

Fig. 6: Thermogravimetric analysis and DTG curves from 30 to 900 °C for regular sawdust G-filter

To get a clear picture of the surface and structural characters of the regular, CFM and NVC G-filters, SEM was employed.

Fig. 8(A) provides a smooth micrograph indicating possibility of lower pore dimension compared to the material in Fig. 8(B). Nanoparticle-embedded CF pods powder used for making the ceramic (NVC water filter) showed more amorphous nature with representation of large surface area (Fig. 8(B)). Presence of Fe and an increase of Al is observed in Fig. 8(B) compared to Fig. 8(A). Micrographs also reveal the porosity of both regular G-filter and CFM G-filter variants. NVC G-filters are found to have more porosity and larger pore dimension as illustrated from Table 3.

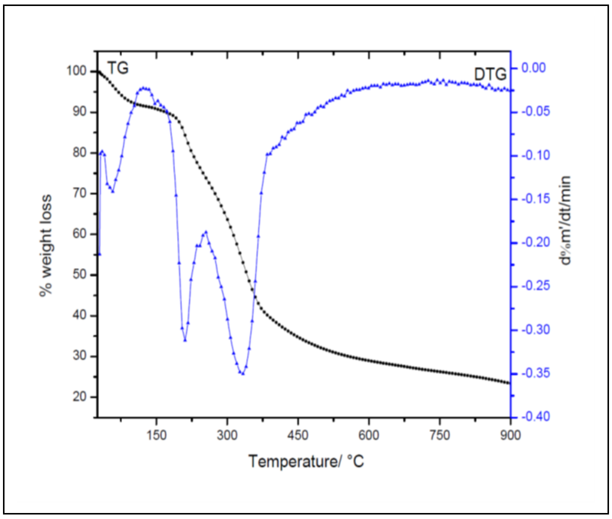

Fig. 7: Thermogravimetric analysis and DTG curves from 30 to 900 °C for *Cassia fistula* Modified G-filter

Table 3: The pore dimensions observed using scanning electron microscopy

Filter Variants	Porosity (%)	Average pore radius (µm)	Standard Deviation of pore radius (µm)
Regular G-filter	27.29	2.1416	1.7647
NVC G-filter	33.99	2.7994	2.4603

Table 4. Porosity calculation using water absorption technique

Properties	Initial weight (dry sample)	Weight after saturation	Porosity (%)
Regular G-filter	1.9367 g	2.3682 g	43.15
(CFM) G-filter	1.2085 g	1.7699 g	56.14

