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

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ABSTRACT

In Ethiopia (Ziway town) an excess fluoride (≥1.5mg/L) consumption in drinking water (ground water and Lake Ziway) sources causes a health problem on the communities. The surrounding of inhabitant's peasant farmers of drinking water sources was extremely relying on this polluted fluoride concentration of water. This investigation was focused on defluoridation of drinking water by natural zeolite modified with a cationic surfactant in a batch system and Hexadecy Trimethyl Ammonium Bromide (HDTMA) were used for zeolite modification. The zeolite treatments had an aggregate size of 1.4 to 2.4 mm. The cationic Surfactant-Modified Zeolite, and raw Zeolite were used in all experiments. The removal efficiency of the treatment was influenced by pH of solution (5.5 ± 0.2 – 8.5 ± 0.2), initial concentration of fluoride (1-10mg/L) with rapid fluoride removal at concentration of 5.5 g/L, dose of Surfactant-Modified Zeolite (2.5-18 g/L), contact time (30-180 Minute), and effect of temperature was investigated at (80-120 ℃) which has increased the performance of removals as temperature increase. The study was examined, at the constant Blank of 10 mg/L, 5 g/L of Hexadecy Trimethyl Ammonium dosage noted the highest fluoride removal potential at the end of the 3 hours runtime: Sodium Low Silica X (Na-LSX) (88.4 %), Sodium Linde Type A (Na-LTA) (64.6 %) and Reagent only zeolite (ZR) (79.8 %). Incompatible to 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 60 minutes of runtime.

Key words: Adsorption, Cationic surfactant, Drinking water, Fluoride, Natural modified Zeolite

1. INTRODUCTION

Fluoride is one of the most electronegative elements which attracted by positively charged ion of group IA (Sodium, Potassium) and IIA (Calcium, Magnesium). Bone and tooth having highest amount of calcium in the body which attracts the maximum amount of fluoride and is deposited as calcium fluoroapatite crystals (Waghmare *et al.*, 2015, Rahmani et al., 2010, Donkor et al., 2016).

The United States Public Health Service has established the optimum concentration for fluoride in the water with the range of 0.7 mg/L to 1.2 mg/L while World Health Organization recommendation for fluoride permissible limit is 1.5 mg F/L (WHO, 2008). However, in the main Ethiopian Rift Valley about 14 million people rely on water sources that contain high concentrations of fluoride (Donkor, Buamah and Kwakye-Awuah, 2016, Mekonnen, 2014, Rahmani *et al.*, 2010, Wang and Peng, 2010). According to this report, 100 % of the hot springs, 75 % of the lakes, 54 % of the shallow wells and 35 % of the bore holes characterized in the main Ethiopian Rift Valley contain above 5 mg/L fluoride. The occurrence of high fluoride in groundwater / surface water in particular has led to the development of defluoridation techniques based on the concepts of adsorption (Zeolite Medias), precipitation, and membrane processes.

Adsorption is the most appropriate method because it has a combination of affordability and effectiveness (Stanić, 2014). Thus, defluoridation of drinking water is the best alternative technology in order to reduce health menace. This adsorption (Zeolite's media) are micro porous crystalline solid structures made of silicon, aluminum and oxygen that form a framework with cavities and channels. Cations, water and small molecules may reside within these cavities and channels (Bell, 2018). Principally, the alkali or alkaline earth metal cations usually attached to the zeolite structure are sodium, potassium, magnesium, lithium, barium and calcium (Inoguchi, 2019).

 The most common synthetic/modified zeolites used in industrial applications are zeolite X, A, Y and P and some of naturally occurring zeolites are: analcime, chabazite, clinoptilolite, erionite, ferrierite, heulandite, laumonite, mordenite, and phillipsite. This natural zeolite modified with cationic surfactants are environmentally and economically acceptable hydrated aluminosilicate minerals with exceptional ion-exchange and adsorption properties which used for treating

drinking water or waste water treatment (Rahmani *et al.*, 2010, Kumar *et al.*, 2019;   Donkor, Buamah and Kwakye-Awuah, 2016).

Clinoptilolite is one of the most common natural zeolites, easily obtained from mines, suitable as a sorbent due to its natural characteristics. According to (Onyango *et al.*, 2010 , Rahmani *et al.*, 2010, Elsheikh, Kalthom and Zainab, 2017, Donkor, Buamah and Kwakye-Awuah, 2016) clinoptilolite family minerals are classified by the dominant exchangeable cation of K, Na, Ca and Mg clinoptilolite. Surfactant modified clinoptilolite was an effective sorbent for both organic compounds and inorganic anions from water which consist of aluminosilicate mineral of porous structure that have valuable properties (cation exchange, molecular sieving, catalysis and adsorption)(Rahmani *et al.*, 2010, Daković, 2010, Donkor, Buamah and Kwakye-Awuah, 2016, European Environment Agency, 2019).

