



Defluoridation of drinking water by modified natural zeolite with Cationic surfactant, in the case of Ziway town, Ethiopia

Dessalegn Geleta Ebsa

Lecturer in Faculty of Civil and Environmental Engineering, Water Supply and Environmental Engineering Department, Jimma Institute of Technology, Jimma University, Ethiopia

ARTICLE INFO

Keywords:

Cationic surfactant
Defluoridation
Drinking water
Modified clinoptilolite

ABSTRACTS

Excessive fluoride intake in drinking water sources in Ethiopia (Ziway town) causes health issues in the residents. The goal of this study was to utilize the defluoridation of drinking water using clinoptilolite zeolite modified with a cationic surfactant Hexadecyl Trimethyl Ammonium Bromine. The treatment's removal efficiency has been optimized by the pH of the solution (5.5 ± 0.2 – 8.5 ± 0.2), initial fluoridated water (1–10 mg/L) to fast fluoride removal at a potency of 5.5 g/L, dose of surfactant modified zeolite (2.5–18 g/L), contact time (30-min, and the effect of temperature (80–120 °C), which better removal efficiency as temperature increased. The study was examined, at the constant Blank of 10 mg/L, 5 g/L of Hexadecyl Trimethyl Ammonium Bromine dosage records the highest fluoride removal potential at the end of the 60 min runtime: Sodium Low Silica X (Na-SX) (88.4%), Sodium Linde Type A (Na-LTA) (64.6%) and Reagent only Zeolite (ZR) (25%). Incompatible with this reflection, the model waters with pH maintained at 5.5 ± 0.2 and 6.5 ± 0.2 verified rapid fluoride removal (89.7% and 72.3% respectively) within the first 3 h of runtime. The best performance of this treatment efficiency were obtained at pH (5.5–8.5), stock solution ≤ 10 mg/L, adsorbent dose ≤ 18 , and more delayed time. The findings of this study indicated that unmodified clinoptilolite zeolite was incapable of adsorbing fluoride ions, but the surfactant-modified zeolite adsorbed fluoride but requires adequate pH control, temperature, and running times. The coincidence of large amount of natural zeolite and high level of fluoride in drinking water in Ethiopian rift valley areas pulls the very vital aspect, which requires the modified treatment technology.

1. Introduction

Fluoride is an electronegative element that is attracted to the positively charged ion of alkali metals and alkaline earth metals (Sodium, Potassium, Calcium, Magnesium, etc.). Alkaline earth metals have low ionization energy, low electron affinity, low electronegativity, highly reactive, and often form divalent cations, whereas alkaline metals have also the same property as alkaline earth, but it's the most reactive metals, due in part to their larger atomic radii and low ionization energies (Pandey, 2021). This group of metals have high reactive with group 7 elements (e.g. Fluorine), which have high electronegativity. The maximum concentration of calcium in the body is present in bones and teeth, which draw the most fluoride and deposit it as calcium fluorapatite crystals (Ram et al., 2021).

According to the U.S. Public Health Service, the optimum fluoride concentration in the water supply was between 0.7 mg/L to 1.2 mg/L, the World Health Organization recommendation for fluoride's permissible limit is 1.5 mg/L (Ali et al., 2016). But, in Halaba district of

Southern Ethiopia fluoride levels from boreholes are high (2.6–7.0 mg/L) yet the incidence of fluorosis is modest (Demelash et al., 2019). Drinking water users living in the vicinity of four drinking water systems that have been in operation for more than 35 yrs out of 625 persons were surveyed, 5% had severe dental fluorosis and 42% had mild forms (Demelash et al., 2019). Water samples collected from defluoridation plants in Wonji-Shoa plantation and factory villages revealed elevated fluoride concentration ranging from 3.8 mg/L to 12.7 mg/L. Among 115 springs sampled in the Rift Valley, (90.0% of the 20 hot springs and 12.6% of the 95 cold springs) had fluoride levels above 1.5 mg/L (Sara Datturi, Assefa Kumsa, Seifu Kebede, 2017). The total samples collected, 53.3% were from deep wells, 24% shallow wells, 16.1% from springs, 3.7% from rivers and 1.2% from lakes (Steenbergen et al., 2011). In Ethiopia's major Rift Valley almost 14×10^6 people rely on fluoride-rich water sources (Tekle-haimanot et al., 2006). The public drinking water supply source of Ethiopian Rift Valley (Ziway town), the Nalgonda method (use of aluminum sulphate and lime) is practiced. The Nalgonda technique was developed and adapted in India by the National

E-mail address: dessalegn.geleta@ju.edu.et.

<https://doi.org/10.1016/j.clet.2023.100596>

Received 21 September 2022; Received in revised form 22 December 2022; Accepted 7 January 2023

Available online 11 January 2023

2666-7908/© 2023 Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

Environmental Engineering Research Institute to be used at either community or household level (Asma M., *et al.*, 2022). It uses the process of aluminum sulphate based coagulation flocculation-sedimentation, where the dosage is designed to ensure F^- removal from the water. In Ethiopia, under the fluorosis mitigation project promoted by UNICEF and the Federal Water and Energy Ministry, the Nalgonda technique has been piloted in several rural communities (Ahmad Z *et al.*, 2022). Most communities of kebeles 02, 07, and 04 were used their drinking water supply sources directly from ground water sources using chlorination treatment in this Great Rift Valley, in rural areas majority of the population were used their drinking water supply from hot springs. Ground water usually contains dissolved mineral ions that can affect the water's usage depending on the type and concentrations of the ions involve. Accordingly the fluoride concentrations in wells selected for dental fluorosis analysis for the communities received clinical dental fluorosis examination for Ziway town and its rural area drinking water source for Cheleki 18 mg/L, Wonji camp.9.7 mg/L, Wulumbula 10.4 mg/L, and Wegea 13.2 mg/L, are some of them among 13 water supply sources sampled for dental fluorosis (Zhang *et al.*, 2020). Therefore, it is too difficult for defluoridation of drinking water supply sources for this area by using Nalgonda and sand filtration alone, and the main objective study were removal of fluoride concentration by modified natural zeolite with Cationic surfactant. Mostly, the alkali metals and alkaline earth metals of cations surfactant usually attached to the zeolite structure are sodium, potassium, magnesium, lithium, barium, and calcium (Dong *et al.*, 2021). The use of cationic surfactants to modify zeolites in particular greatly increases the adsorption potency and affinity for anions removal in an aqueous solution (Rahmani *et al.*, 2010).