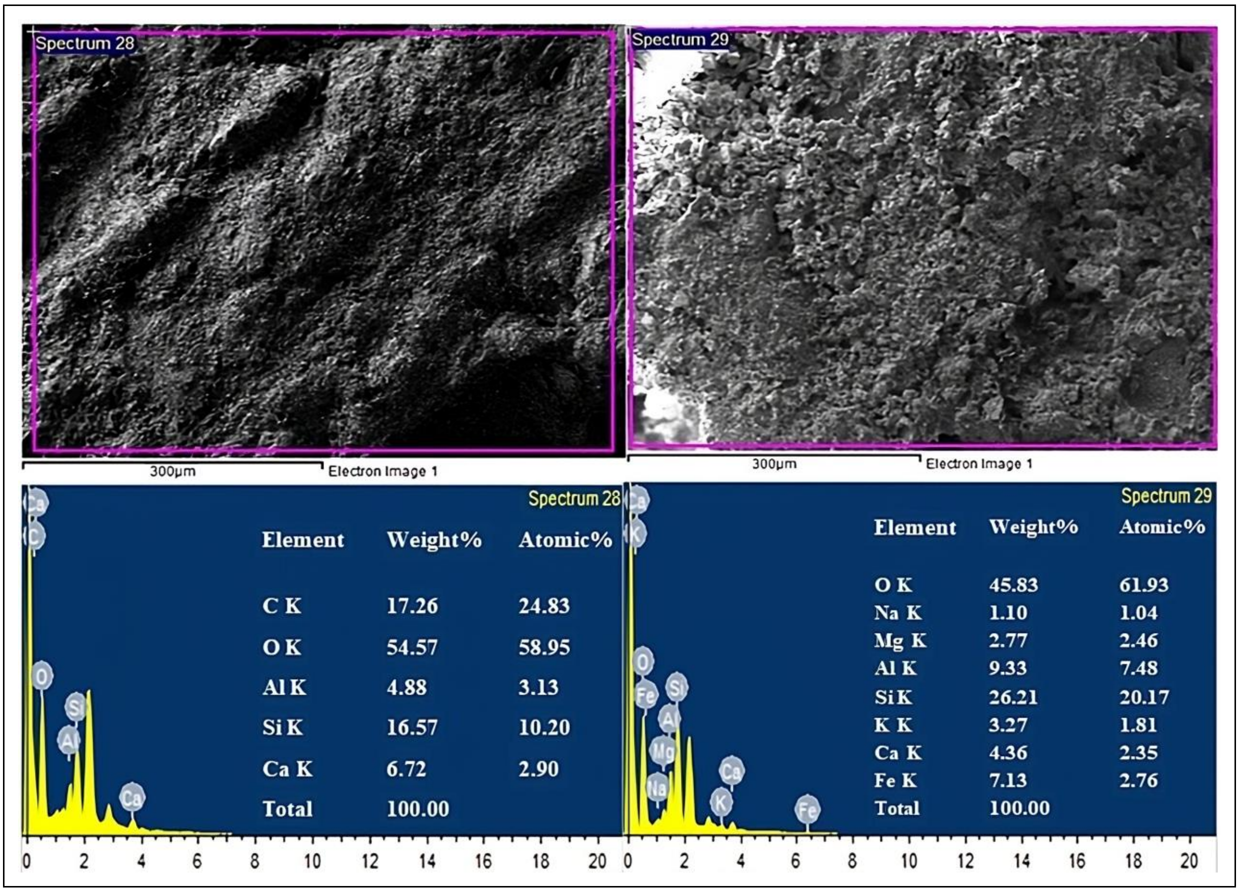

Fig. 8: Micrograph of 250-mL G-filter ceramic material (A) and nano-particle embedded CF-based ceramic NVC G-filter material (B)

Upon comparison, it was observed that the density of pores with a diameter of 1 µm was significantly reduced in NVC G-filters, in contrast to regular G-filters. There was a notable increase in the frequency of pores within 4-6 µm range in CFM G-filters compared to regular G-filters. These findings shed light on the altered porosity profile of CFM G-filters, indicating potential implications for their filtration efficiency and performance in water purification applications. The porosity is measured by water absorption into the ceramic. It is represented as percentage (Table 4), indicating the amount of water mass absorbed compared to the total dry mass of the samples.

Timed gravity-based flow experiments by passing 100 mL of water through the 250-mL saturated porous vessels is shown in Fig. 9. The 250-mL CFM G-filters and the NVC G-filters were found to be more percolative than regular G-filters. This would mean faster water filtration through CFM G-filter and NVC-G filter compared to regular G-filters (Ahmad *et al.* 2023).

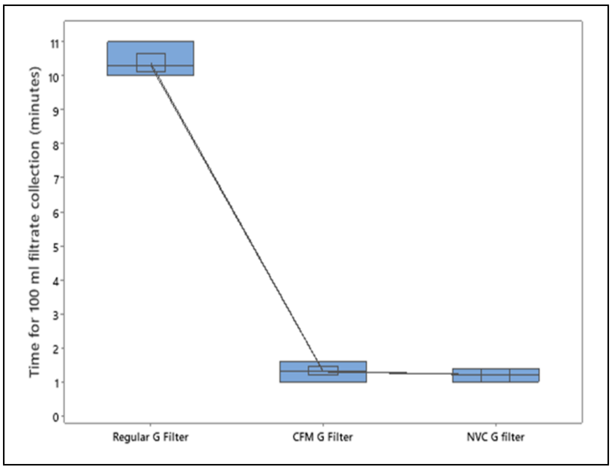

Fig. 9: Gravity based flow of 100 mL water passing through the 250-mL saturated porous vessels

This accelerated filtration rate through CFM and NVC G-filter materials presents an opportunity to deliver a larger volume of filtered water in a short time. In this study, removal of fluoride was also measured using CF modified G-filters.

Table 5. Fluoride removal measurement for the first two sequential runs through the 250-mL G-filter variants

Fluoride removal	Benchtop pH/ISE Meter		Ion Chromato-graphy	
	First Run	Second Run	First Run	Second Run
Initial concentration (ppm)	15	15	15	15
Regular G-filter (ppm)	15	15	15	15
CFM G-filter (ppm)	12	10	13.147	10.372
NVC G-filter (ppm)	10	7	10.372	7.995

The ISE meters and ion chromatography were used to detect fluoride removal when fluoride contaminated water was passed through the G-filter variants. The results were observed for the first two sequential runs (Table 5). The CF based G-filter decreased the content of fluoride in the filtrate collected from the respective filters. The CFM and NVC filters exhibited remarkable fluoride removal capabilities, with NVC achieving approximately 33% removal in the first run and approximately 53.33% in the second run, as confirmed by ion-selective electrode tests. Ion chromatography further supported these findings, revealing 37.66% removal in the first run and 46.97% in the second run.

4. CONCLUSION

Our study demonstrates the promising potential of Cassia fistula modified and novel clay ceramic water filters in addressing fluoride contamination in drinking water sources, particularly in Rajasthan, India. The CFM and NVC ceramics demonstrated several advantages over regular G-filter materials. They exhibited significantly higher pore volume and greater surface area. Additionally, NVC-based filters showed higher porosity compared to regular G-filter ceramics. Notably, CFM and NVC filters filtered water approximately 10 times faster than regular G-filters, suggesting enhanced filtration efficiency and faster production of clean drinking water. Utilizing local plant materials, such as Cassia fistula pods in the fabrication of filters similar to CFM and NVC G-filters presents a promising solution for addressing fluoride contamination of water.

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CONFLICTS OF INTEREST

The authors declare that there is no conflict of interest.

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