Title: 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 ($\geq$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 were used for zeolite modification. The Batch experiments also conducted to test for preferential removal of fluoride from water by surfactant-modified zeolite. 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 influence by pH of solution ($5.5 \pm 0.2 - 8.5 \pm 0.2$), initial concentration of fluoride(1-10mg/L), dose of surfactant-modified zeolite (2.5-18 g/L), contact time (30-180 Minute), and effect of temperature was investigated. The study investigated that, at the constant Blank of 10 mg/L, 5 g/L of Hexadecy Trimethyl Ammonium Bromide dosage noted the highest fluoride removal potential at the end of the 3hours runtime: Na-LSX (88.4 %), Na-LTA (64.6 %) and 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

INTRODUCTION

Fluoride, is one of the most electronegative elements which have a negative charge and attracted by positively charged ions of group IA and IIA (Calcium, Sodium, 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). 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. Thus, defluoridation of drinking water is the best alternative technology in order to reduce health menace, due to excessive consumption of fluoride. The natural zeolite modified with cationic surfactants are environmentally and economically acceptable hydrated aluminosilicate minerals with exceptional ion-exchange and sorption 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 $(Na_2, K_2, Ca , Mg)_3)(Al_6 Si_{30} O_{72}. 20H_2O)$ (Ologundudu, Odiyo and Ekosse, 2016). Modification of zeolite can be conducted by different methods including ion exchange in which the exchangeable cation of the parent zeolite is replaced HDTMA-Br.

The interaction between surfactant and clinoptilolite is the ion exchange of HDTMA-Br with extra structural cations on the surface up to external cation exchange capacity of clinoptilolite which can removes fluoride concentration from drinking water sources.

3. MATERIALS AND METHODS

3.1. 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 co-ordinate of 7° 52′– 8° 8′ N; and 38° 04′–38° 56 ′E, with an 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.

3.2. Sample collection

Drinking water samples will collects from sampling sites in the 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. A cross-sectional study was conducted to removes the concentration fluoride in the drinking water and de-fluoridation by using natural zeolite with cationic surfactant from community water supply and private tap of the town.

3.3. Analysis of defluoridation

The removal of fluoride concentration by natural zeolite with cationic surfactants will analyzed by standard procedures of the water quality guidelines according WHO. This can be measured or set as the existence fluoride elements and free and compounds which may exist in aqueous from and the removal efficiency. Samples were collected and filtered through a 0.45 μm membrane before being analyzed. The concentrations of ORII and MB were determined by measuring the maximum absorbance at a fixed wavelength of 484 and 664 nm, respectively, using UV mini-1240 spectrophotometer.

The removal efficiency of ORII was calculated as: -

$$\text{Removal efficency} = \left\{1 - \frac{C_t}{C_o}\right\} * 100\% \qquad \{1\}$$

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

90 $$qe = \left\{ \{Co - Ce\}\frac{V}{W} \right\} \qquad \{2\}$$

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

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

95 adsorbent used.

3.4. SMZ Preparation

The zeolite used in this study was a natural clinoptilolite-rich tuff obtained from the St. Cloud mine near Winston, NM. The mineral composition was 74% clinoptilolite, 5% smectite, 10% quartz/cristobalite, 10% feldspar, and 1% illite. The zeolite had an external surface area of 15.7

100 m2/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 and column experiments.

The SMZ used in the laboratory experiments was produced by treating 1000 g of zeolite with

105 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 (*Bowman et al. 2001*), had an HDTMA loading of 180 mmol HDTMA/kg zeolite.

110 **4. RESULTS AND DISCUSION**

4.1. 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

115 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.

120   Table 1 Modification of natural zeolites cationic surfactants'

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

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 were under took for adsorption of batch experiments in different scenarios likes variation of

125   HDTMA dosages, at variation of pH, at variation of mixing time and the duration of adsorption in order to follow up best fluoride removal efficiency were considered.