The aluminum has lower positive charge than silicon, the framework usually has a net negative charge which is balanced by exchangeable cation such as $(Na_2, K_2, Ca\,, Mg)_3)(Al_6Si_{30}\,O_{72}. 20H_2O)$ (Ologundudu, Odiyo and Ekosse, 2016). Uniquely most natural and synthetic(modified) zeolites have high selectivity for cations (HDTMA) which have a wide application in water purification, mainly in the uptake of heavy metal pollutants, ammonia, and radioactive species (Mehdizadeh, 2017). According to (Peng, 2018), the surface modification of both natural and synthetic zeolites can be achieved through acid treatment, ion exchange, and surfactant modification. The use of cationic surfactants (Hexa-Decyl Trimethyl Ammonium (HDTMA) to modify zeolites in particular, greatly increase the adsorption potency and affinity for anions removal in aqueous solution (Margeta, 2013).

Modification of zeolite can be conducted by different methods including ion exchange in which the exchangeable cation of the parent zeolite is replaced HDTMA. The interaction between surfactant and clinoptilolite is the ion exchange of HDTMA with extra structural cations on the surface up to external cation exchange capacity of clinoptilolite which can removes fluoride concentration from drinking water sources. Hence, the main outcome of this study was to remove excess fluoride concentration in drinking water which is highly affect health society using natural available material by simple modification with cationic surfactants. The study also has a great contribution on adaption of new technology, low cost, design simple and nearly available material.

2. MATERIALS AND METHODS

2.1. Description of the study area

The study is carried out in the Oromia Regional state, of Batu town which located at the Ethiopian Rift Valley at the elevation of 1643 meters above sea level. The town of Batu lies on the western shore of the lake, extending along that shoreline and growing at a very fast rate in recent years.

2.2. Sample collection

Drinking water samples was collected from Batu town, mainly in the drinking water distribution system. The sampling sites for this study is deliberately selected based on the anthropogenic impact on surface water and the number of populations utilizing the water from different drinking water sources. Among different water sources two sample from river sources (Bulbula River mouth 38.743261° E 7.899822° N, located in kebele 05, which give services for 4567 population and Meki River 38.848733° E, 8.051128° N found in kebele 02, which give services for population 6754). The other points of sample collected were from boreholes (Around floriculture industries 38.740261° E, 7.917644 ° N 3895 of population where service and Korekonch 38.755692 ° E, 7.995050 ° N which services 5489 population). The safe sourcing schemes are multi-village sized. Data were also collected on local acceptance, perceptions, and functionality of the water supply systems. The study was conducted to removes the concentration of fluoride in the drinking water and defluoridation by using natural zeolite with cationic surfactant from community water supply and private tap of the town.

2.3. Analysis of defluoridation

The removal of fluoride concentration by natural zeolite with cationic surfactants was analyzed by standard procedures of the water quality guidelines (precautions during collection of samples, transportation handling and storage of samples). This procedure should be considering, if samples are taken for off- site testing at laboratories, it is essential that they are preserved during transportation to prevent change to their hydro-chemical properties. They should be preserved, stored in a dark, covered cool box at a stable temperature between 4 and 10 degrees. They should be analyzed within 24 hours of collection and which was collected and filtered through a 0.45 µm membrane before being analyzed. This were analyzed the concentrations of fluoride and membrane before by measuring the maximum absorbance at a fixed wavelength of 484 and

664 nm, respectively, using ultra violet mini-1240 spectrophotometer. Thus, way the overall removal efficiency of the study was calculated as: -

$$\text{Removal efficency} = \left\{1 - \frac{Ct}{Co}\right\} * 100\% \tag{1}$$

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

$$qe = \left\{\{Co - Ce\}\frac{V}{W}\right\} \tag{2}$$

130 $$qt = \left\{\{Co - Ct\}\frac{V}{W}\right\} \tag{3}$$

Where qe and qt (mg/g) are the adsorption capacity at equilibrium and t min; Co is the initial concentration of fluoride concentration in solution, while Ce and Ct (mg/L) are the concentrations of fluoride concentration at equilibrium and min, respectively; V (L) is the volume of solution and W (g) is the mass of adsorbent used.

135 ## 2.4. SMZ Preparation

The hydrothermal treatment methods employed in zeolite formation usually involves appropriate pretreatments processes such as grinding, acid washing, calcination and fusion with additives of the starting materials investigated. Results showed that the nature of the alkali-metal cation did not have a critical structure-determining role in the synthesis but did contribute to other
140 properties of the material including the rate of crystallization, the Si/Al ratio of the resulting crystals, the crystal size, and the morphology. Potassium ions greatly increased the rate of crystallization and decreased the nucleation time. (Mehdizadeh, 2017) Hydrothermally treated a (K, Na)-aluminosilicate slurry containing starting materials with Si/Al :(Na + K)/Si: K/ (Na + K): H₂O/Al molar ratio of 6.0:0.42:0.5:52.5 and found that plate-like particles of (K, Na)-
145 clinoptilolite were formed. (Stanić, 2014) Synthesized clinoptilolite according to the process reported by (Peng, 2018) and concluded that highly crystalline clinoptilolite could be obtained from the batch composition of 2.1Na₂O: Al₂O₃:10Si₂O:110H₂O. 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
150 available clinoptilolite mineral as the source of alumina and silica. Zeolite LTA (Linde Type A) was synthesized from locally available clinoptilolite and bauxite mineral as the source of silica