The most common synthetic/modified zeolites used in industrial applications are zeolite (X, A, Y, and P) and naturally occurring zeolites (analcime, chabazite, clinoptilolite, erionite, ferrierite, heulandite, laumontite, mordenite, and phillipsite)(Zhang *et al.*, 2020). Clinoptilolite mineral is one of the most typical natural zeolites, easily accessible from mines, and excellent as a sorbent because to its natural characteristics. Surfactant modified clinoptilolite was an effective sorbent for both organic compounds and inorganic anions from water which consist of alumino silicate mineral of porous structure that have valuable properties (Zhang *et al.*, 2020).

Aluminum has a slightly positive charge than silicon, the framing typically has a net negative charge that is countered by a replaceable cation like $(Na_2, K_2, Ca, Mg)_3$, $(Al_6 Si_{30} O_{72} \cdot 20H_2O)$ (Gul *et al.*, 2022; Guoru *et al.*, 2021; Muhammad *et al.*, 2022). Most of the natural and modified zeolites have high selectivity for cations for which have a wide application in water purification, mainly in the uptake of heavy metal pollutants, ammonia, and radioactive species (Joseph *et al.*, 2019). Zeolite modification can be accomplished through various approaches, including ion exchange, in which the original zeolite's exchangeable cation is replaced by Hexadecyl Trimethyl ammonium bromide. The ion exchange of Hexadecyl Trimethyl ammonium bromide (HDTMA-Br) with clinoptilolite can be eliminate fluoride concentration from drinking water sources, due to this interaction. There is no any advanced treatment technology or modified treatment technology used for this area, and most of the researchers studied were focused on determination fluoride concentration in daily intake in water supply sources. This have a negative implication on the health condition of the society living around that area. The outcomes of the study were to remove excess fluoride in drinking water, which is high affects society's health by using naturally available material by simple modification with cationic surfactants.

2. Materials and methods

2.1. Materials and chemicals

The study was used different materials, Chemicals and Reagents were used during this study. For-instance Crusher (jaw, mortar and

pestle) for Size reduction No.16 mesh, Sieve (sieve sample), Analytical balance, Incubator shaker Vacuum filter, and Centrifuge. Chemicals and Reagents used for the study were NaCl (determine the surface chemistry), Sodium fluoride, NaOH and HCl (adjustment of pH), Clinoptilolite (adsorbent) distilled water, HDTMA-Br, and Nitric acid are some it.

2.2. Study design flow diagram

In order to gain the output of the study was gathered different samples and literature reviews as described in Fig. 1.

2.3. Sample collection

Drinking water samples were collected from the Ziway area from ground water and surface sources and additional from the drinking water distribution system. Among different water sources, two samples were taken from river sources (Bulbula river mouth 38.74326° E, 8.051128° N which was located in kebeles 05, and giving services for 4567 populations and Meki river 38.848733° E, 8.051238° N which found in kebeles 02, which give services for 6754 population). The other points of sample collection were from boreholes (floriculture industries 38.740261 E, 7.917644 N of the population where services and Korekonch 38.755692 E, 7.99505 N which services 5489 of the population).

2.4. Analysis of defluoridation

The removal of fluoride concentration by natural zeolite with cationic surfactants was analyzed by standard procedures of the water quality guidelines. This can be measured or set as the existence of fluoride elements and free compounds, which may exist in an aqueous form, and the removal efficiency, and the overall removal efficiency of the study was calculated as :

$$\text{Removal efficiency} = 1 - \frac{C_t}{C_o} * 100\% \quad (1)$$

Where; C_t is the dye concentration at time t and C_o is the initial dye concentration. The quantity 125 of fluoride concentration adsorbed on the Cetriamonium bromide-modified cornstalk biochar was calculated by the following equation:

$$q_c = (C_t - C_e) \frac{V}{W} * 100\% \quad (2)$$

$$q_t = (C_o - C_t) \frac{V}{W} * 100\% \quad (3)$$

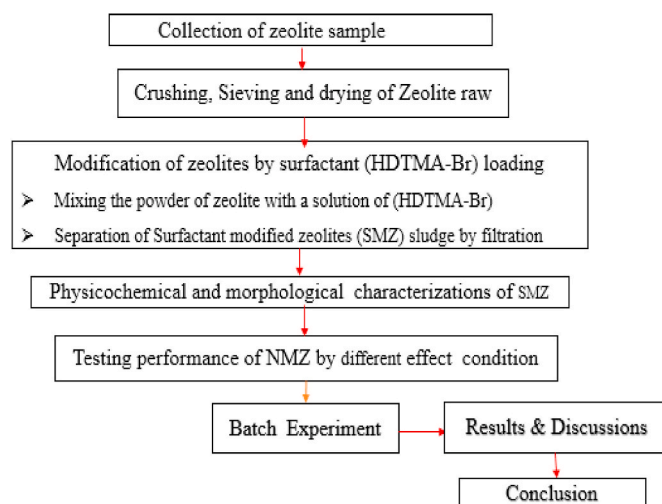


Fig. 1. Study design flow chart.

