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KINETICS AND EQUILIBRIUM STUDIES OF FLUORIDE ADSORPTION FROM DRINKING WATER ONTO ALUMINIUM MODIFIED ZEOLITE NA-LSX

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ABSTRACT

Fluoride related health issues such as dental and skeletal fluorosis have become a global concern in recent times. Adsorption is one of the affordable defluoridation techniques. This study reports the potentiometric determination of fluoride adsorbed onto Aluminium modified zeolite Na-LSX (AMZL) from aqueous solution at 25°C and various experimental conditions: pH (4.5-9), initial fluoride concentrations (3-15 mg/L), adsorbent dosage (2.5-12.5 g/L) and contact time (4-6 days) in a batch system. The obtained adsorption data was fitted to Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherms. Error functions, $\chi 2$, SSE, SAE were used in conjunction with

R^2 to ascertain the best fitted isotherm. The various kinetic models Lagergren's pseudo-first-order, Ho's pseudo-second-order, Intra-particle Diffusion and Elovich models were used to evaluate the kinetics of fluoride adsorption. The maximum fluoride uptake unto AMZL occurred at pH 5.5 over a period of 360 min. An increase in adsorbent dosage and pH affected fluoride removal. The presence of bicarbonate ions had a negative effect on the adsorption of fluoride however, chloride and nitrate did not affect the adsorption of fluoride. By the use of error functions, $\chi2$, SSE, SAE and the coefficient of regression, R^2 values, Langmuir isotherm model gave the best description of fluoride adsorption onto AMZL. The maximum fluoride adsorption capacity of AMZL based on Langmuir model was found to be 4.122 mg/g. The Ho's pseudo-second order kinetics best fitted the fluoride adsorption data obtained. The adsorption mechanism was found to be predominantly physisorption than chemisorption.

Keywords: adsorption, equilibrium isotherms, kinetics, alum modified zeolite

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1. INTRODUCTION

One of the numerous anions that have been found in aqueous solutions in higher concentrations and also detrimental to humans is fluoride. Fluoride originates from geological and anthropogenic sources. Thus, the occurrence of fluoride in high concentrations in surface waters, ground waters and wastewaters are common. Concentrations as high as 80-90mg/l has been found in industrial wastewaters (Zhang et al., 2011) and 0.1-11.6 mg/L in ground waters (Buamah et al., 2013) in the northern region of Ghana. These concentrations are above the world health organization's guideline of 10mg/l for wastewater disposal and 1.5mg/l for drinking water.

Several defluoridation technologies have been identified and researched into. These include membrane technology such as electrodialysis and reverse osmosis, coagulation methods such as chemical precipitation, electrochemical techniques such as electrocoagulation and electrosorption, and adsorption that makes use of natural and synthetic adsorbents.

However, some of these technologies are often found not to be appropriate and sustainable when technical and economic conditions are considered. Adsorption has been found to be more popular amongst the other methods because of its simplicity, versatility, high efficiency relatively low cost and its regenerative nature. Materials such as oxides and hyroxides, biosorbents, industrial products and by products, geomaterials and carbonaceous materials have been used as adsorbents for the removal of fluoride (Habuda-Stanic et al., 2014).

Zeolite a geomaterial, is gradually becoming a formidable material that is used in various industries for a number of applications. In recent years the use of zeolites as adsorbents for cation and anion removal in aqueous solutions has been investigated by a number of researchers (Majdan et al., 2003; Princz et al., 2005; Onyango et al., 2004; Samatya et al., 2007). Notable factors that make zeolites more attractive for adsorption are their ion exchange ability, large surface area and abundance in nature or availability of synthesized forms. Zeolites exchange interlayer cations easily however, they have negative surface charges and therefore cannot attract or adsorb anions easily (Samatya et al., 2007; Zhang et al., 2011). According to Onyango et al., 2006, this limitation is as a result of their negative zeta potential in solution over a wider pH range. This causes columbic repulsive forces between the adsorbate anions and the zeolite surface. In order to overcome this disadvantage, zeolite surfaces are tailored or modified to target the removal of specific anions in aqueous solutions. The modification of natural and synthetic zeolites can be achieved through acid treatment, ion exchange, and surfactant application (Bansiwal et al., 2006; Samatya et al., 2007; Zhang et al., 2011). Modification with metal ions using inorganic compounds through ion exchange, have proven to be more effective in the removal of fluoride than other modifiers (Shounkova, 2011).