and alumina respectively. Sodium metasilicate and sodium aluminate laboratory reagents were used to synthesize another zeolite nicknamed zeolite ZR. For this SMZ preparations, zeolite (natural clinoptilolite) which was a rich tuff obtained from national mining area in East Wellega zone. The study was investigating mainly mineral composition zeolite using X-Ray Diffraction was 74% aluminosilicate slurry, 5% smectite, 10% quartz/cristobalite, 10% feldspar, and 1% illite and had an external surface area of 15.7 m^2/g. The internal cation exchange capacity was 800 meq/kg and the external cation exchange capacity was 90-110 meq/kg (Bowman et al. 2000). The zeolite was crushed and sieved to two different grain sizes: 1.4 to 0.4 mm (14-40 mesh) for the field test and 0.18 to 0.15 mm (80-100 mesh) for the laboratory batch experiments. The SMZ used in the laboratory experiments was produced by treating 1000 g of zeolite with 3000 mL of a 0.10 M HDTMA-Cl (Aldrich, Milwaukee, WI) solution and shaking for 24 hrs. The HDTMA-zeolite was rinsed with two 180 mL aliquots of Type I water (purified with Milli-Q system, Millipore Corp., Bedford, MA) and air-dried. The final HDTMA loading was 157 mmol HDTMA/kg zeolite. The SMZ for the field test, bulk produced at the St. Cloud mine and described by (Odiyo, J. O. and Ekosse, *eta'al* (2016), had an HDTMA loading of 180 mmol HDTMA/kg zeolite.

3. RESULTS AND DISCUSION

3.1. Modification and Preparation of Zeolite Cationic Surfactant's

As per described in Table 1 for both unmodified and modified different surface chemistry (Na-LST, Na-LTA and ZR) of natural cationic surfactants proportions were justified. This percentage of natural zeolites weights has been taken with accordingly the proposed for modified of cationic surfactant of natural zeolite formations. Hence the modified natural zeolites of cationic surfactant's were oxidized by same elements and replaced by carbon in place of iron, cupper and sulfur in 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 replacing other compound's /elements as indicated in Table1.

Table 1: Modification of natural zeolites with cationic surfactants

Unmodified modified	Na-LSX			Unmodified modified	Na-LTA			Unmodified	ZR modified		
ID	weight (%)	ID	weight (%)	ID	weight (%)	ID	weight (%)	ID	weight (%)	ID	weight (%)
O_2	68.48	O_2	48.05	S	0.3	S	0.23	Na	8.85	Na	7.02
Na	8.41	Na	5.6	Na	10.78	Na	6.56	O_2	72.23	O_2	47.08
Al	9.19	Al	6.09	Si	11.27	Si	6.15	Al	8.46	Al	7.8
Si	13.05	Si	8.49	O_2	66.65	O_2	45.33	Si	10.14	Si	9.34
S	0.22	S	0.18	Al	11	Al	6.09	S	0.32	S	0.19
K	0.19	K	0.12			C	35.64			C	28.57
Fe	0.33	Fe	0.21								
Cu	0.13	C	31.26								

From this Table 1, same elements were common before and after the modification of zeolite with cationic surfactants (e.g., Na-LTA and ZR) whereas same types of modified zeolite with this surfactant were changed before and after modification (e.g., Na-LSX types). This indicates that changed element (replaced to other element) since modification have a good pore space and highly activated for adsorption of fluoride concentration than others. Apart from this in each types of zeolite, after their modification commonly their structural composition has attached to carbon element which processed since this modification of zeolite.

Techniques used for zeolite characterization provide information about the structure, morphology, chemical composition as well as its catalytic and adsorptive abilities. Modification of natural zeolite using cationic surfactant was purposely requires for activating and reshaping the framework structure of zeolite or an isomorphic substitution of silicon by aluminium (Si/AL atoms in the crystal zeolite structure. As indicated in the above Table1, among the types of synthesized/modified natural zeolites with cationic surfactant's, Zeolite Na-LSX was found to be the best performing adsorbent than Zeolite Na-LTA and ZR at constant Ph 5.5 and 105 ℃. The percent composition of Si and Al elements from the Energy Dispersive X-ray analysis shown in Table 1 gives Si/Al ratios of 1.39, 1.01, 1.197 for zeolite Na-LSX, Na-LTA and ZR respectively. This result of modification indicates, in the 1st and 2nd columns (unmodified and modified of Na-LSX) have the better morphological structural pore space and activated composition of elements

which was highly adsorbs the fluoride concentration. This show that, zeolite sodium Low Silica (Na-LSX) have pure crystal products and uniform particle sizes which more performance to removes fluoride concentration in drinking water. During this modifying of natural zeolite/ clinoptilolite, same of the modified /synthesized zeolite by using common cation surfactant (HDTMA) the existing elements were remain constant in both after and before modified. This result was recorded in both Na-LTA and ZR types, where as in the Na-LSX composition one heavy element (copper was) lost since this modification.

As indicated in the above preparation of natural zeolites, the prepared sampled could be used for laboratory in order to follow up the efficiency of cationic modified surfactants for fluoride removal from drinking water as discussed. The prepared raw material and modified of cationic surfactant's was used for adsorption of batch experiments in different scenarios of variation with HDTMA dosages, pH, mixing time and the duration of adsorption in order to follow up best fluoride removal efficiency were considered.

3.2. Batch adsorption experiments

The 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. This conditions such as the HDTMA concentration or dosage and the contact time used in modifying the zeolites, as well as the pH of the fluoride contaminated water were varied in order to investigate their effects on fluoride uptake.