Where q_e and q_t (mg/g) are the adsorption capacity at equilibrium and t min; C_0 is the initial concentration of fluoride concentration in solution, while C_e and C_t (mg/L) are the concentrations of fluoride at equilibrium and min, respectively; V (L) is the volume of solution and W (g) is the mass of adsorbent used.

2.5. Surfactant modified zeolite (SMZ) preparation

The hydrothermal treatment methods employed in zeolite formation usually involve appropriate pretreatments processes. The rate of crystallization and nucleation time were both considerably accelerated by potassium ions. According to (Badessa et al., 2020), the surface of nanoparticles of (K, Na) clinoptilolite was produced by hydrothermally processing a (K, Na)-aluminum-silicate slurry containing starting ingredients with a Si/Al : (Na + K)/Si: K/(Na + K): H₂O/Al with a molar ratio of 6.0:0.42:0.5:52.5. Furthermore (Dey et al., 2022; Manikandan et al., 2013), crystalline clinoptilolite could be obtained from a batch composition of 2.1Na₂O: Al₂O₃:10Si₂O:110H₂O, according to the process reported by (Yahya et al., 2020). Two protocols each were adopted to synthesize zeolites Na-LSX (Sodium Low Silica X) and zeolite LTA (Linde Type A) using different alumina and silica sources. Zeolite Na-LSX was synthesized using a locally available clinoptilolite mineral source (alumina and silica). Zeolite LTA (Linde Type A) was synthesized from locally available clinoptilolite and bauxite minerals as the source of silica and alumina respectively.

Sodium Meta silicate and sodium aluminate laboratory reagents were also used to synthesize another zeolite nicknamed zeolite ZR. Zeolite LTA (Linde Type A) was synthesized from locally available clinoptilolite and bauxite minerals as the source of silica and alumina respectively. Sodium silicate and sodium aluminate laboratory reagents were also used to synthesize another zeolite nicknamed zeolite ZR. The ability for internal intercalation has been 800 meq/Kg, and the capabilities for exterior electrostatic interaction were 90–110 meq/Kg (Chengying B., et al., 2021). The zeolite was crushed and sieved into two different grain sizes for the test performed and the laboratory batch studies: 1.4 to 0.4 mm (14–40 mesh) for the test run and 0.18 to 0.15 mm (80–100 mesh) for the laboratory batch studies.

3. Results

3.1. Modification of clinoptilolite zeolites

The unmodified and modified (Table 1) different surface chemistry (Na-LST, Na-LTA, and ZR) of natural cationic surfactants proportions were justified. This percentage of natural zeolite weights has been taken accordingly to the proposed modified cationic surfactant of natural zeolite formations. The modified natural zeolites of cationic surfactants have been oxidized by the same elements and replaced by carbon in place of iron, copper, and sulfur in the case of modified cationic surfactants of Na-LSX. In the same manner for both modification of Na-LTA and modification of ZR zeolites, carbon elements were oxidized without

Table 1
Modification of natural zeolites cationic surfactants'

Unmodified		Na-LSX modified		Unmodified Na-LTA		Na-LTA modify		ID	Un modified		ZR modified	
ID	V (%)	V (%)	V (%)	V (%)	V (%)	V (%)	V (%)		V (%)	V (%)	V (%)	V (%)
O ₂	68.5	48.1	0.3	0.2	0.2	O ₂	8.9		7			
Na	8.4	5.6	10.8	6.6	6.6	Na	72.2		47.1			
Al	9.2	6.1	11.3	6.2	6.2	Al	8.5		7.8			
Si	13.1	8.5	66.7	45.3	45.3	Si	10.1		9.3			
S	0.2	0.2	11	6.1	6.1	S	0.32		0.2			
K	0.2	0.1		35.6	35.6				28.6			
Fe	0.3	0.2										
Cu	0.1	31.3										

Where V is represented Volume.

replacing other compounds/elements as indicated in Table 1.

3.1.1. Batch experiments

A series of batch adsorption experiments were conducted (using zeolite Na-LSX and Na-LTA) to determine the fluoride removal potentials for unmodified and modified zeolites.

3.1.2. Removal of fluoride using unmodified zeolites

This batch experimental process was conducted to investigate the fluoride removal potential of all considered unmodified natural zeolites (Na-LSX, Na-LTA, and ZR) (Fig. 2).

As indicated in Fig. 2, beyond the initial 45 min until the end of runtime, all the unmodified zeolites maintained maximum adsorption levels indicating a period of near equilibrium.

3.1.3. Effect of varying HDTMA-Br dosage on fluoride uptake

Based on this issue, the study investigated which cationic surfactant dosage (HDTMA-Br) was recorded as the lowest and highest fluoride concentration in drinking water as (Fig. 3) (see Fig. 4).

3.1.4. Effect of reaction time on fluoride removal

The intention of this experiment was to determine the effect of reaction time variations on fluoride removal efficiency.

3.1.5. Effect of pH on fluoride removal

The influence of pH on fluoride absorption was studied using modified zeolites Na-LSX, Na-LTA, and ZR at pH values of 5.5 ± 0.2 , 6.5 ± 0.2 , and 7.5 ± 0.2 . The solutions were maintained at their required pH using 0.1 N NaOH, 0.5 and 1 N HCl solutions. In addition, a batch setup was concurrently run without pH adjustments using modified Na-LSX, Figs. 7 and 8 depict the results obtained.

