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Enhanced Defluoridation Using Aluminium-Modified Freshwater Mussel Shell Biosorbent

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Abstract

Groundwater fluoride contamination poses a significant public health challenge, necessitating affordable and sustainable defluoridation technologies. This study investigated raw and aluminium-modified freshwater mussel shell biochars, prepared by pyrolyzing Lake Victoria mussel shells at 800 °C, as low-cost adsorbents for fluoride removal from water. Surface characterization and batch adsorption experiments optimized pH, adsorbent dosage, fluoride concentration, contact time, and temperature. Aluminium modification introduced Al–O/Al–OH functional groups and significantly enhanced the surface area and porosity of the mussel shell biosorbent. The Energy-Dispersive X-ray Spectroscopy confirmed aluminium incorporation and fluoride binding, while X-ray Diffraction analysis indicated enhanced crystallinity in modified forms of the shells. The modified mussel biochars exhibited better removal efficiencies at higher concentrations compared to the unmodified forms. Additionally, modified mussel shell exhibited the highest adsorption capacity of 0.202 mg/g at optimal pH 7 and temperature of 25 °C. The reaction mechanism followed Freundlich model ($R^2 > 0.96$), suggesting multilayer adsorption on heterogeneous surfaces. Kinetic modeling showed that adsorption best fits the pseudo-second-order model, indicating chemisorption as the dominant mechanism. The modified mussel biochars sorbent applied to real samples reduced fluorides permissible levels. This study paves way for simple, cost effective and efficient approaches to water defluoridation and environmental management.

Key words: Fluorides, Mussel shells, Aluminium chloride, Characterization, Adsorption and Kinetics

1.0 Introduction.

There has been an increase in fresh water consumption and waste water generation due to the increasing world population and the increased agricultural water use demands. As a result, both surface and ground waters have become contaminated (Kimambo *et al.*, 2019). This has been worsened by lack of proper storage facilities, and poor water management especially in developing nations (Narsimha and Sudarshan, 2017). Human health and environmental safety are at a greater risk when drinking water that contains anionic substances such as fluoride. Some of the health issues that can result from fluoride exposures of over 1.5 ppm are dental and skeletal fluorosis. Consequently, several defluoridation techniques have been applied in reduction of fluoride in water. Among these methods are precipitation, adsorption, ion-exchange, coagulation, electrolytic treatment, and membrane processes. Most of these conventional defluoridation techniques have setbacks that include; huge primary setting-up cost, lack of selectivity, low adsorption capacity, and regeneration or application issues (Ingle *et al.*, 2014). To address some of these limitations, the adsorption process has increasingly grown into use.

The use of adsorbents on contaminants removal has been embraced by several researchers. Among these are magnesia chitosan composite, *Mytilus coruscus* shells and Aluminium hydroxyapatites (Otieno *et al.*, 2024). In addition, cheap, highly acceptable and readily available animal shells have been explored as materials for defluoridation (Yin *et al.*, 2024). Calcium-based adsorbents such as sea shells have been reported to have high affinity for fluoride ions (Gazeau *et al.*, 2013). However, poor surface area and a narrow pH range are limitations of adsorption with an unmodified shell, thus the modification of the mussel shell biochars using electropositive Aluminium salt (Sadhu *et al.*, 2021). This would provide more active adsorption sites for the fluoride ions. Studies involving aluminium chloride have also indicated improvement of fluoride adsorption through ligand

exchange mechanisms (Ahmad *et al.*, 2022). Aluminium chloride can be incorporated into biosorbents before pyrolysis (Du *et al.*, 2014) or after pyrolysis of the shells (Meilani *et al.*, 2021). Herein, Mussel shells from fresh water, Lake Victoria were pyrolyzed and modified with aluminium chloride and used to remove high fluoride ions from drinking water.

2.0 Materials and Methods

2.1. Preparation of Mussel shell biosorbent.

Fresh water mussel shells were randomly collected from the shores of Lake Victoria in Homabay County, Kenya. The shells were washed several times with distilled water to remove sand, algae, and other impurities, after which they were sun-dried for 12 hours. The dried shells were milled into fine powder and stored for further experiments. The mussel shell powder (MSP) were rinsed using 0.1 M hydrochloric acid (HCl) and dried at 100 °C for 4 hours. The dried powders were then pyrolyzed at 800 °C in a muffle furnace (MC5-12-3KW Biobase bioindustry Shandong) for 6 hours to obtain mussel shell biosorbents (MB).

For modification of the biosorbents, MB samples were soaked separately in aluminum chloride solution. The pH of the mixture was adjusted to 7.0 using 2.0 M sodium hydroxide (NaOH) and magnetically stirred at 200 rpm for 3 hours. The mixtures were then allowed to stand undisturbed for 24 hours. After settling, the samples were filtered and washed five times using excess deionized water and anhydrous ethanol. The modified biosorbents were finally dried in an oven at 105 °C for 3 hours and preserved for subsequent adsorption experiments.

2.3. Chemicals and reagents

Hydrochloric acid (35%), sodium hydroxide pellets (98.5%), nitric acid, sodium fluoride (98%), phosphoric acid (98%), and anhydrous ethanol (99.5%) of analytical grade were used throughout the study without further purification. Deionized water obtained from Tom Mboya University Chemistry Laboratory was used in all preparations. Sodium fluoride (NaF) was used as the source of fluoride ions, while hydrochloric acid was employed during regeneration studies. Solutions of 0.1 M HCl and 0.1 M NaOH were used for pH adjustments, whereas sodium acetate buffer was applied to maintain solution pH.

2.4. Preparation of fluoride solution

A stock fluoride solution was prepared by dissolving 2.21 g of sodium fluoride in one litre of distilled water. The stock solution was diluted appropriately to obtain fluoride standards of 2, 4, 6, 8, and 10 ppm.

2.5. Batch experiment and optimization studies

Batch adsorption experiments were conducted to evaluate the effects of pH, contact time, fluoride concentration, adsorbent dosage, temperature, and competing ions on fluoride adsorption.

2.5.1 Effect of fluoride concentration

Fluoride solutions of 2–10 ppm were separately mixed with 1.0 g of modified mussel shell biosorbent at optimum pH and agitated at 150 rpm for 180 minutes at 25 °C.

2.5.2 Effect of Contact time

A total of 1.0 g of mussel shell biosorbent was mixed with 50 mL of a 10 ppm fluoride solution. The mixtures were shaken at 150 rpm for 5, 10, 30, 60, 90, 120 and 180 minutes in triplicate to determine the optimal contact time.

2.5.3 Effect of adsorbent mass

A 50 ml fluoride solution of 10 ppm was agitated at 150 rpm for 180 minutes using adsorbent dosage of 1.0 g, 2.0 g, 4.0 g, 6.0 g, 8.0 g and 10 g of Mussel shell biosorbent at the optimal pH and temperature of 25 °C.