4.3. Batch adsorption: Removal of fluoride using unmodified zeolites

This batch experimental process was conducted to investigate the fluoride removal potential of the all considered unmodified natural zeolites (Na-LSX, Na-LTA, and ZR). As per justified in Fig 1 depicts the fluoride removal performances by unmodified zeolites (Na-LSX, Na-LTA, and ZR) without any pH adjustment within (7.5 to 8.5). The below Fig 1, indicated that the removal of fluoride by using unmodified natural zeolite or adsorption fluoride concentration using natural zeolites prior its modification with cationic surfactant.

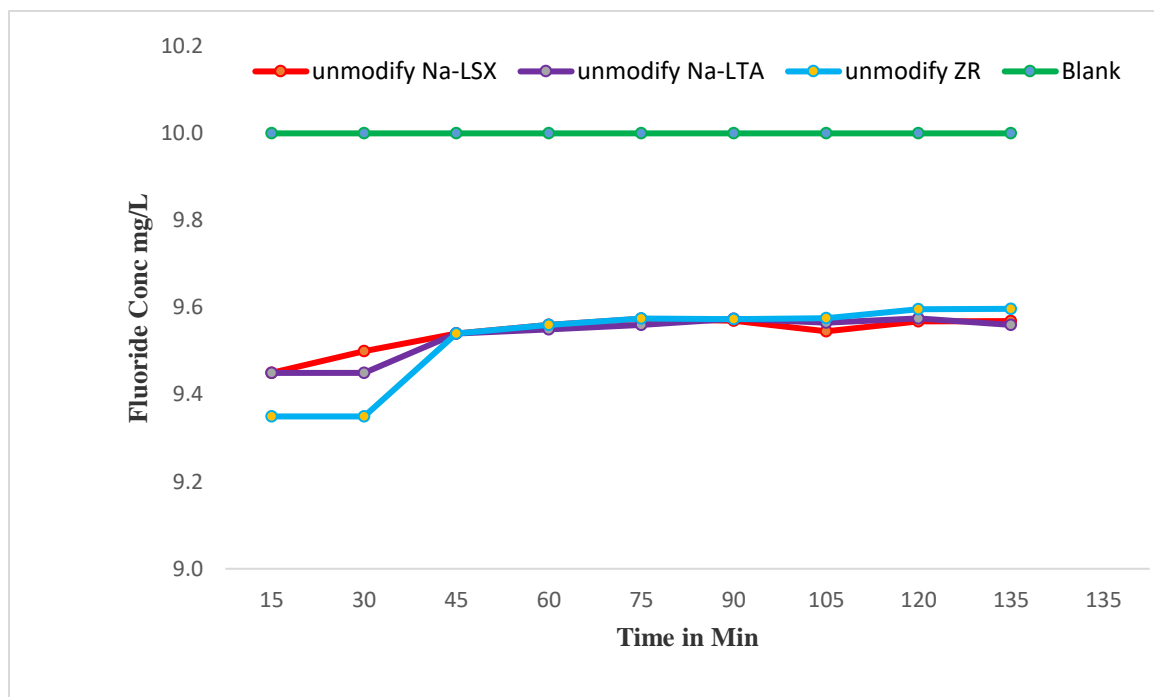



Figure 1: Fluoride removal using unmodified zeolites: Na-LSX, Na-LTA, ZR *(*Model water composition: (F^-) i = 10 mg/L, Blank = 10 mg F^-/L without adsorbent).

As evident from Fig 1, the only slight fluoride removal by the unmodified zeolites occurred in the initial 15 minutes of the run time. Beyond this, the fluoride concentration of the solution leached back into solution till 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 pH of the fluoride-contaminated solution plays an important role in the sorption of fluoride onto adsorbents. The pH values recorded for the test rose from an initial pH of 7.5 to 8.5. This increase in pH is probably responsible for the leach back of fluoride anions into solution. Fig 2, depicts the fluoride removal performances by the three unmodified zeolites when the pH of the fluoride-concentration 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 suggests that the fluoride removal was only due to adsorption by the unmodified zeolites and as it described in Fig 2, when the pH of the solution was maintained at 6.5 ± 0.2 the adsorption of fluoride significantly increased. Probably, the interference from the OH^- anions was reduced, providing additional free adsorption sites for the fluoride ions. Due to this, there was a sharp decrease in fluoride concentrations within the initial 45 minutes 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 indicated in Fig 2, beyond the initial 45 minutes till the end of runtime, all the unmodified zeolites maintained maximum adsorption levels indicating a period of near equilibrium.