3.2. Discussions

Same of modified zeolites elements were common before and after the modification of zeolite with cationic surfactants (Na-LTA and ZR), but, (Na-LSX) changed before and after modification. The changed elements, designates the modified zeolites have a good pore space and highly activated for adsorption of fluoride concentration than others unmodified zeolite. This requires activating and reshaping the framework structure of zeolite or substitution of silicon with aluminum (Si/Al atoms in the crystal zeolitic structure. Indeed, the modified natural zeolites with cationic surfactants, Zeolite Na-LSX was found to be the best performing adsorbent than Zeolite Na-LTA and ZR at constant pH 5.5 and 105 °C. The percentage composition of Si and Al elements from the Energy Dispersive X-Ray analysis (Table 1) gives Si/Al ratios of 1.39, 1.01, and 1.197 for zeolite Na-LSX, Na-LTA, and ZR respectively. Almost all of the geopolymer gels can be transformed into zeolite at a higher molar ratio of Si/Al. It confirms that the molar ratio of Si/Al has a significant effect on the phase transformations and microstructure. The NaA zeolite is the main phase when the molar ratio is less than 1.25, and the main phase is transformed to analcime as the molar ratio increases

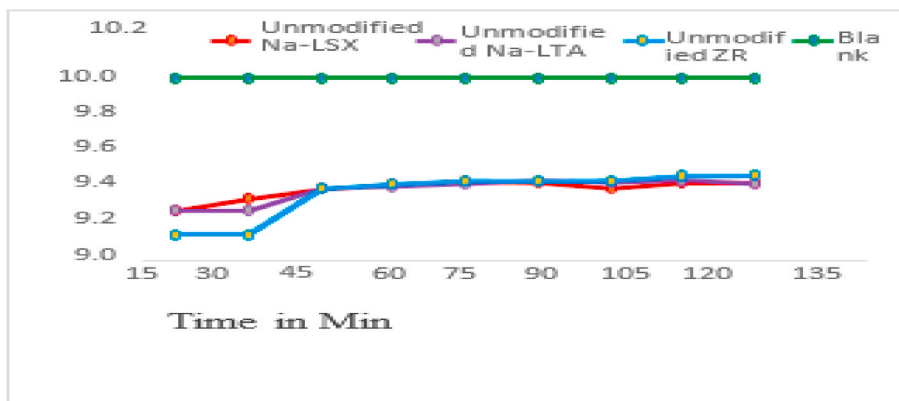


Fig. 2. Fluoride removal using unmodified zeolites : (Na-LSX, Na-LTA, ZR).

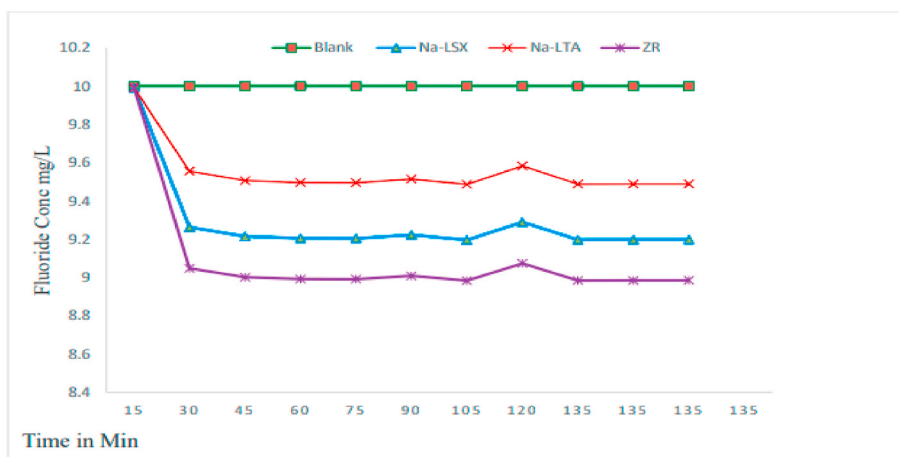


Fig. 3. Fluoride removal using unmodified zeolites under controlled of 6.5 ± 0.2 .

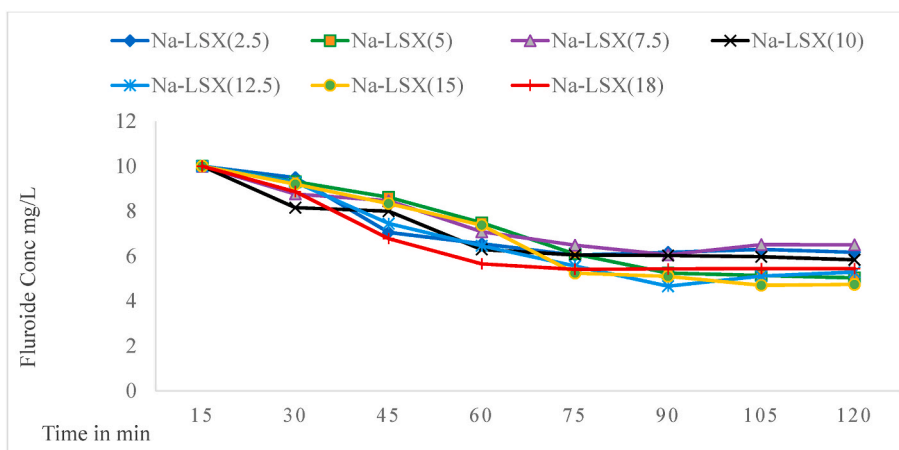


Fig. 4. Fluoride removal using zeolite Na-LSX modified with different dosage of HDTMA-Br.

from 1.5 to 2 (Mohammadi et al., 2013). More Zeolites with low silica content and a Si/Al ratio approaching one generally exhibit more hydrophilic characteristics than high silica zeolites with a high Si/Al ratio, which influenced hydrophilicity by the nature of the charge-balancing cations in the pores (Mohammadi et al., 2013). This result of a modification indicates, in the 1st and 2nd columns have a better morphological structural pore space and activated composition of elements that highly adsorbed the fluoride concentration. This shows, Na-LSX has pure crystal products and uniform particle sizes which more performance to

removes fluoride concentration in drinking water. During this modification of natural zeolite/clinoptilolite, same as the modified zeolites by cation surfactant, the existing elements remained constant both after and before modification. This result was recorded in both Na-LTA and ZR types, whereas in the Na-LSX composition one heavy element (copper) was lost since this modification.