Modification and application of natural and synthetic zeolites as fluoride adsorbents have been documented in literature. Zhang et al. (2011) using natural zeolitic materials sourced from China and modified with Ca^{2+}, achieved a maximum fluoride capacity of 1.766 mg/g from an aqueous solution with initial concentration of 100 mgF^{-}/L. Sun et al. (2011) tested Fe^{3+} modified natural stillbite and found the fluoride adsorption capacity to be 2.31mg/g using initial concentration of 10mg/L. Onyango et al. (2004) used Al^{3+} and La^{3+} modified Zeolite F9 for fluoride removal. They observed that alum modified Zeolite F9 had a higher adsorption capacity (37.5mg/g) for initial aqueous concentration range of 10-80 mg F-/L.

Even though zeolites are being used as adsorbents, limited work has been done using low silica zeolites Na-LSX and Na-A. They are known to have higher Cation exchange capacities (CEC). The higher the zeolite’s cation exchange capacity, the effective the surface modification and the higher the fluoride removal potential. Low silica zeolites have the advantage of removing higher amounts of fluoride, when they undergo cation exchange with higher valency metal salts.

In this study aluminium modified zeolite Na-LSX (AMZL) was utilized for fluoride adsorption and evaluated. The effects of varying conditions such as modification with AMZL, dosage, pH and presence of co-existing ions on fluoride adsorption were evaluated.

2 Equilibrium isotherm and kinetic models

Equilibrium isotherm models such as the Langmuir, Freundlich, Timkin, and Dubinin–Radushkevich, were employed to derived equilibrium data. Error analysis was done to determine the best fit isotherm.

2.1 Equilibrium isotherm models

The isotherms deal with adsorption capacities of adsorbents, adsorbent-adsorbate binding intensities and other sorption properties. Analysis of isotherm data is important for determining adsorption capacity of adsorbents which is one of the main parameters that is essential for designing an adsorption treatment system. To model the fluoride adsorption onto AMZL, the equilibrium experimental data was fitted to the following isotherm models; Langmuir, Freundlich, Dubinin–Radushkevich and Temkin equations so as to determine sorption capacities, intensities and energies of the adsorption system. The coefficients of determination (R^2) values in tables 1 were also used to determine the best-fit isotherm model (Allen et al., 2003; Kumar and Sivanesan, 2006)

2.1.1 Langmuir model

The Langmuir isotherm model assumes that the adsorption of adsorbate unto adsorbent takes place on a homogeneous surface. It further assumes that the adsorption sites are energetically the same. Equation (1&2) shows the model and linearized form for Langmuir isotherm respectively.

$$Q_e = \frac{QK_LC_e}{1+K_LC_e} \qquad (1)$$

$$\frac{C_e}{Q_e} = \frac{1}{Q_{max K_L}} + \frac{C_e}{Q_{max}} \qquad (2)$$

The constants Q_e and C_e are the equilibrium adsorption capacity and concentration of adsorbate in solution respectively. Q_{max} (mg/g) is the maximum adsorption capacity which corresponds to complete monolayer coverage on adsorbent (AMZL). And KL (L/mg), is a constant related to the affinity of the binding sites.

2.1.2 Freundlich model

Freundlich isotherm model is an indication of surface heterogeneity of an adsorbent. The model equation is expressed mathematically as in equation (3)

$$Q_{e=K_f C_e}{}^{1}/_{n} \qquad (3)$$

Data is often fitted to the linearized equation as in equation (4);

$$Log\ Q_e = LogK_f + \frac{1}{n}\ Log\ C_e \qquad (4)$$

The constants Q_e and C_e are the equilibrium adsorption capacity and concentration of adsorbate in solution respectively. K_f is the Freundlich isotherm constant (mg/g), which is a close indication of adsorption capacity. 1/n is the adsorption intensity and is related to the strength of adsorption in the adsorption process (Voudrias et al, 2002). If 1/n = 1 then the partition between the two phases is independent of concentration. If the value of 1/n is below one, it indicates a normal adsorption. On the other hand, if 1/n is greater than one then there is a cooperative adsorption (Dada et al., 2012.

2.1.3 Dubinin-Radushkevich (DR)

In order to determine the energy required for the adsorption process and adsorption mechanism involved in the uptake of fluoride, the Dubinin-Raduskevich isotherm model was applied. This model is based on the Gaussian energy distribution onto a heterogeneous surface (Dabrowski, 2001). The model and linear equation are presented in equation 5 and 6 below.

$$\frac{Q_e}{Q_s} = \exp\left(-K_{DR} \in^2\right) \qquad (5)$$

$$InQ_e = InQ_s - K_{DR} \in^2 \qquad (6)$$

Where the Є is the Polanyi potential given as

$$\in = RTIn(1 + \frac{1}{C_e}) \qquad (7)$$

Q_e, C_e, Q_s, K_{DR}, R and T are the equilibrium amount of fluoride on AMZL, equilibrium concentration in solution, adsorption capacity (mg/g), constant related to adsorption energy, gas constant (8.314 J/mol K) and temperature in Kelvin respectively.