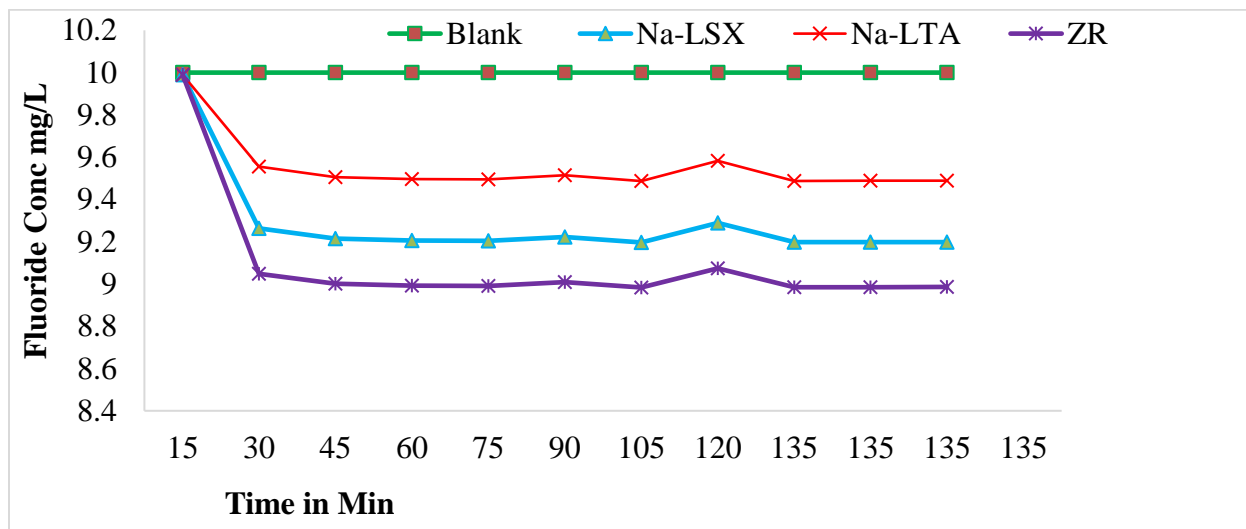



Figure 2: Fluoride removal using unmodified zeolites under controlled of 6.5± 0.2

*(*Model water composition: (F^-) i = 10 mg/L, Blank = 10 mg F^-/L without adsorbent)

As the study results (Fig 2), indicates, 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.

4.4.   Batch adsorption: Effect of varying HDTMA dosage on fluoride uptake

As pre described in Fig, 1 and 2 depict the fluoride removal potentials of unmodified zeolites Na-LSX, Na-LTA and ZR with runtime under controlled pH and without adsorbents. Hence, each zeolite was modified with a variety of HDTMA dosages concentrations (2.5, 5, 7.5, 10,12.5, 15, and 18) g/L. Evidently each modified zeolite exhibited significant fluoride removal till the end of the runtime for all the HDTMA modification dosages. Based on this issue, the study was investigated that on which cationic surfactant dosage (HDTMA) were recorded the lowest and highest fluoride concentration from drinking water as indicated in Fig 3 below.

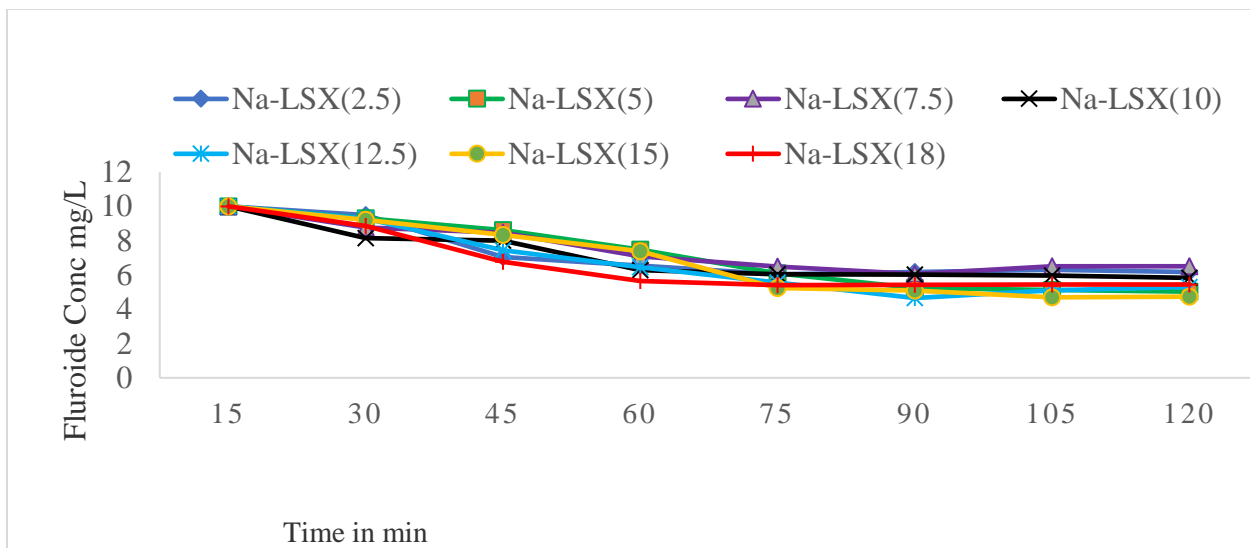



Figure 3: Fluoride removal using Na-LSX modified zeolite with different dosage of HDTMA
*(*Model water composition: (F^-) i = 10 mg/L, Blank = 10 mg F^-/L without adsorbent)

270 The study was investigated, that effect of fluctuating HDTMA dosage on fluoride adsorption by increasing 2.5 g/L and with the variation of 15 minutes intervals until the ends of 120 minutes. Accordingly, the effective dosage cationic surfactant was observed during the study and 5g/L of the dosage were effective and hence beyond to this the adsorption of modified zeolite were almost constant. As described in Fig 8, this 5 g/L HDTMA dosage recorded the highest fluoride

275 removal potential at the end of the 3 hours runtime: Na-LSX (88.4 %), Na-LTA (64.6 %) and ZR (25 %).