4.2.   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

130   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

135   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).
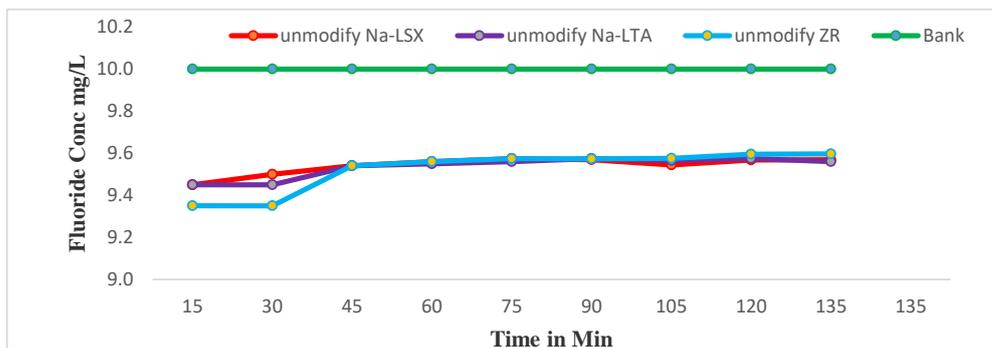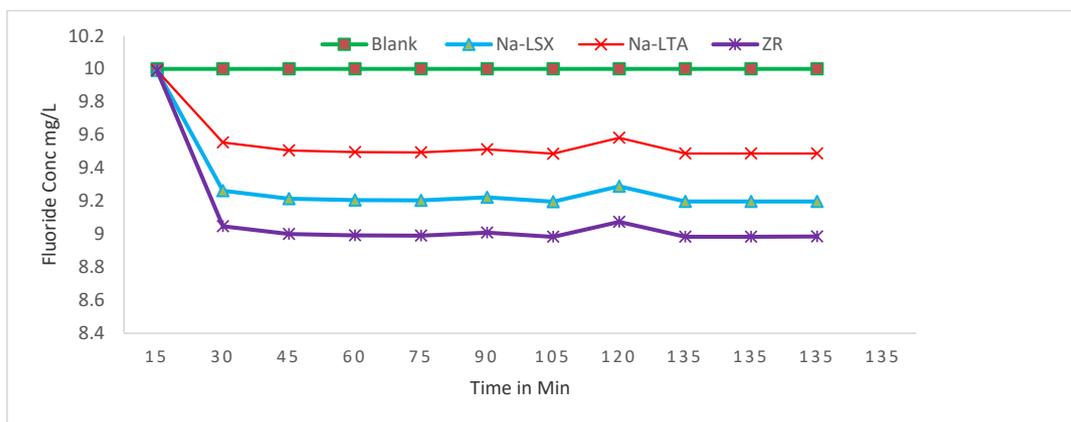

Figure 1: Fluoride removal using unmodified zeolites: Na-LSX, Na-LTA, ZR (Model water composition: (F^-) i = 10 mg/L, Blank = 10 mg F^-/L without adsorbent).

As evident from Figure 4.1, the only slight fluoride removal by the unmodified zeolites occurred in the initial 15 minutes of the runtime. 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 4.2, depicts the fluoride removal performances by the three unmodified zeolites when the pH of the fluoride-contaminated solutions was maintained at 6.5 ± 0.2. From Figure 4.1, a remarkable fluoride uptake was observed within the initial 30 minutes of runtime for all the zeolites. The synthesized zeolite from only laboratory reagents gave the highest fluoride removal (88.4 %) at the end of the 3 hours runtime. Zeolite Na-LSX and Na-LTA followed with lesser fluoride removals of 64.6 and 25% respectively. The result of the blank setup however 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. It can be observed from Fig 4.3, that 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

160   sites. This seemingly hydrophilic nature of the unmodified zeolites might have also enhanced the

affinity and rapid uptake of fluoride anions.