The prepared raw material and modified cationic surfactants were used for adsorption of batch experiments in different scenarios of variation with HDTMA-Br dosages from 2.5 to 18 mg/L. Increasing the

dosage of HDTMA-Br from 0.17 to 7 g/L caused more removal of chromate, which was consistent with the finding of the present study (Kumar and Arunabha, 2018). This was occurred, due to the fact that the surfactant molecules made two layers on the zeolite surface; one side was hydrophilic and the other side was hydrophobic. The removal efficiency of unmodified zeolites adsorbent was only slight fluoride removal by the unmodified zeolites occurred in the initial 15 min of the runtime. Beyond to this, fluoride concentration of the solution leached back into the solution until the end. This poor fluoride uptake could be attributed to the repulsion between the negatively charged zeolite surface and the negatively charged fluoride ions. The surface loading for optimum fluoride removal is less than or equal to 0.1042 mg/g. A dose of 24 g corresponding to the capacity of 0.0889 mg/g of adsorbent was considered for further adsorption studies (Mohammadi et al., 2013). The pH values recorded for the test rose from an initial pH of 7.5–8.5. Fig. 3 describes the fluoride removal performances by the three unmodified zeolites when the pH of the fluoride-contaminated solutions was maintained at 6.5 ± 0.2 . The result of the blank setup indicates that there was no fluoride removal over the entire duration of the experiment. This depicts the fluoride removal performances by unmodified zeolites (Na-LSX, Na-LTA, and ZR) without any pH adjustment (7.5–8.5). This suggests that the fluoride removal was only due to adsorption by the unmodified zeolites and as it described in Fig. 3 when the pH of the solution was maintained at 6.5 ± 0.2 the adsorption of fluoride significantly increased. This is the reason for piercing fluoride concentrations decrease within the initial 45 min of the test indicating rapid attachment onto the free sites. This superficially hydrophilic nature of the unmodified zeolites might have also enhanced the affinity and rapid uptake of fluoride anions. As expressed in Fig. 2, beyond the initial 45 min until the end of runtime, all the unmodified zeolites maintained maximum adsorption levels indicating a period of near equilibrium. The high fluoride removal performance by zeolite ZR could be attributed to its inherent nature, that is the combined properties of zeolite Na-LSX and Na-LTA. The illustrated Figure, (2 and 3) represent the fluoride removal potentials of unmodified zeolites Na - LSX, Na-LTA, and ZR with a runtime under controlled pH and without adsorbents, and each zeolite was modified with a variety of HDTMA-Br dosages concentrations (2.5, 5, 7.5, 10, 12.5, 15, and 18) g/L. The effect of cationic surfactant dosage for adsorption of fluoride removal of the study to modify the natural zeolite types (Na-LTA) 5 g/L of HDTMA-Br were most effective dosage for adsorption of 1–10 mg/L. The study investigated the effect of fluctuating HDTMA-Br dosage on fluoride adsorption by increasing 2.5 g/L and with the variation of 15 min intervals until the end of 120 min.

The effective dosage of cationic surfactant was observed during the study, and 5 g/L of the dosage were effective, above this value, the adsorption of modified zeolite was almost constant. Accordingly (Fig. 8),

stated at 5 g/L HDTMA-Br have the highest fluoride removal potential at 3 h of runtime: Na-LSX (88.4%), Na-LTA (64.6%), and ZR (25%). Application of the modified Nano zeolite with a concentration of 0.8 g/L, shows a higher potential of humic acid adsorption from water, and its modification by 0.5–10 g/L HDTMA-Br can remove 70% of humic acid (25–96%) on an average (Bhaumik and Kumar, 2014). The maximum removal efficiency for humic acid is 96% and 86% for the surfactant dosage of 7 and 10 g/L respectively, which show that in experiments with surfactant dosages less than 3 g/L, the turbidity is increased (Rango et al., 2012) (see Fig. 5).

The intention of this experiment was to determine the effect of reaction time variations on fluoride removal efficiency. Equal amounts of zeolite Na-LSX were modified by stirring in equal volumes of 5 g/L HDTMA-Br with the aid of a flocculator. Fig. 6 perceived that fluoride removal is rapid for all the modification times within the first 120 min of runtime and above 120 min, the performance of adsorption (removal efficiency) was almost constant. Mostly, fluoride removal performance increased with increasing modification time until 24 h, and between 24 and 36 h, fluoride removal was slightly increased at 36 h, the removal efficiency of fluoride was remains steady towards the end of the test indicating a period of near-equilibrium (see Fig. 9).

According to (Dey et al., 2022), the amount of HDTMA-Br sorbed onto the zeolite during modification is a function of the initial HDTMA-Br concentration and the sorption time (i.e., reaction or contact time). Inferences from their work suggest that provided the concentration of HDTMA-Br used in the modification of the zeolite is above the external cation exchange capacity of the zeolite, HDTMA-Br coating on the surface increases with increasing modification reaction time. As increasing, the contact time for the HDTMA-Br zeolite modification favors its sorption equilibrium and the formation of bilayer coating on the zeolite surface. This effect was observed during the fluoride adsorption whereby the fluoride removal performance of zeolite Na-LSX increased with increasing modification reaction time. The longer reaction times favored the coating of HDTMA-Br on the zeolite surface. The fluoride removal performance increased from 61 to 64.6% from 2 h through to 24 modification times at the end of runtime (Fig. 6). This also determined that the 24-h adjustment reaction time resulted in the highest removal efficiency potential (64.6%), whereas 36 h resulted in nearly identical performance (88.4%).