2.5.4 Effect of Temperature

A 50 mL fluoride solution of 10 ppm was agitated at 150 rpm for 180 minutes using 1.0 g of mussel shell biosorbent at the optimal pH. The adsorption process was repeated at temperatures of 30, 40, 50, and 60 °C.

2. 5.5 Effect of Competing Ions

Solutions containing 30 mgL⁻¹ and 50 mgL⁻¹ concentrations of selected anions namely sulfate (Na₂SO₄), chloride (NaCl), carbonate (Na₂CO₃), and phosphate (Na₃PO₄) were prepared using analytical-grade reagents. Equal volumes of a 30 mgL⁻¹ fluoride solution were then combined with

each competing ion solution and 1.0 g of modified mussel shell biosorbent material under study. The mixtures were agitated at a constant speed of 150 rpm, temperature 25 °C and optimal pH 7 for a duration of 180 minutes using a mechanical shaker to ensure adequate contact between the fluoride ions, competing ions, and sorbent.

2.5.6 Effects of pH

For pH studies, 200 mL fluoride solutions were adjusted to pH values of 2, 4, 6, 7, 8, 10, 12, and 14 using 0.1 M HCl and 0.1 M NaOH. A fixed amount (1.0 g) of mussel biosorbents was added and the mixtures agitated at 150 rpm for 180 minutes at 25 °C

2.6. Characterization

The morphology of the mussel biosorbents was examined using a FEI XL40 ESEM (Germany) Scanning Electron Microscopy, equipped with two EDAX Sapphire Si (Li) EDS detectors for elemental composition determination. The EDAX system operated at an acceleration voltage of 20.0 kV, with a take-off angle of 49.3°, and a live acquisition time of 655.4 seconds. The detector featured an energy resolution of 126.6 eV at the Mn K α line, and spectral data was collected over a range of 0 to 40.96 keV using 4096 channels with a dispersion of 10 eV per channel. Functional groups were analyzed using a Perkin Elmer FTIR spectrometer controlled by Spectrum software version 10.03.02 in the range of 4000–400 cm⁻¹. Brunauer–Emmett–Teller (BET) analysis was conducted using a Micromeritics TriStar II Plus version 3.00 to determine the surface area, pore size, and pore volume of the biosorbents using nitrogen adsorption at 77 K. Crystalline phases were characterized using a panalytical empyrean x-ray diffractometer, UK. The X-ray Diffractometer instrument operated with a copper (Cu) anode as the X-ray source, generating Cu

K α radiation with wavelengths of $\lambda_1 = 1.54060 \text{ \AA}$ (K α_1) and $\lambda_2 = 1.54443 \text{ \AA}$ (K α_2), with a K α_2 /K α_1 ratio of 0.5. The scan was performed over a 2θ range of 4.00° to 89.99° , with a step size of 0.0130° and a step time of 66.045 s, using a continuous scan mode. A fixed divergence slit of 0.2177° was employed and the system was operated at 40 kV and 40 mA, under ambient conditions (25°C).

2.7. Regeneration studies

Regeneration studies were carried out by washing the used biosorbents with 250 mL of 1.0 M HCl for five consecutive cycles. After each cycle, the sorbents were rinsed three times with distilled water and reused for subsequent adsorption experiments.

2.8 Application of modified mussel shell biosorbent to natural water system

Water samples were collected from Paga, Koguta and Waondo boreholes located at Lambwe Valley in Mbita Sub-County, Kenya, and stored in tightly sealed containers. Parameters including pH, conductivity, turbidity, alkalinity, total dissolved solids (TDS), total suspended solids (TSS), and chloride content were determined. Portions of 50 mL water samples were treated with 1.0 g of mussels biosorbent and agitated at 150 rpm for 180 minutes hours at 25°C . Residual fluoride concentrations were then measured using a fluoride ion-selective electrode.

3.0 Results and Discussion.

To determine the possibility of modification and accessibility of functional groups responsible for removal of excess fluoride ions from contaminated water, characterization of the prepared fresh water mussel shell biosorbents was carried out using FTIR, SEM, EDS, BET and XRD techniques and the results presented and discussed.

3.1. FTIR Characterization

The Fourier Transform Infrared Spectroscopy (FTIR) spectra of unmodified mussel shell biosorbent (MB), modified mussel shell biosorbent (MBM), and fluoride-loaded modified mussel shell biosorbent presented in Figure 1 were analyzed to determine the functional groups involved in fluoride adsorption.

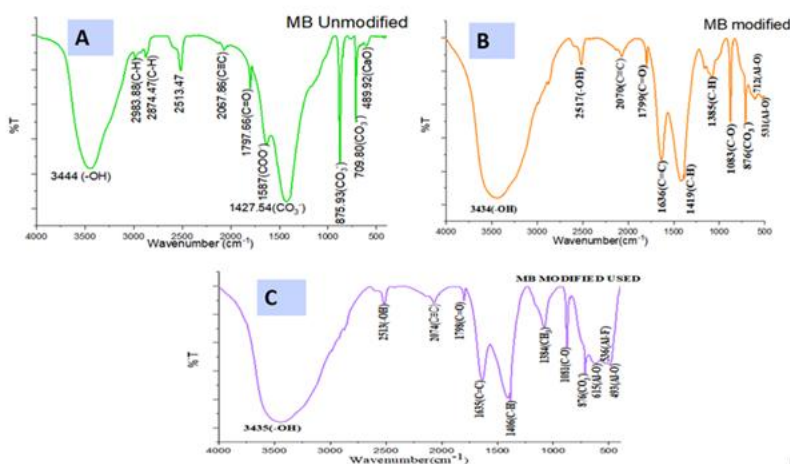


Figure 1: Fourier Transform Infrared Spectra of (A) MB Unmodified, (B) MB Modified and (C) MB Modified Used

The spectra revealed significant changes after modification and fluoride adsorption. The broad absorption band observed around 3400 cm^{-1} was attributed to O–H stretching vibrations, indicating the presence of hydroxyl groups and adsorbed water molecules on the biosorbent surface (Vijayaraghavan, 2021). The intensity of this band increased after modification, suggesting successful incorporation of hydroxyl-containing aluminium compounds. Peaks around $1420\text{--}1470\text{ cm}^{-1}$ correspond to carbonate (CO_3^{2-}) asymmetric stretching vibrations, confirming the calcium carbonate composition of the mussel shell (Kattoura *et al.*, 2018). The band near 1797.66 cm^{-1} is characteristic of C=O stretching, indicative of the presence of carbonate (Vijayaraghavan, 2021).