Beyond the initial 45 minutes till the end of runtime, all the unmodified zeolites maintained

maximum adsorption levels indicating a period of near equilibrium. At equilibrium, the rate of

fluoride adsorption is equal to the rate of desorption in solution.

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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)

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.

170   4.4.   Batch adsorption: Effect of varying HDTMA dosage on fluoride uptake

From the Fig, 1 and 2 respectively depict the fluoride removal potentials of modified zeolites Na-

LSX, Na-LTA and ZR with time. Each zeolite was modified with varying HDTMA dosages of

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.

175   As depicted in Fig 3, the 5 g/L HDTMA dosage recorded the highest fluoride removal potential at

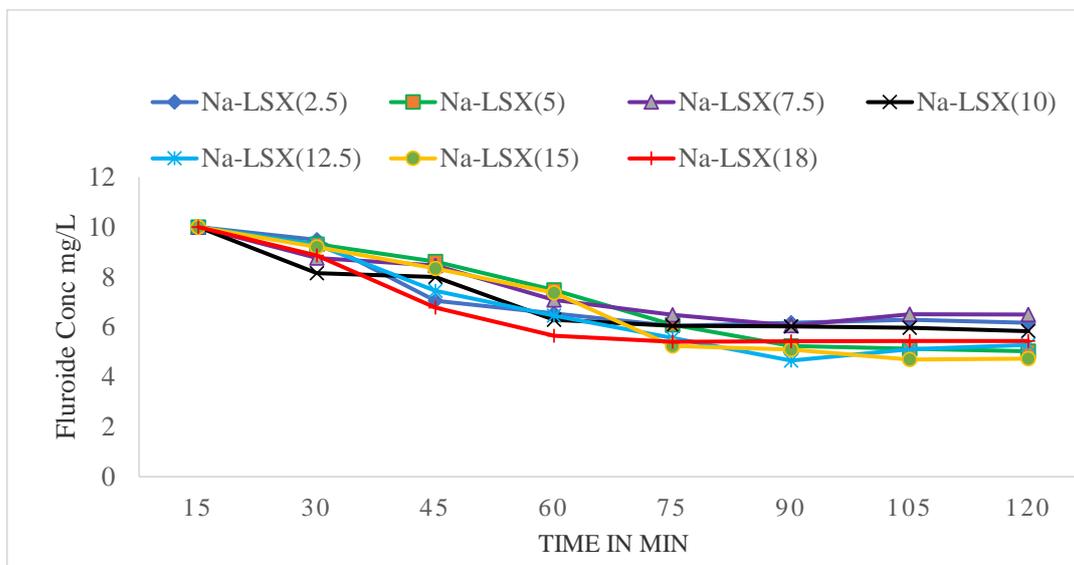the end of the 3 hours runtime: Na-LSX (88.4 %), Na-LTA (64.6 %) and ZR (79.8 %).

Figure 3: Fluoride removal using zeolite Na-LSX modified with different dosage of HDTMA