The slight discrepancy could be due to interference from the release of excess, loosely bound HDTMA-Br molecules from the 36 h of modification reaction time. Because of this, the formation of a complete bilayer HDTMA-Br coating probably occurred at the 24 h of modification reaction time. This translated into the increased fluoride removal during the batch adsorption process. At the end of the 3-h runtime, the zeolite prepared using merely laboratory reagents (Na-LSX) had the maximum

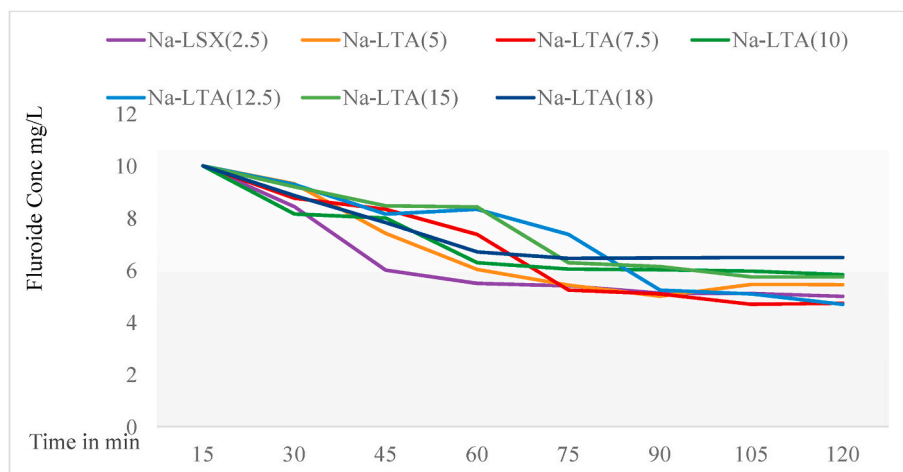


Fig. 5. Fluoride removal using zeolite Na-LTA modified with different dosage of HDTMA-Br.

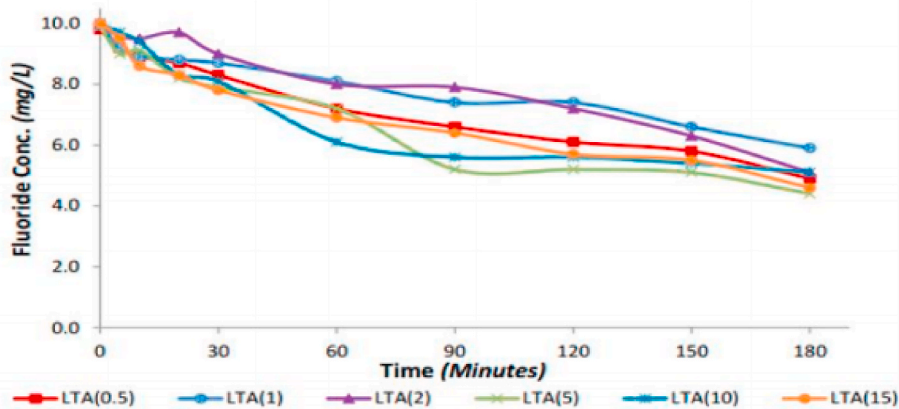


Fig. 6. Fluoride removal using zeolite Na-ZR modified with different dosage of HDTMA-Br.

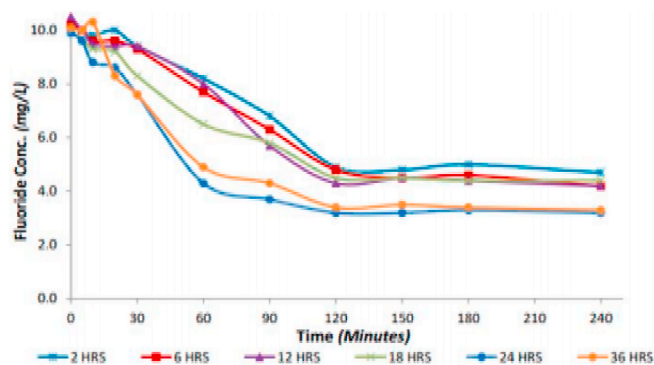


Fig. 7. Fluoride removal using zeolite Na-LTA modified with different times with HDTMA-Br.

fluoride removal (88.4%), because beyond this time the removal efficiency was almost constant or horizontal. Zeolite Na-LTA and ZR proceeded by reduced fluoride removals of 64.6 and 25%, respectively. In HDTMA-Br dosages of 7 and 10 g/L, the maximum removal efficiency for HA was 96 and 86%, respectively, with a slight variation in the pH value and turbidity unit (Mohapatra et al., 2009). The only slight fluoride removal occurred within the first 5–10 min of runtime, which represents only 5% fluoride removal from the initial 10 mg/L concentration. This, fluoride ions leached back into the solution and thus increased the concentration of fluoride to about the initial concentration (10 mg/L) with pH maintained at 5.5 and 6.5 experienced rapid fluoride removal (88.4 and 64.6%, respectively) within the first 60 min s of

runtime.