The modified biosorbent exhibited additional peaks around 780–800 cm^{-1} and 600–700 cm^{-1} , associated with Al–O and Al–OH vibrations. This confirmed successful modification using aluminium chloride. After the adsorption of fluoride ions, spectral shifts were observed with a slight reduction in the intensity of the –OH band (3435 cm^{-1}) and emergence of a spectral peak shoulder at 536.21 cm^{-1} . These could be related to Al–F bond formation, indicating an effective binding of fluoride ion onto the aluminum sites (Gallios *et al.*, 2017). These findings demonstrated that modification enhanced the number of active adsorption sites and improved fluoride adsorption capability.

3.2 SEM Characterization of Mussel Shell Biosorbent

Scanning Electron Microscopy (SEM) images were used to investigate the surface morphology of mussel shell powder (MSP), unmodified mussel shell biosorbent (MB), modified mussel shell biosorbent (MB.M), and fluoride-loaded modified biosorbent (MB modified used) as in Figure 2.

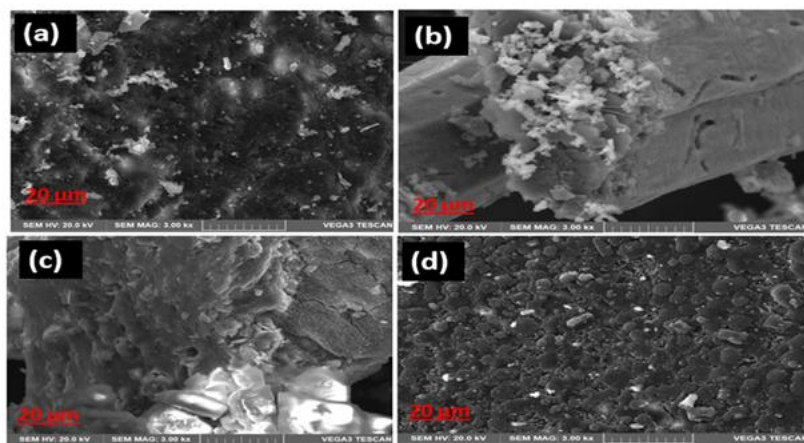


Figure 2: Scanning Electron Microscopic Images of (a) MSP, (b) MB. Unmodified, (c) MB. Modified, (d) Used MB

The raw mussel shell powder exhibited relatively smooth and compact surfaces with limited pore structures. After pyrolysis, the unmodified mussel biosorbent showed increased roughness and

development of pores due to thermal decomposition of organic matter (Mourhly *et al.*, 2019; Sadhu *et al.*, 2021). The modified mussel shell biosorbent displayed highly irregular surfaces with numerous cavities and porous structures (Wan Mahari *et al.*, 2022). The increased porosity and roughness indicated that aluminium modification significantly altered the surface morphology and enhanced the available adsorption sites (Kattoura *et al.*, 2018). After fluoride adsorption, the surface pores of used MB appeared partially blocked and covered by precipitated materials, indicating successful fluoride adsorption onto the biosorbent surface. The SEM observations confirmed that modification improved the structural properties of the biosorbent, thereby increasing its adsorption efficiency.

3.3. EDS Characterization of Mussel Shell Biosorbent

Energy Dispersive X-ray Spectroscopy (EDS) analysis was performed to determine the elemental composition of the modified mussel shell biosorbent (Figure 3).

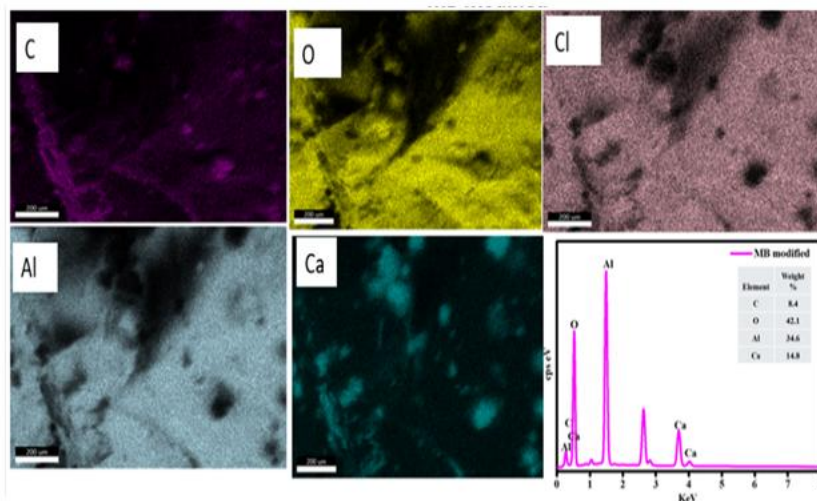


Figure 3: Scanning Electron Microscopic- Energy Dispersive X-ray mapping images and spectrum of MB modified (MB.M)

The observed spectra confirmed the presence of calcium (Ca), oxygen (O), carbon (C), and aluminium (Al) as the major elements. Calcium and carbon originated from calcium carbonate, which forms the major composition of mussel shells (Li & Skelly, 2023). The appearance of aluminium peaks after modification confirmed successful incorporation of aluminium species onto the biosorbent surface. The EDS mapping images further revealed uniform distribution of aluminium on the biosorbent surface, indicating effective modification. The presence of Al confirmed successful modification of the mussel shell biosorbent for defluoridation (Lawrinenko *et al.*, 2017).

3.4. BET Analysis for Mussel Shell Biosorbent

Brunauer–Emmett–Teller (BET) analysis was conducted to determine the specific surface area, pore volume, and pore size distribution of the mussel shell biosorbents. The nitrogen adsorption–desorption isotherms presented in Figure S1 indicated that the modified mussel shell biosorbent possessed a larger surface area and pore volume compared to the unmodified form. This increase was attributed to pyrolysis and aluminium modification, which enhanced pore formation and structural development (Ren *et al.*, 2022; Shimizu and Matubayasi, 2024). The modified biosorbent exhibited improved mesoporous characteristics suitable for fluoride adsorption. Increased surface area provided more active adsorption sites, thereby improving adsorption efficiency (Marin *et al.*, 2024). The BET findings supported the SEM observations, which also indicated enhanced porosity after modification. The quantitative BET surface area and related parameters were also investigated and the results presented in table 1

Table 1: Properties of Mussel Shell Biosorbents from BET Analysis

Adsorbent material	BET S.A(M ² /g)	pore diameter(Å)	Adsorption capacity (Q _m) cm ³ /g STP	pore volume distribution (cm ³ /g)	surface interaction energy(C)
unmodified mussel shell biosorbent	3.8137	191.614	0.8762	0.0196	14.0289
modified mussel shell biosorbent	6.1035	150.381	1.4023	0.0236	14.023

From table 1, it was observed that the BET surface area increases significantly from 3.8137 m²/g for the unmodified mussel shell biosorbent to 6.1035 m²/g in the modified mussel shell biosorbent sample indicating that the modification process greatly enhanced the surface availability for adsorption (Meilani *et al.*, 2021). In terms of pore diameter, the unmodified mussel shell biosorbent exhibits a larger average pore size of 191.614 Å, which reduces to 150.381 Å in the modified mussel shell biosorbent. The decrease in pore diameter suggests the formation of smaller mesopores during the modification process, leading to a tighter pore structure favorable for certain adsorption applications, such as fluoride removal (Mourhly *et al.*, 2019). The adsorption capacity (Q_m) exhibited an improvement, increasing from 0.8762 cm³/g STP in the unmodified mussel shell biosorbent to 1.4023 cm³/g post-modification. This suggests that a greater availability of active sites and more accessible pore volume (Ren *et al.*, 2022). The pore volume distribution also improved slightly, increasing from 0.0196 cm³/g to 0.0236 cm³/g, further supporting the development of a more porous structure in the modified biosorbent (Ren *et al.*, 2022).