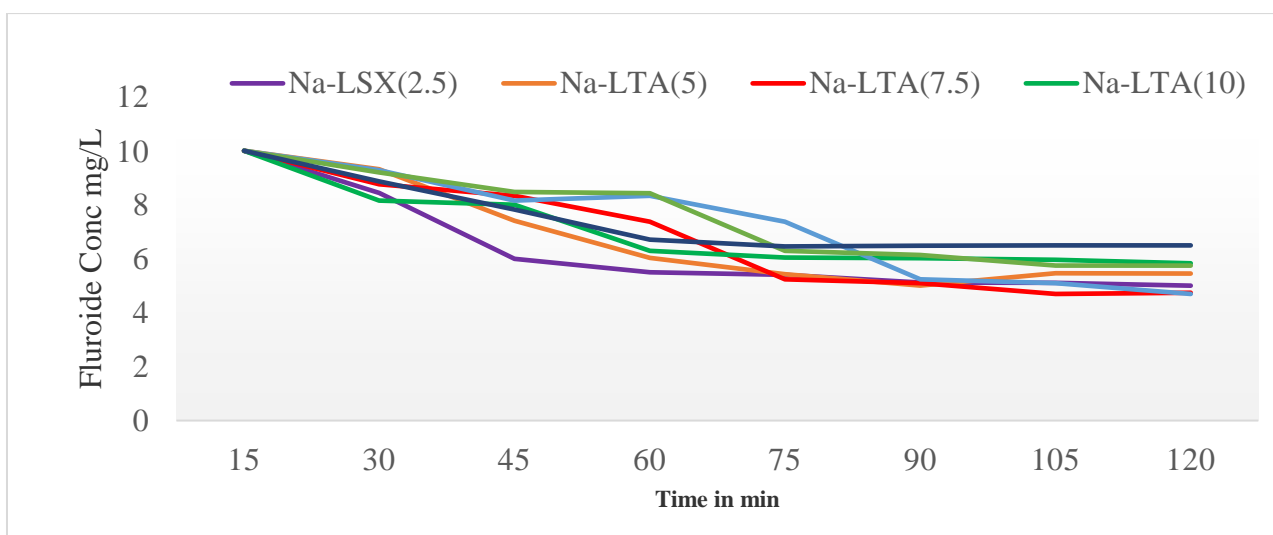



Figure 4: Fluoride removal using zeolite Na-LTA modified with different dosage of HDTMA *(*Model water composition: (F^-) i = 10 mg/L, Blank = 10 mg F^-/L without adsorbent)

280 As per described in Fig 3, on the effect of cationic surfactant of dosage for adsorption of fluoride removal for the study in order to modify the natural zeolite types (Na-LTA) and hence 5g/L of HDTMA were most effective dosage for adsorption of 1-10 mg/L.

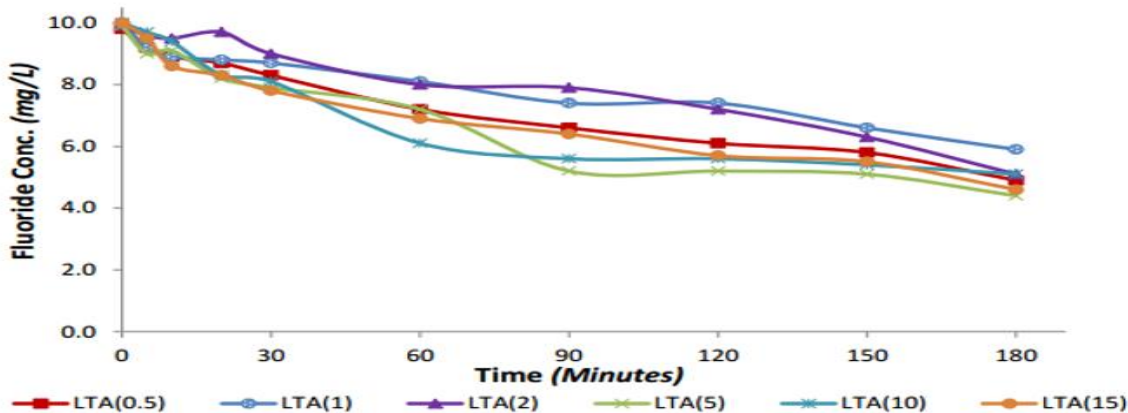



Figure 5: Fluoride removal using zeolite Na-ZR modified with different dosage of HDTMA

285 *(*Model water composition: (F^-) i = 10 mg/L, Blank = 10 mg F^-/L without adsorbent)

4.5. Batch adsorption: Effect of modification reaction time on fluoride removal

This batch adsorption experiment was carried out to determine the effect of modification reaction time on fluoride removal performance. Equal amounts of zeolite Na-LSX were modified by stirring in equal volumes of 5 g/L HDTMA with the aid of a flocculator. The modifications were

290 varied for 30 minutes. From Fig 6 it is observed that fluoride removal is rapid for all the modification times within the first 120 minutes of runtime and above 120 minutes the performance of adsorption /removal efficiency was almost constant. Generally, fluoride removal performance increased with increasing modification time till 24 hours. Beyond 24 hours to the 36 hours, fluoride removal decreased slightly. Fluoride removal remains steady towards the end

295 of the test indicating a period of near equilibrium.