4. Conclusions

Drinking water supply for the study area was highly polluted by fluoride concentration, which is extremely above WHO guidelines. The modified Clinoptilolite was successfully conducted using varying HDTMA-Br dosages (0.5, 1, 2, 5, 10, and 15) g/L, and used 10 mg/L of initial fluoride solution, this publicized that the fluoride removal potential of the Clinoptilolite Nano zeolite modified increased with increasing HDTMA-Br dosage. The operational parameters such as adsorbent dose, contact time, pH, and initial fluoride concentration were found to have an effect on the removal efficiency of modified zeolite. The 5 g/L HDTMA-Br dosage used to modify zeolite Na-LSX gave the best fluoride removal potential which was preferably chosen for further batch removal processes and significantly dependent on pH.. To maintain the pH of fluoride solution (6.5 ± 0.2), for unmodified and modified zeolite Na-LSX recorded considerable fluoride uptakes. At the optimum operation conditions, the adsorbents modified Clinoptilolite with cationic surfactant exhibited highest fluoride removal efficiency of 84.4 and 89.7%, respectively, for 5 mg/L of initial fluoride concentration at the pH maintained at 5.5 ± 0.2 and 6.5 ± 0.2 . The investigated 5 mg/L HDTMA-Br dosage, 24 h modification reaction time, and a controlled pH of 5.5 ± 0.2 , maximum fluoride removal (88.4%) was obtained using modified zeolite Na-LSX as adsorbent. This represents 88.4%, 64.6% and 25% decreased fluoride removal from the controlled pH of 5.5 ± 0.2 , 6.5 ± 0.2 , and 7.5 ± 0.2 respectively. This study showed that modification of Nano zeolite by cationic surfactants, to reduce its negative surface charge, markedly improve its efficiency in the adsorption of fluoride from an aqueous solution. The HDTMA-Br/

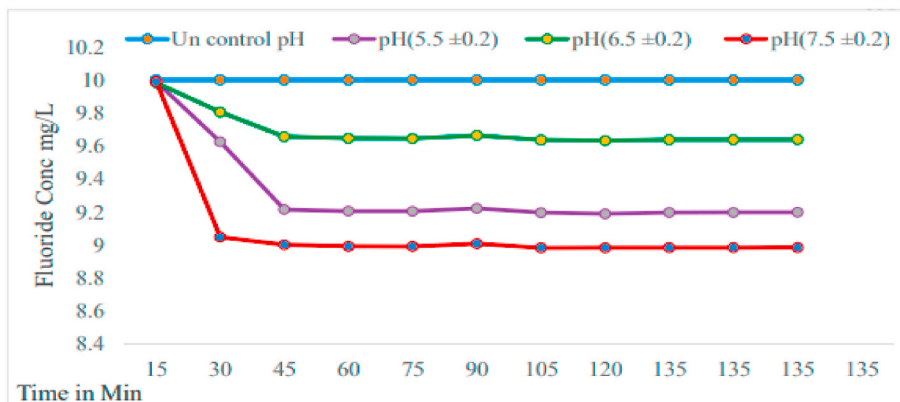


Fig. 8. Fluoride removal with pH maintained using modified Na-LSX at pH (5.5 ± 0.2 , 6.5 ± 0.2 , and 7.5 ± 0.2).

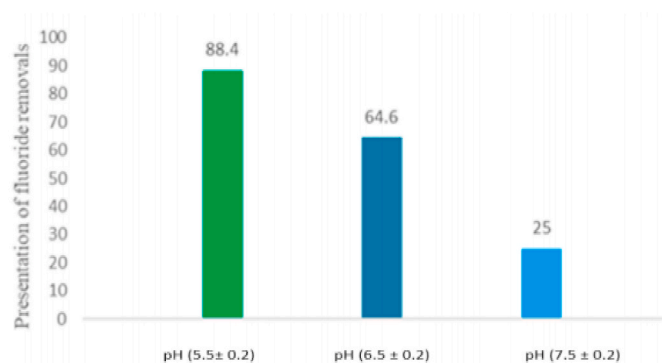


Fig. 9. Fluoride removal underperformance with pH maintained using modified Na-LST at pH (5.5 ± 0.2, 6.5 ± 0.2, and 7.5 ± 0.2) and uncontrolled pH using modified Na-LST absorbents.

Clinoptilolite ratio, and pH have to coincide in isoelectric point can be an optimum ratio for the modification.

Ethical issue

The author wants justify that this research paper do not be compliance to with any Ethical issue.

Declaration of competing interest

The authors declare that no conflict of interest concerning the research, authorship, and/or publication of this article.

Data availability

The data that has been used is confidential.

Acknowledgments

The author would like to thank all the participants and psychometric experts who supported the research.

References

- Ali, A., Saeed, K., Maboob, F., 2016. Removal of chromium (VI) from aqueous medium using chemically modified banana peels as efficient low-cost adsorbent. *Alex. Eng. J.* 55 (3), 2933–2942. <https://doi.org/10.1016/j.aej.2016.05.011>.
- Badessa, T.S., Wakuma, E., Yimer, A.M., 2020. Bio-sorption for effective removal of chromium (VI) from wastewater using *Moringa stenopetala* seed powder (MSSP) and banana peel powder. *BMC Chemistry* 71 (14), 1–12. <https://doi.org/10.1186/s13065-020-00724-z>.
- Bhaumik, R., Kumar, N., 2014. Optimizing adsorption of fluoride from water by modified banana peel dust using response surface modelling approach. *Appl. Water Sci.* (1), 1–21. <https://doi.org/10.1007/s13201-014-0211-9>.
- Demelash, H., Demelash, H., Beyene, A., Abebe, Z., Melese, A., 2019. Fluoride concentration in ground water and prevalence of dental fluorosis in Ethiopian Rift Valley : systematic review and. *BMC Publ. Health* 19, 1–9.
- Dey, S., Naga, K., Anusha, Veerendra, G.T.N., Sambangi, A., 2022. The removal of iron from synthetic water by the applications of plants leaf biosorbents. *Cleaner Engineering and Technology* 9, 100530. <https://doi.org/10.1016/j.clet.2022.100530>. June.