3.5 XRD Analysis of Mussel Shell Biosorbent

X-ray Diffraction (XRD) analysis was carried out to investigate the crystalline phases of the mussel shell biosorbents and the results presented in Figure 4.

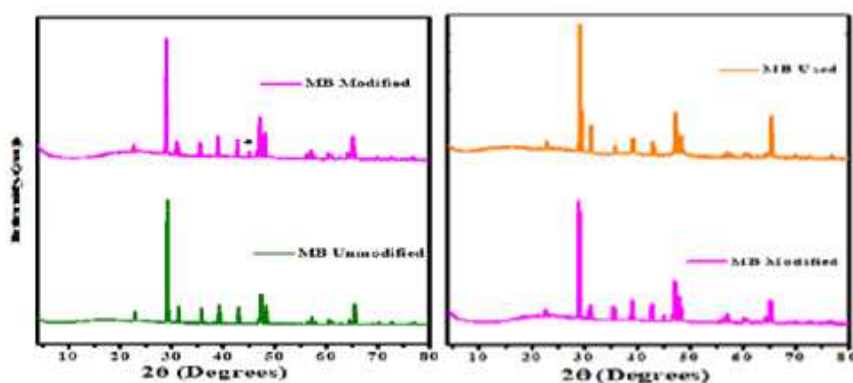


Figure 4: Diffractograms of MB Modified, MB Unmodified Biosorbent and MB Modified used

The diffractograms displayed revealed dominant peaks corresponding to calcium carbonate crystalline phases, particularly calcite and aragonite (Floquet *et al.*, 2015). After pyrolysis and modification, changes in peak intensities and sharpness were observed, indicating increased crystallinity. The modified biosorbent exhibited additional diffraction peaks associated with aluminium oxide and aluminium hydroxide phases, confirming successful surface modification. The enhanced crystallinity and formation of new crystalline phases contributed to improved fluoride adsorption properties (Du *et al.*, 2014, Lee *et al.*, 2021). To determine the effect of fluoride remediation in the crystal structures, the XRD patterns of used shells were obtained. Notably, from the diffractograms of the used mussel shell biosorbent (MB used) new diffraction peaks emerged at approximately $2\theta \approx 8.3^\circ$, 47.0° , and 55.8° , which correspond to the (111), (220), and (311) planes

of calcium fluoride (CaF_2), as referenced in JCPDS Card No. 87-0971. The appearance of these peaks indicated that reactions occurred between fluoride ions and Ca^{2+} on the biochar surface, resulting in precipitation of CaF_2 . This confirms a fluoride removal mechanism involving ion exchange or surface precipitation (Dhillon *et al.*, 2017). The presence of CaF_2 peaks after adsorption signifies the chemical stability of the biochar materials and highlights their efficacy in adsorbing fluoride through mineral precipitation pathways (Dar and Kurella, 2023).

4.0. Optimization Studies

4.1. Effects of pH on Fluoride Adsorption Using Mussel Shell Biosorbent

The effect of pH on fluoride adsorption using modified and unmodified mussel shell biosorbents was investigated over a pH range of 2–14 as shown in the Figure 5.

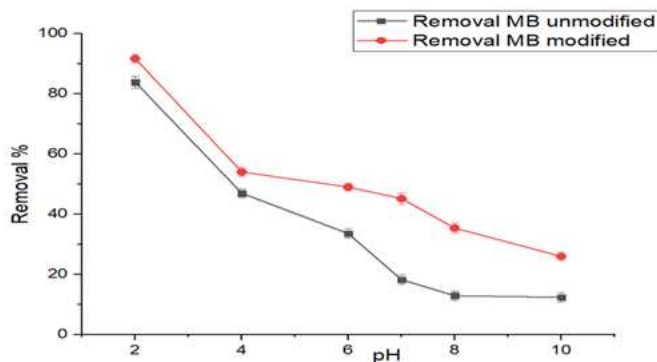


Figure 5: Shows the Effect of Solution pH on Fluoride Removal Using Modified and Unmodified Mussel Shell Biosorbents

From Figure 5 it can be observed that the fluoride ion removal percentage efficiency for the modified mussel shell biosorbent was at maximum of 91% at pH 2 compared to that of unmodified mussel shell biosorbent that was 83.89% at the same pH. This high adsorption capacity at pH 2

could be due to increased positive charge due to aluminium ions on the adsorbent surface (Neeti *et al.*, 2024). This also explains the higher fluoride removal percentage of modified mussel shell biosorbent compared to unmodified mussel shell biosorbent. However, both biosorbents have pH_{pzc} values above 2, indicating that the surface is most positively charged at low pH, promoting high fluoride removal (Kumari *et al.*, 2019). At pH 2 coulombic attraction could be favored because of more positive charges on the adsorbents surface (Chigondo *et al.*, 2018).

It was also noted that at low pH the biosorbent surface tends to be positively charged due to protonation of surface functional groups (Sadhu *et al.*, 2021). This enhances electrostatic attraction between the negatively charged fluoride ions and the adsorbent as also reported by (Sadhu *et al.*, 2021). When the pH increased to pH 4, the percentage removal decreased to 54.04% and 46.80% respectively for the modified and unmodified adsorbent. The negatively charged adsorbent surface causes coulombic repulsion to F⁻ ions at pH values higher than pH p_{zc} (Chigondo *et al.*, 2018). Furthermore, at relatively higher pH 8-10, the solution contains more hydroxyl ions than hydrogen ions, leading to competitive adsorption between hydroxyl and F⁻ ions on the active sites, this reduces the percentage removal capability of the sorbent material as observed in the graph. The adsorbent material also become deprotonated/ more electronegative resulting to fixation of hydroxide ions in preference to F⁻ thereby leading to a decrease in adsorption efficiency (Kumari *et al.*, 2019).

4.2. Effect of Initial Fluoride Concentration

The adsorption capacity increased with increasing fluoride concentration from 2 to 10 ppm as shown in Figure 6.