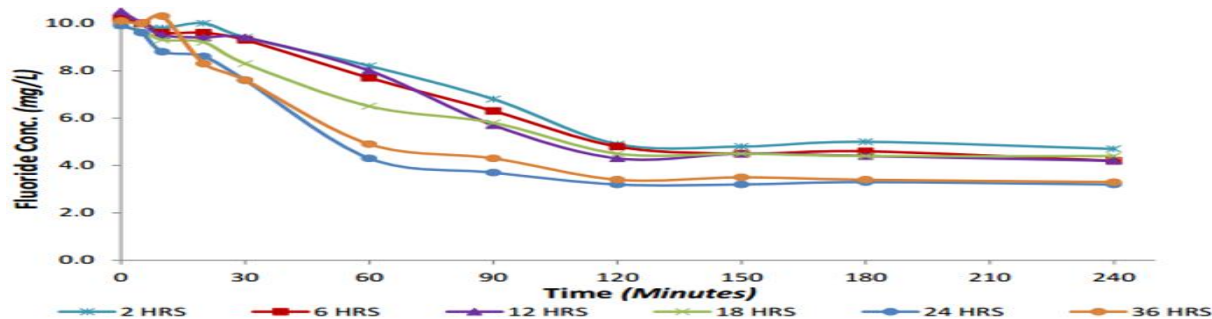



Figure 6: Fluoride removal using zeolite Na-LTA modified with different times with HDTMA

(Model water composition: (F^-) i = 10 mg/L, Blank = 10 mg F^-/L without adsorbent)

According to Apreutesei *et al.* (2008), the amount of HDTMA sorbed onto the zeolite during modification is a function of the initial HDTMA concentration and the sorption time (i.e., reaction or contact time). Inferences from their work suggest that provided the concentration of HDTMA used in the modification of the zeolite is above the External Cation Exchange Capacity of the zeolite, HDTMA coating on the surface increases with increasing modification reaction time. Hence increasing the contact time for the HDTMA-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. By increasing modification or reaction time, the HDTMA molecules had ample time to rearrange themselves to form a bilayer coating on the zeolite surface. Thus, longer reaction times favored the coating of HDTMA on the zeolite surface. From Fig 6, fluoride removal performance increased from 61 to 73 % from 2 hours through to 24 hours modification times at the end of runtime. It is also observed that the 24 hours modification reaction time exhibited the highest fluoride removal potential (73%) whilst the 36 hours resulted in a slightly lower performance (88.4%). The slight discrepancy could be due to interference from the release of excess, loosely bound HDTMA molecules from the 36 hours modification reaction time. In view of this, the formation of a complete bilayer HDTMA coating probably occurred at the 24 hours of modification reaction time. This translated into the increased fluoride removal during the batch adsorption process.

4.6. Batch adsorption: Effect of pH on fluoride removal

The effect of pH on fluoride uptake using modified zeolite Na-LSX, Na-LTA and ZR were conducted considering the following pH: 5.5 ± 0.2, 6.5 ± 0.2 and 7.5 ± 0.2. The solutions were

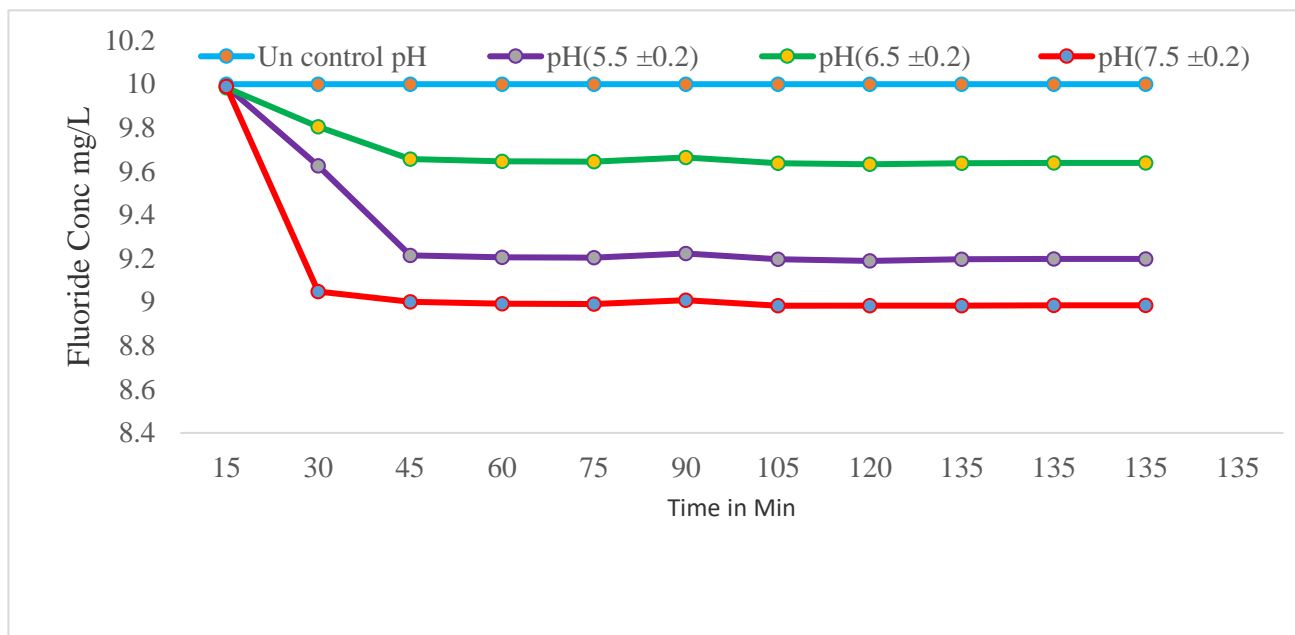
maintained at their required pH using 0.1 N NaOH, 0.5 and 1 N HCl solutions. In addition, a batch setup was concurrently run without pH adjustments using modified Na-LSX, Fig 7 and 8