- Dong, C., Wu, X., Gao, Zh, Yang, P., Yawar, M., Khan, A., 2021. A novel and efficient metal oxide fluoride absorbent for drinking water safety and sustainable development. *MD* 13 (2), 883.
- Gul, S., Ahmad, Z., Asma, M., Ahmad, M., Rehan, K., Munir, M., Bazmi, A.A., Ali, H.M., Mazroua, Y., Salem, M.A., Akhtar, M.S., Khan, M.S., Chuah, L.F., 2022. Effective adsorption of cadmium and lead using SO₃H-functionalized Zr-MOFs in aqueous medium. *Chemosphere* 307 (1), 135633. <https://doi.org/10.1016/j.chemosphere.2022.135633>. Available at:
- Guoru, M., Chengying, B., Meirong, W., Peigang, H., 2021. Effects of Si/Al ratios on the bulk-type zeolite formation using synthetic metakaolin-based geopolymer with designated composition. *MD* 11, 1310. <https://doi.org/10.3390/cryst11111310>.
- Joseph, L., Jun, B., Flora, J.R.V., Min, Ch, Yoon, Y., 2019. Removal of heavy metals from water sources in the developing world using low-cost materials : a review. *Chemosphere* 229 (1), 142–159. <https://doi.org/10.1016/j.chemosphere.2019.04.198>.
- Kumar, N., Arunabha, M., 2018. Potentiality of a fruit peel (banana peel) toward abatement of fluoride from synthetic and underground water samples collected from fluoride affected villages of Birbhum district. *Appl. Water Sci.* 8 (3), 1–10. <https://doi.org/10.1007/s13201-018-0729-3>.
- Manikandan, S.C.S., Ramanathan, A.L., Nagar, A., 2013. A study on the defluoridation in water by using natural soil. *Appl. Water Sci.* 279 (1), 1–11. <https://doi.org/10.1007/s13201-013-0122-1>.
- Mohammadi, A., Bina, B., Ebrahimi, A., Hajizadeh, Y., 2013. Effectiveness of nanozeolite modified by cationic surfactant in the removal of disinfection-by-product precursors from water solution. *Int. J. Environ. Health Eng.* 1 (1), 3–7. <https://doi.org/10.4103/2277-9183.94387>.
- Mohapatra, M., Anand, S., Mishra, B.K., Giles, Dion E., Singh, P., 2009. Review of fluoride removal from drinking water. *J. Environ. Manag.* 91 (1), 67–77. <https://doi.org/10.1016/j.jenvman.2009.08.015>.
- Muhammad, H., Munir, Sh, Feroze, N., Ramzan, N., 2022. Fe-zeolite catalyst for ozonation of pulp and paper wastewater for sustainable water resources. *Chemosphere* 297 (1), 134031. <https://doi.org/10.1016/j.chemosphere.2022.134031>.
- Pandey, S.K., 2021. Novel and polynuclear K and Na based super alkali hydroxides as super bases better than Li-related species and their enhanced properties: an ab initio exploration. *Am. Chem. Soc. Omega* 6, 31077–31092. <https://doi.org/10.1021/acsomega.1c04395>.
- Rahmani, A., Nouri, J., Kamal Ghadiri, S., Mahvi, A.H., Zare, M.R., 2010. Adsorption of fluoride from water by Al³⁺ and Fe³⁺ pretreated natural Iranian zeolites. *Int. J. Environ. Res.* 4 (4), 607–614. <https://doi.org/10.22059/ijer.2010.246>.
- Ram, A., Pandey, S.K., Tiwari, H.K., Kumar, A., Supriya, Ch, Singh, S.Y.V., 2021. Groundwater quality assessment using water quality index (WQI) under GIS framework. *Appl. Water Sci.* 11 (2), 1–20. <https://doi.org/10.1007/s13201-021-01376-7>.
- Rango, T., Kravchenko, J., Atlaw, B., Mccornick, P.G., Jeuland, M., Merola, B., Vengoso, A., 2012. Groundwater quality and its health impact : an assessment of dental fluorosis in rural inhabitants of the Main Ethiopian Rift. *Environ. Int.* 43, 37–47. <https://doi.org/10.1016/j.envint.2012.03.002>.
- Sara, D., Assefa, K., Seifu, K., F. van, S., M. van, B., 2017. The right to smile: fluoride and fluorosis in central Rift Valley (Ethiopia). *Int. J. Environ. Res. Publ. Health* 8 (13), 756.
- Steenbergen, F.Van, Haimanot, R.T., Sidelil, A., 2011. High fluoride , modest fluorosis : investigation in drinking water supply in Halaba. *J. Water Resour. Protect.* 3 (2), 120–126. <https://doi.org/10.4236/jwarp.2011.32014>.
- Tekle-haimanot, R., Melaku, Z., Kloos, H., Reimann, C., 2006. The geographic distribution of fluoride in surface and groundwater in Ethiopia with an emphasis on the Rift Valley. *Sci. Total Environ.* 367 (1), 182–190. <https://doi.org/10.1016/j.scitotenv.2005.11.003>.
- Yahya, M.D., Aliyu, A.S., Obayomi, K.S., Olugbenga, A.G., Abdullahi, U.B., Aliyu, A.S., 2020. Column adsorption study for the removal of chromium and manganese ions from electroplating wastewater using cashew nutshell adsorbent Column adsorption study for the removal of chromium and manganese ions from electroplating wastewater using cashew nutshe. *Cogent Eng.* 7 (1), 1–19. <https://doi.org/10.1080/23311916.2020.1748470>.
- Zhang, Z., Chen, K., Zhao, Q., Huang, M., Ouyang, X., 2020. Comparative adsorption of heavy metal ions in wastewater on monolayer molybdenum disulfide. *Green Energy and Environ.* 6 (5), 751–758. <https://doi.org/10.1016/j.gee.2020.06.019>.