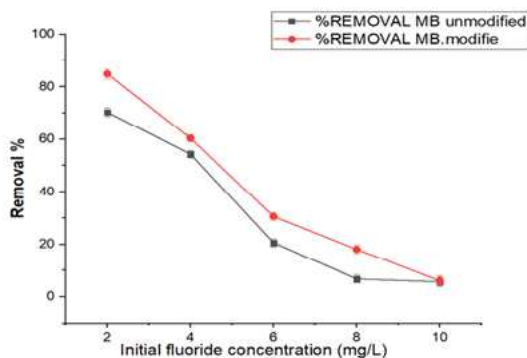


Figure 6: Effect of Initial Concentration on the Sorption Capacity of Unmodified and Modified Mussel Shell Biosorbents.

It was observed from figure 6 that for both unmodified mussel shell biosorbent and modified mussel shell biosorbent, the percentage of fluoride absorbed by both biosorbents gradually dropped as its initial fluoride content rose from 2 to 10 ppm. At 2 ppm, modified mussel shell biosorbent exhibited superior fluoride removal efficiency, achieving 85% removal efficiency compared to 70% removal efficiency for unmodified mussel shell biosorbent. At lower initial fluoride concentration of 2 mg/L, 85% removal efficiency is attained. This indicates that when the initial fluoride concentrations increase, the sorbent's capacity decreases. At higher fluoride concentrations, the active sites of the sorbent were saturated (Rout *et al.*, 2015). On another hand, at low fluoride ion concentrations, the adsorbent possessed enough active sites for the majority of the fluoride ions to interact with them. As a result, the percentage of fluoride ions removed rose until the equilibrium was achieved (Dhongde *et al.*, 2017; Zeng *et al.*, 2023). This confirms the significance surface modification which enhanced the adsorption performance as shown by the modified mussel shell biosorbents (Trivedi *et al.*, 2025).

It was also observed that at higher fluoride concentration of between 6 and 10 ppm the percentage removal efficiency of the two adsorbents decreased to less than 10%. This could be due to saturation of active adsorption sites (Trivedi *et al.*, 2025). Similarly, competition for active sites

grows as the concentration of fluoride ions in the solution rises, ultimately resulting in the sites' depletion (Sadhu *et al.*, 2021).

4.3 Effect of Contact Time

The influence of contact time on fluoride adsorption was examined using the modified mussel shell biosorbent as presented in Figure 7.

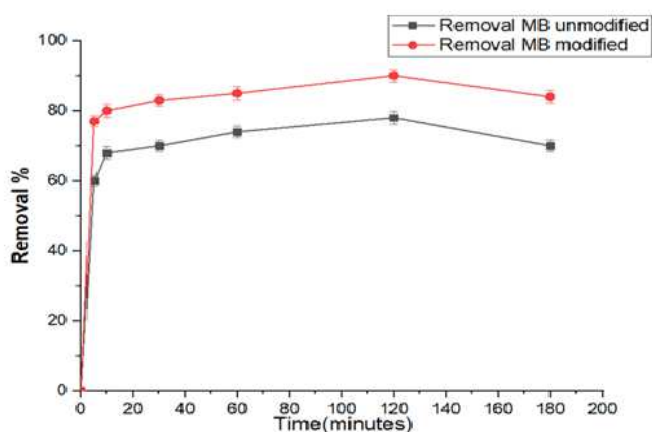


Figure 7: Effects of Contact Time on Fluoride Removal by Modified and Unmodified Mussel Shell Biosorbent

It can be observed from figure 7 that fluoride adsorption increased rapidly during the initial stages of adsorption due to availability of abundant active sites. Equilibrium was achieved after approximately 180 minutes. The unmodified mussel shell biosorbent showed significantly lower removal efficiency, with a gradual increase over time and a maximum removal of about 75% after 180 minutes. This could be due to limited adsorption sites that were filled faster by the adsorbed fluoride ion (Neeti *et al.*, 2024).

It was also noted that the modified mussel shell biosorbent exhibited a high fluoride removal percentage and this could have been due to a larger concentration gradient between the liquid and

solid phase in the system (Rahdar *et al.*, 2019). The rapid adsorption at the beginning was attributed to strong electrostatic attraction between fluoride ions and the biosorbent surface. As adsorption progressed, the remaining active sites became limited, leading to slower adsorption rates. Noticeably, fluoride removal percentage levelled off significantly past the 120 minutes for both the modified and unmodified sorbent materials which denoted the attainment of the equilibrium phase (Kusrini *et al.*, 2019; Neeti *et al.*, 2024). Modified mussel shell biosorbent demonstrated faster adsorption kinetics compared to the unmodified biosorbent.

4.4. Effects of Adsorbent Dosage

The effects of dosage on removal of excess fluoride ions from water was investigated using mussel shell adsorbents and the results presented in Figure 8.

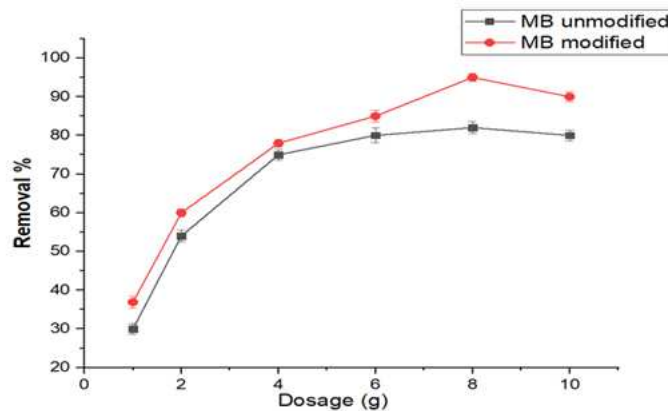


Figure 8: Effects of Adsorbent Dose on Fluoride Removal Using Modified and Unmodified Mussel Shell Biosorbents.

Fluoride removal efficiency increased with increasing adsorbent dosage due to the availability of more adsorption sites (Sadhu *et al.*, 2021). However, adsorption capacity per unit mass decreased at higher dosages due to possible aggregation of particles and overlapping of adsorption sites (Trivedi *et al.*, 2025). The modified mussel shell biosorbent achieved higher fluoride removal efficiencies than the unmodified form.

4.5. Effects of Temperature

It can be observed that the fluoride removal percentage using the unmodified mussel shell biosorbent increases from 15.27% at 30 °C to a peak of 45.90% at 50 °C, before dropping to 32.87% at 60 °C as shown in Figure 9.