depict the results obtained.

Figure 7: Fluoride removal with pH maintained using modified Na-LSX at pH (5.5± 0.2, 6.5± 0.2, and 7.5± 0.2) *(Model water composition: (F^-) i = 10 mg/L, Blank = 10 mg F^-/L without adsorbent).*

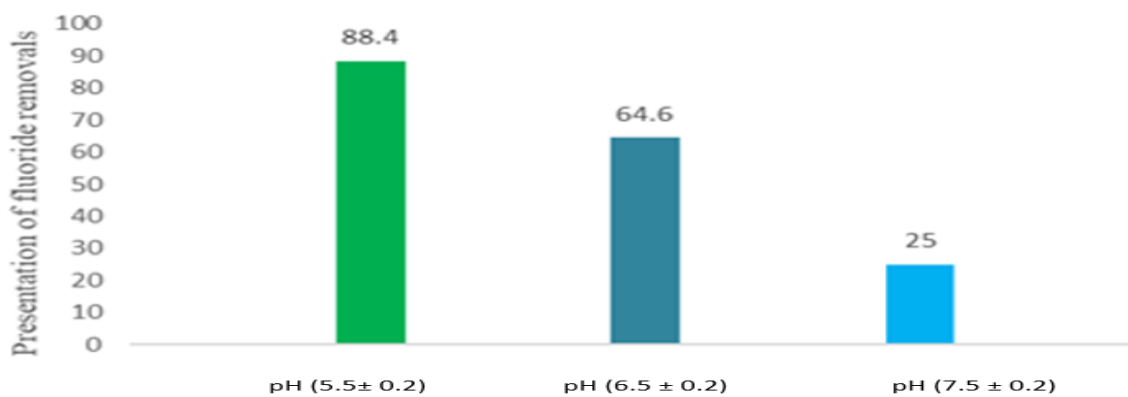



Figure 8: Fluoride removal under performance of with pH maintained using modified Na-LST at pH (5.5± 0.2, 6.5± 0.2, and 7.5± 0.2) and uncontrolled pH using modified Na-LST absorbents.

This diagram (Fig 8), was generalized the results obtains from Fig 1-7 including Table 1 which can be remarkable fluoride uptake was observed within the initial 30 minutes of runtime for all the zeolites (Na-LSX, Na-LTA and ZR). The synthesized zeolite from only laboratory reagents (Na-LSX) gave the highest fluoride removal (88.4 %) at the end of the 3 hours runtime. Zeolite Na- LTA and ZR followed with lesser fluoride removals of 64.6 and 25 % respectively. The only slight fluoride removal occurred within the first 5 to 10 minutes of runtime, which represents only 5 % fluoride removal from the initial 10 mg/L concentration. After this, the fluoride ions leached back into solution and thus increased the concentration of fluoride to about the initial concentration (10 mg/L). Contrary to this reflection, the model waters with pH maintained at 5.5 and 6.5 recorded rapid fluoride removal (88.4 and 64.6 % respectively) within the first 60 minutes of runtime. After this, almost steady fluoride concentration is recorded till the experiment was terminated. Meanwhile, the model water adjusted to a pH of 7.5 resulted in a gradual to steady decrease in fluoride removal performance over the entire duration of the batch removal process (i.e., 10 to 8.5 mg fluoride/L). During the fluoride removal process, the bromide ions bonded to the HDTMA layer is exchanged with the fluoride ions in solution. The free bromide ions that are released into solution perhaps interact with the sodium ions that were formerly bound to the fluoride and hydroxide entities.

4. CONCLUSIONS

The ground water supply for the study were highly polluted by fluoride concentration which is unfit for use. The SMZ was successfully conducted using varying HDTMA dosages (0.5, 1, 2, 5, 10, 15 g/L). Using an initial 10 mg/L fluoride solution, the batch adsorption revealed that the fluoride removal potential of the SMZ increased with increase in HDTMA dosage. The 5 g/L HDTMA dosage that was 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. Without pH control, the solution pH rose from 7.5 to 9.5 and no considerable fluoride removal was recorded in this basic region. Upon maintaining pH of fluoride solution at 6.5 ± 0.2, both unmodified and modified zeolite Na-LSX recorded considerable fluoride uptakes. Under the tested conditions (5 mg/L HDTMA dosage, 24 hours 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.

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