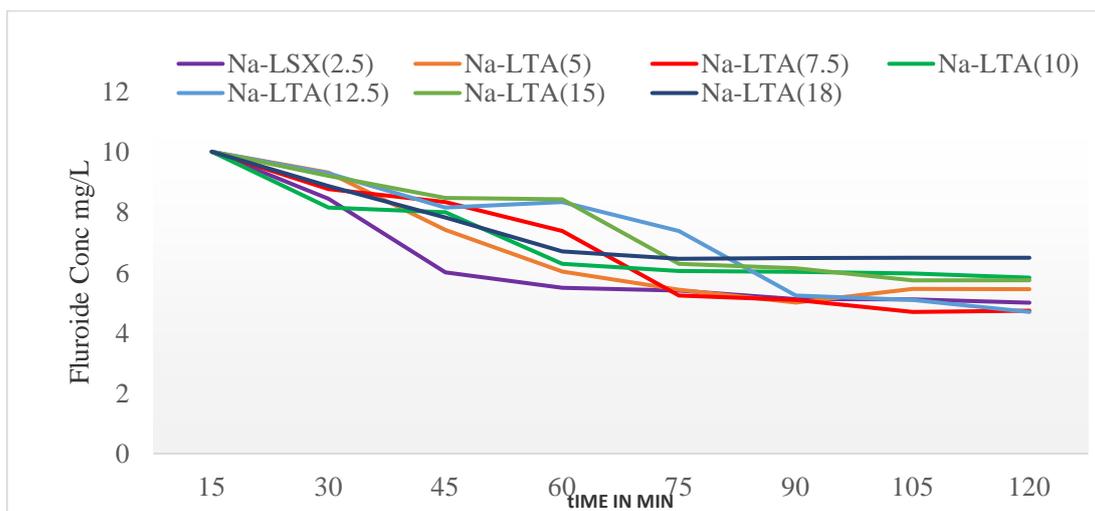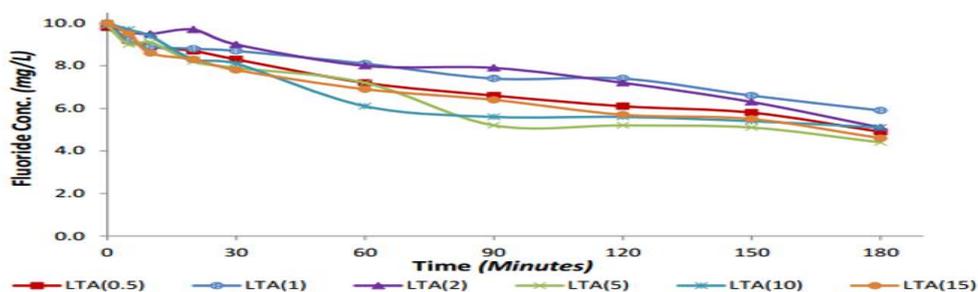(Model water composition: (F^-) i = 10 mg/L, Blank = 10 mg F^-/L without adsorbent)

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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)

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Figure 5: Fluoride removal using zeolite Na-ZR modified with different dosage of HDTMA
(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 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. Generally, fluoride removal performance increased with increasing modification time till 24 hours. Beyond the 24 hours to the 36 hours, fluoride removal decreased slightly. Fluoride removal remains steady towards the end of the test indicating a period of near equilibrium.
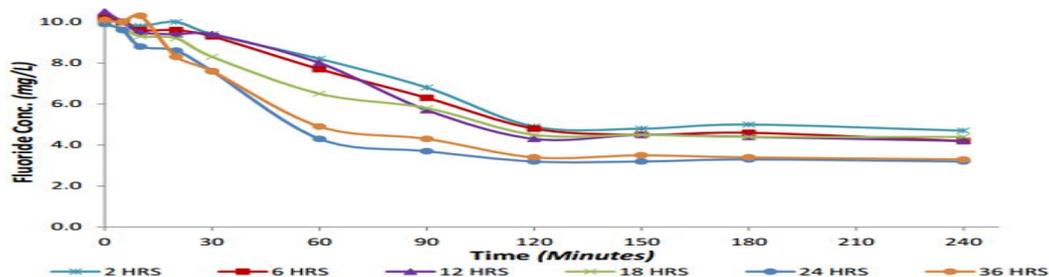

Figure 6: Fluoride removal using zeolite Na-LTA modified with different times with HDTMA

(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 ECEC 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

205   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 zeolitic surface. From Fig 4.6, fluoride removal

210   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 (73 %). The slight discrepancy could be due to interference from the release of excess, loosely bound HDTMA

215   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 was conducted considering

220   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.