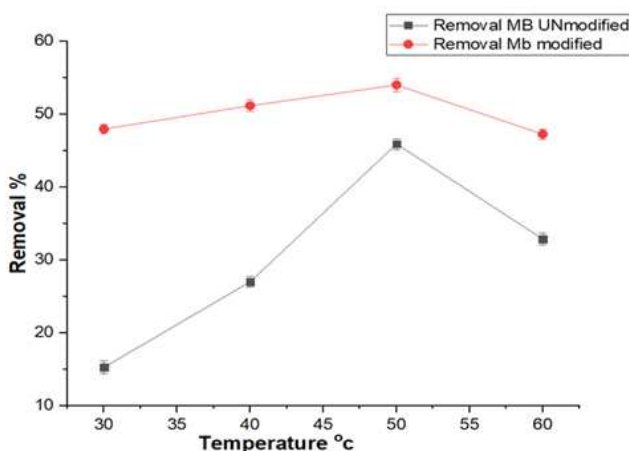


Figure 9: Effects of Solutions Temperature on Fluoride Removal by Modified and Unmodified Mussel Shell Biosorbents

This rise and fall trend indicate that fluoride adsorption onto unmodified is endothermic up to an optimum point (50 °C), beyond which desorption or decreased affinity may occur due to thermal agitation (de Carvalho Costa *et al.*, 2024; Revellame *et al.*, 2020). Similarly, modified mussel shell biosorbent showed an increased adsorption percentage at lower temperature (30 °C) with 47.96% removal efficiency to a peak of 53.99% removal at 50 °C, before falling to 47.25% at 60 °C. The better adsorption percentage at lower temperature indicated greater thermal stability and higher affinity for fluoride by the modified sorbent material, likely due to improved surface area, porosity, and electrostatic attraction enhanced by aluminum modification (Dar and Kurella, 2023). Similar studies on fluoride adsorption being endothermic and increasing with temperature until optimal point and further increasing thermal agitation was done by Tamjidi and Ameri. (2020)

4.6. Effects of Competing Ions on Mussel Shell Biosorbent

The presence of competing ions such as sulfate, chloride, carbonate, and phosphate reduced fluoride adsorption efficiency to varying extents. The bar graphs in Figure 10 illustrates the effects of these competing ions on fluoride adsorption onto the modified sorbent material.

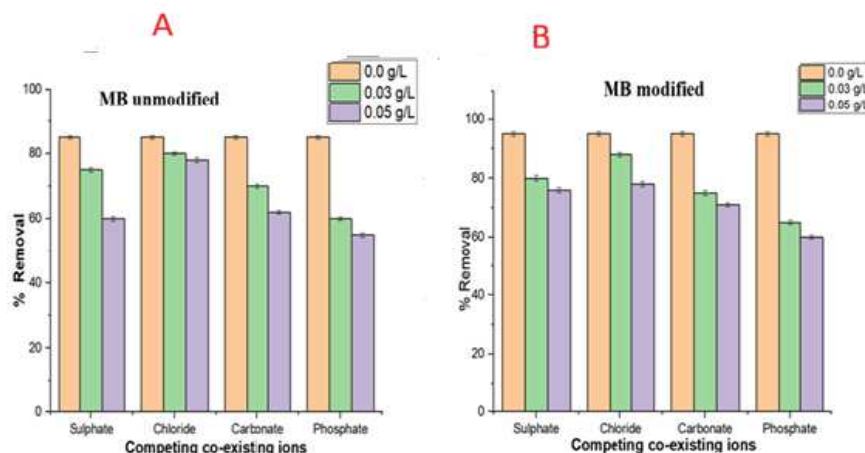


Figure 10: Effects of Competing Ions on Fluoride Removal by Unmodified (A) and Modified (B) Mussel Shell Biosorbents.

It is observed that in the unmodified mussel shell biosorbent Figure 10A, fluoride removal in the presence of chloride ions remained relatively high, decreasing slightly from 80% to 78% when the concentration of chloride was increased from ions 0.03 g/L and 0.05 g/L. This minimal effect is consistent with chloride's monovalent charge and weak affinity for common active sites in presence of fluoride. Conversely, SO_4^{2-} caused a more substantial decline, with removal dropping from 75% to 60% with similar increase in sulphate ions concentration, indicative of its divalent nature and stronger electrostatic competition for active sites (Singh *et al.*, 2017). The CO_3^{2-} exhibited more notable fluoride removal efficiency from 70% to 62%, likely due to a combination of site competition and pH elevation, which reduces adsorbent surface positivity (Poudyal, 2015). However, the phosphate (PO_4^{3-}) ions exhibited the strongest interference, decreasing fluoride

removal from 60% to 55%, likely due to its high charge and strong ligand exchange capability with metal sites (Muchunku *et al.*, 2023).

Modified mussel shell biosorbent, (Figure 10 B) exhibited high fluoride removal efficiency following the order of $\text{PO}_4^{3-} > \text{CO}_3^{2-} > \text{SO}_4^{2-} > \text{Cl}^-$. The presence of Cl^- exhibited a high removal efficiency of 88% at 0.03g/L due to the low affinity of the chloride ions in ligand formation as they react with formation of weaker bonds with active adsorption sites (Murambasvina and Mahamadi, 2020). For sulphate ion, fluoride removal remained above 75% even at the higher concentration of 0.05g/L, suggesting enhanced tolerance to divalent ion competition, potentially due to improved charge distribution (Azzeddine *et al.*, 2024). For CO_3^{2-} , the fluoride removal efficiency was maintained at between 75% and 70%, a substantial improvement over unmodified mussel shell biosorbent. Phosphate, though still the most competitive ion, had a reduced impact post modification, with removal efficiency remaining at 60% at phosphate concentration of 0.05g/L. While modified mussel shell biosorbent demonstrated improved fluoride adsorption in the presence of competing ions, its effectiveness varied depending on the ionic composition of the water (Telkapalliwar and Shivankar, 2019). The degree of competition between competing ions and the target ions and its subsequent effect on adsorption processes depend on ionic strength, charge and size of the competing ion and the chemical properties of the adsorbent (Murambasvina and Mahamadi, 2020). Despite the presence of competing ions, the modified mussel shell biosorbent maintained relatively high fluoride adsorption efficiency.

4.7. Adsorption Isotherm Experiments

Adsorption isotherm studies showed that fluoride adsorption onto modified mussel shell biosorbent followed the Freundlich isotherm model more closely than the Langmuir model as can

be observed in Table 2 and Figure S2. This indicated that the adsorption process was taking place on a heterogeneous surface that varied with surface coverage as was observed on the spectroscopic results. The high correlation coefficient values obtained for the Freundlich model suggested multilayer adsorption on heterogeneous surfaces (Kong *et al.*, 2024)

Table 2: Isotherm Model Parameters for Fluoride Adsorption on Modified mussel Shell Biosorbents

Adsorbent	Langmuir		R ²	Freundlich		R ²	Best isotherm
	Q _{max} (mg/g)	b (L/mg)		K _f (mg/g)	1/n		
Mussel shell unmodified	0.629	0.168	0.5211	0.0278	0.21	0.7302	Freundlich
Mussel shell modified	1.034	0.584	0.9209	0.202	0.30	0.9821	Freundlich

The modified mussel shell biosorbent gave a removal capacity (K_f) of 0.202 mg/g. This value was higher than that reported by Muchunku *et al.* (2023) in a study on defluoridation of groundwater by activated carbon derived from water hyacinth (*E. Crassipes*) by Phosphoric Acid Activation which gave an adsorption capacity of 0.1801 mg/g. The heterogeneity factor, 1/n, ranged between 0.21 and 0.53 was observed as seen in table 2, falling within the favorable adsorption range ($0 < 1/n < 1$) (Ashraf *et al.*, 2022).

4.8. Adsorption Kinetics of Fluoride

The kinetic behavior of fluoride adsorption onto modified and unmodified shell biosorbent was evaluated using two kinetic models; the Pseudo-First-Order and Pseudo-Second-Order models. It was observed that modified adsorbent exhibited higher correlation coefficients ($R^2 = 0.8917$ for

PFO and 0.9874 for PSO) compared to the unmodified adsorbent, indicating improved adsorption performance. The PSO model provides the best fit for both materials, suggesting that chemisorption is the dominant adsorption mechanism governing MB uptake as presented in Figure S3. The linearized data on various kinetic model parameters are presented in table 3.

Table 3: Kinetic Model Parameters for Fluoride Adsorption onto Modified and Unmodified Shell Biosorbents

Adsorbent	Pseudo First Order (PFO)			Pseudo Second Order (PSO)		
	$q_e(\text{mg/g})$	$K_1(\text{mg/g/min})$	R^2	$q_e(\text{mg/g})$	$K_2(\text{mg/g/min})$	R^2
Mussel shell unmodified	2.338	0.00552	0.735	0.107	0.3459	0.9445
Mussel shell modified	1.177	0.00826	0.907	0.209	1.082	0.9874

It was observed that the modified mussel shell biosorbent showed higher q_e of 0.209 mg/g while that of unmodified mussel shell biosorbent was 0.107 mg/g. This enhancement is consistent with reports by (Corral-Capulin *et al.*, 2018; Telkapalliwar and Shivankar, 2019) that chemical modification of biosorbents could significantly increase fluoride uptake through increased surface area, pore structure development, and the introduction of functional groups that promote fluoride binding.

5.0. Regeneration of Mussel Shell Biosorbent

The modified and used mussel shell was regenerated using 1.0 molar HCl and the results presented in Figure 11.

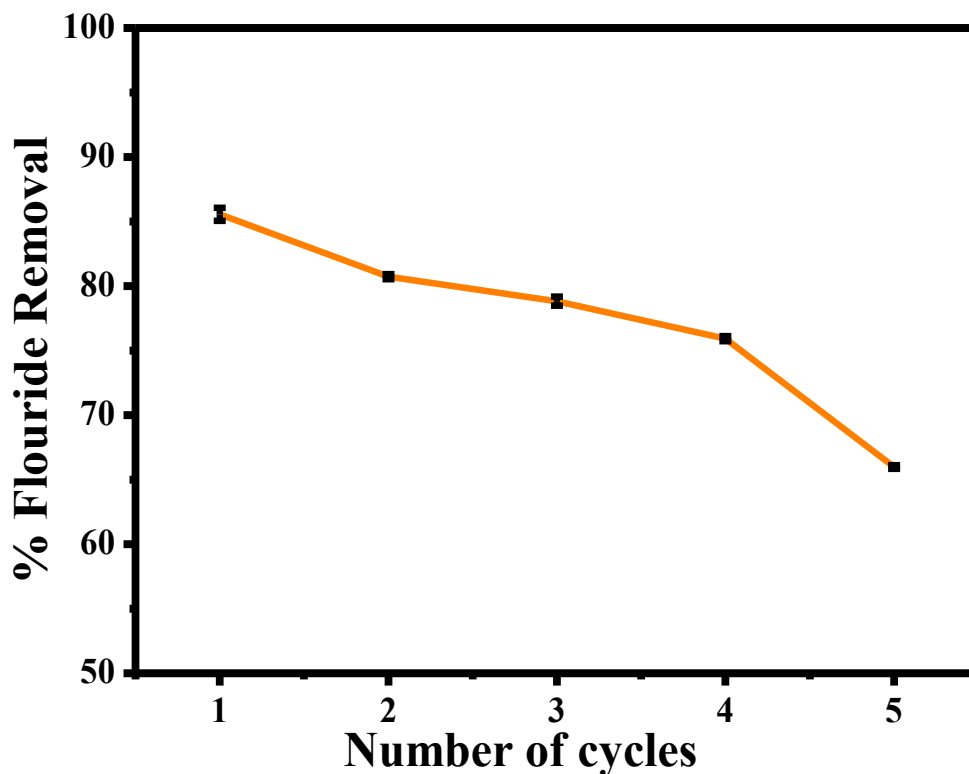


Figure 11: Regeneration Study for Used Modified Mussel Shell Biosorbent

The results in Figure 11 revealed that the material maintained high adsorption efficiency across five consecutive regeneration cycles. The results show that fluoride removal efficiency decreased progressively from 84.5 % in the first cycle to 63% by the fifth cycle. This gradual decline can be attributed to the progressive occupation and saturation of active binding sites on the adsorbent surface, as well as possible structural degradation of the biosorbent during repeated regeneration treatments (Kiprono, 2024). Maintaining of the high fluoride removal efficiency after multiple regeneration cycles demonstrates the robustness and stability of the modified mussel shell biosorbent (Chang *et al.*, 2019). Equally the high efficiencies maintained after several regeneration

cycles suggests that the regeneration process not only restores adsorption sites but could also activate the biosorbent surface by protonating it, thereby enhancing its affinity for fluoride ion (Mukkanti & Tembhurkar, 2024) . The sustained efficiency of the regenerated modified mussel shell biosorbent across successive cycles demonstrates its reusability without appreciable loss of adsorption capacity, an advantageous property for economical water treatment applications.

6.0 Application of Modified Mussel Shells Biosorbents in Real Water Samples

Water samples collected from Koguta, Waondo and Paga within Lambwe valley in Kenya were utilized to examine the efficacy of modified snail shell and mussel shell biosorbents in defluoridation. The mean physical parameters for the sampled water from Koguta, Waondo and Paga boreholes within Lambwe valley in Kenya were analyzed and the results presented in table 4.