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In addition, a batch setup was concurrently run without pH adjustments using modified Na-LSX.
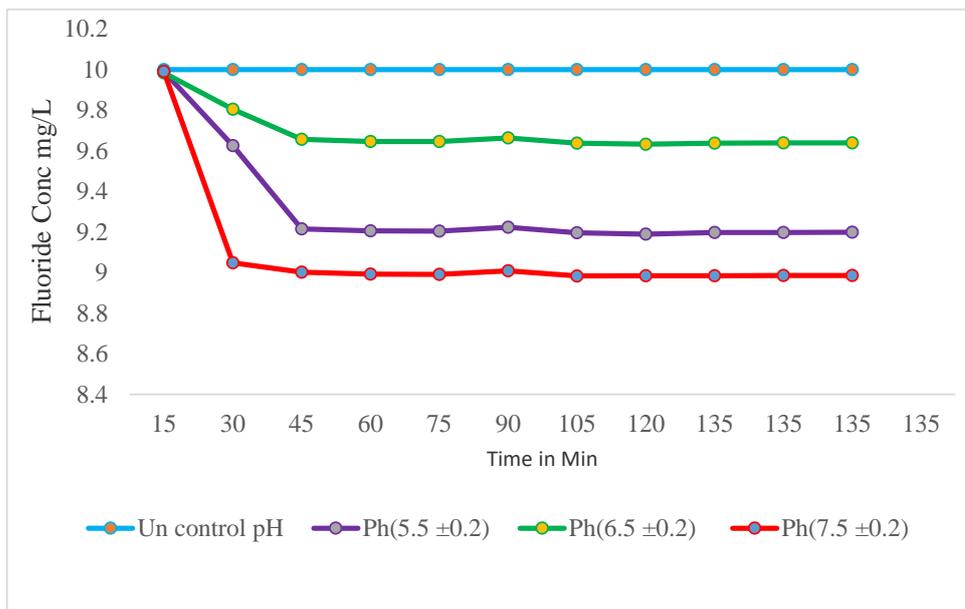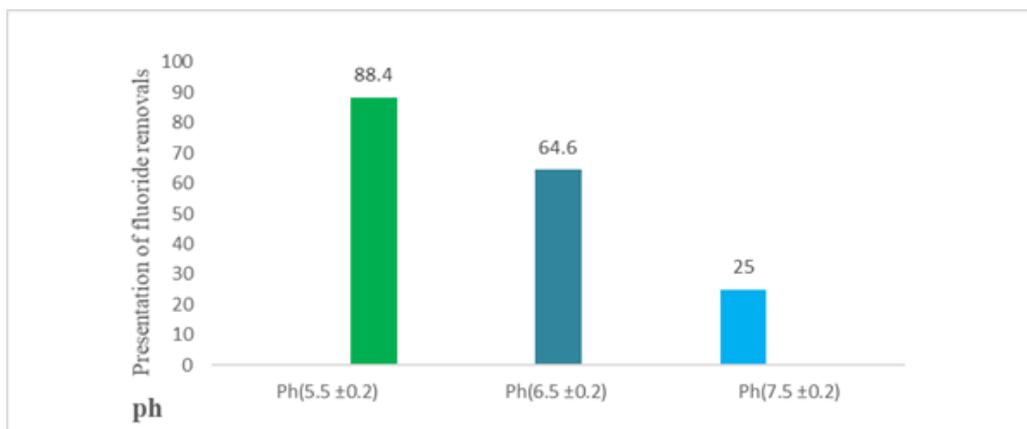
230   Fig 7 and 8 depict the results obtained.

Figure 7: Fluoride removal with pH maintained using modified Na-LST 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

235   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.

As evident from Fig 4.8, the modified zeolite Na-LSX with no pH control recorded poor fluoride removal similar to its unmodified zeolite in Fig 4.8. The only slight fluoride removal occurred within the first 5 to 10 minutes of runtime. This 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 observation, 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, an 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.

5. 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

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260 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

265 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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