Table 4: Physico-Chemical Parameters of Lambwe boreholes Water

Parameter	Mean $\pm$ SD	Coefficient of Variation %	WHO Guideline
Electrical Conductivity ($\mu\text{S}/\text{cm}$)	150.033 $\pm$ 0.208	0.14	<1500
Total Dissolved Solids (mg/L)	75.033 $\pm$ 0.153	0.2	<500
Salinity (ppt)	0.083 $\pm$ 0.006	6.93	<0.5
pH	7.857 $\pm$ 0.055	0.7	6.5–8.5
Temperature ($^{\circ}\text{C}$)	26.6 $\pm$ 0.3	1.13	No guideline
Resistivity ($\text{k}\Omega\cdot\text{cm}$)	6.567 $\pm$ 0.058	0.88	Inverse of EC
Total Suspended Solids (mg/L)	0.0 $\pm$ 0	0.0	<5

From the table 4 it can be observed that, the sampled water revealed acceptable quality in most parameters. Electrical conductivity averaged 150.0 $\pm$ 0.208 $\mu\text{S}/\text{cm}$ with minimal deviation, which is well below the WHO limit of 1500 $\mu\text{S}/\text{cm}$. This indicates that the water contains low levels of

dissolved ions and minimal mineralization (Kumar *et al.*, 2020). Similarly, the mean total dissolved solids (75.0 ± 0.153 mg/L) correlated well with conductivity and was far below the guideline value of 500 mg/L, confirming that the water is of good palatability (Kiprono, 2024).

The results also show that salinity was found to be 0.083 ± 0.006 ppt, a value that classifies the water as fresh, and although the relative variation was slightly higher, this was mainly due to sensitivity of the measuring equipment at such low ranges. The pH value of 7.86 ± 0.3 indicated slightly alkaline conditions, typical of groundwater influenced by carbonate minerals (Frisbie *et al.*, 2015) and still within the WHO recommended range of 6.5-8.5. The mean temperature was 26.6°C , reflecting ambient environmental conditions during sampling while resistivity averaged 6.57 ± 0.058 k Ω ·cm.

The modified mussel shell biosorbent was applied in adsorption of fluoride from real borehole water samples collected from Koguta, Waondo, and Paga boreholes and results presented in graph Figure 12.

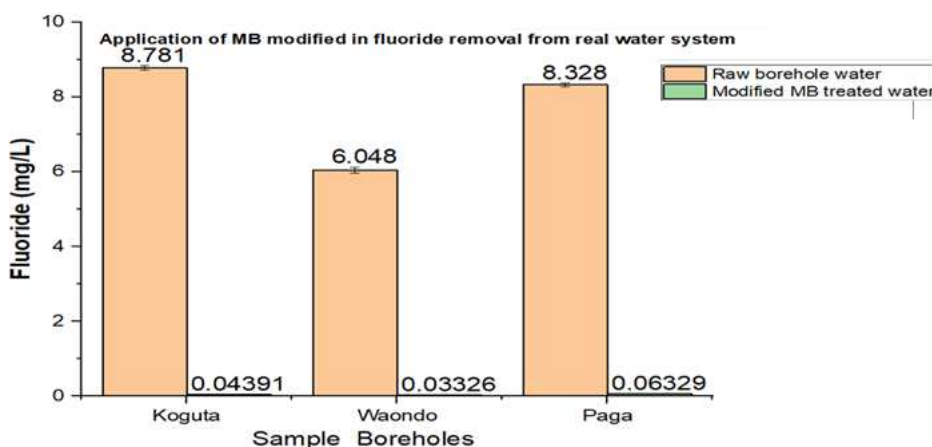


Figure 12: Application of Modified Mussel Shell Biosorbent in Fluoride Removal from Real Water System

Fluoride concentrations in the sampled boreholes were above WHO acceptable limit but upon treatment with modified mussel shell biosorbents, it significantly reduced. For example, the fluoride levels in Koguta water reduced from 8.781 ± 0.05 mg/L to 0.04391 ± 0.002 mg/L, Waondo 6.048 ± 0.09 to 0.03326 ± 0.007 mg/L and Paga 8.328 ± 0.082 to 0.06329 ± 0.005 mg/L. The mussel shell biosorbent demonstrated superior fluoride adsorption capacity, with efficiencies approaching complete removal. This high removal efficiency could be associated with its higher calcium carbonate and surface reactivity in mussel shells (Chang *et al.*, 2019).

CONCLUSION

The results of this study demonstrated that modified freshwater mussel shell biosorbent is an effective, low-cost, and environmentally friendly adsorbent for fluoride removal from contaminated water. Characterization studies using FTIR, SEM, EDS, BET, and XRD confirmed that aluminium modification significantly improved the physicochemical properties of the mussel shell biosorbent. FTIR analysis revealed the introduction of Al–O and Al–OH functional groups, while SEM and BET analyses showed increased porosity and surface area after modification. XRD patterns confirmed the presence of calcium carbonate crystalline phases as calcite and aragonite, whereas EDS analysis verified successful incorporation of aluminium and adsorption of fluoride ions onto the biosorbent surface.

Batch adsorption experiments confirmed that pH, fluoride concentration, contact time, adsorbent dosage, temperature, and competing ions influenced fluoride adsorption efficiency. The modified mussel shell biosorbent achieved optimum fluoride removal at pH 7, where the adsorption sites were most favorable for fluoride uptake. Fluoride adsorption increased with increasing adsorbent dosage and contact time, reaching equilibrium after 180 minutes. Increased temperature enhanced fluoride adsorption, indicating that the adsorption process was endothermic in nature. Although

competing ions reduced adsorption efficiency, the modified mussel shell biosorbent maintained considerable fluoride removal capacity even in the presence of sulfate, chloride, carbonate, and phosphate ions. The modified mussel shell biosorbent exhibited the highest adsorption capacity of 0.202 mg/g, indicating superior performance compared to the unmodified biosorbent. Adsorption isotherm studies showed that fluoride adsorption followed the Freundlich isotherm model, suggesting multilayer adsorption on heterogeneous surfaces. Kinetic studies further established that fluoride adsorption followed the pseudo-second-order kinetic model, indicating that chemisorption was the dominant adsorption mechanism.

Application of the modified mussel shell biosorbent to real borehole water samples from Lambwe Valley successfully reduced fluoride concentrations from levels above the World Health Organization permissible limit to acceptable levels below 1.5 ppm. This confirmed the suitability of the biosorbent for practical water defluoridation applications. Furthermore, regeneration studies demonstrated that the modified mussel shell biosorbent retained high adsorption efficiency after five adsorption desorption cycles, indicating good stability and reusability. Therefore, this study established that modified freshwater mussel shell biosorbent prepared from locally available shell waste has great potential as a sustainable and efficient adsorbent for remediation of fluoride-contaminated water while also contributing to environmental waste management.

Data Availability

The data that support the findings of this study are available from the corresponding author upon request.

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Conflicts of Interest

The authors declare no conflict of interest regarding the design of the study, in the collection, analyses or interpretation of data, in the writing of the manuscript and the publication of this paper.

Ethics, Consent to Participate, and Consent to Publish declarations

Not applicable

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