The Free energy of adsorption (E) for the fluoride-AMZL system can be determined using equation (8)

$$E = \frac{1}{\sqrt{2}} K_{DR} \qquad (8)$$

The magnitude of E may provide useful information with regards to the adsorption mechanism, whether it is a chemical or physical process (Foo and Hameed, 2010). Typical bonding energy range reported for ion-exchange mechanism is 8–16 kJ/ mol. It is also generally noted that values up to -20 kJ/mol is indicative of physisorption process due to electrostatic interaction between charged particles while values < -40 kJ/ mol involve chemisorption (Salifu et al., 2013; Onyango et al., 2006).

2.1.4 Temkin model

This model estimates the bonding energy and type of interaction between fluoride and adsorbent. The Temkin isotherm assumes that the heat of adsorption (a function of temperature) decrease linearly rather than logarithmically with increase of adsorbent coverage due to effects of adsorbent- adsorbate interactions. Equation (9&10) shows the model and linearized form for Temkin isotherm respectively.

$$Q_e = \frac{RT}{b} \ In(A_T C_e) \qquad (9)$$

$$Q_e = B_T \ In \ A_T + B_T \ In \ C_e \qquad (10)$$

A_T is the Temkin isotherm equilibrium binding constant (L/g) that is related to maximum binding energy, $BT = \frac{R_T}{b_T}$ is Temkin Constant related to heat of sorption (J/mol) and b_T is the Temkin isotherm constant that reflects the bonding energy which in turn indicate the type of interaction between for example fluoride and aluminium modified zeolite LSX (AMZL). While R is universal gas constant (8.314J/mol/K) and T is Temperature at 298K (Allen et al., 2003; Foo and Hameed, 2010).

2.2 Kinetic models

According to Mondal and George (2014), the kinetics of any sorption process is the function of different parameters such as structural properties of adsorbent, nature and concentration of adsorbate and adsorbent-adsorbate interactions. Therefore, it is prudent to investigate any selected adsorbent to determine its adsorption mechanism, as well as, its adsorption rate. This information provides useful prediction/answers for the rate of adsorption which in turn give information for modeling the process (Yousef et al., 2011). The rate of adsorption of some adsorbents is fast at the beginning of adsorption, but may slow down after a few minutes. This, according to Nethaji and Sivasamy (2014), is because the anions adsorbed have to undergo various processes in the adsorbent by the following three stages; i) transport of solute from bulk aqueous phase to film of the adsorbent molecules, ii) diffusion of solute from the film to the pores of the adsorbent and iii) adsorption of solutes onto the interior surface of pores. In the present study, the adsorption data was tested with different kinetic equations such as Largergren Pseudo-first order, Ho‘s pseudo- second order, Elovich and intra-particle diffusion models. The applicability of a particular kinetic model for adsorption of fluoride unto AMZL was assessed from the goodness of fit, coefficient of correlation (R_2) and comparison of experimental and predicted amounts of fluoride adsorbed at equilibrium Q_e (mg/g).

2.2.1 Largergren Pseudo first order Model

For this model, the absorption rate is proportional to the concentration of the solute. It is usually used for homogeneous sorbents and physical sorption (Ho et al., 2004). The mathematical representation of first order kinetic model is given in equation (11) This can be interpreted to obtain the linear form in equation (12) using the boundary conditions $Q_t = Q_t$ at t = t and $Q_t = 0$ at t = 0

$$In\left({}^{Q_e}/_{Q_e} - Q_t\right) = K_1 t \qquad (11)$$

$$In\,(Q_e - Q_t) = In\,Q_e - K_1 t \qquad (12)$$

Where Q_e and Q_t are the amounts of absorbed fluoride (mg/g) at equilibrium and at time t (h), respectively, and $K_1(h^{-1})$ is the absorption rate constant. The calculated Q_e and the rate constant K_1 were calculated from the slope of the linear plot of ln (Q_e-Q_t) vrs. t (Figure 3) of the kinetic experimental data using equation (12). If the value of the experimental Q_e (Exp) and calculated Q_e (Cal) are close then the kinetic model fits the data. On the other hand if the calculated and experimental Q_e values are at variance, it implies that the kinetic model does fit the data well.

2.2.2 Ho’s Pseudo Second order Model

According to Ho and Mekay, (2002), the Pseudo order model is based on the assumption that chemisorption may be involved in the rate determining step in which valence forces or exchange of electrons occur between adsorbent and adsorbate. Mathematically represented as:

$$Q_t = Q_{e^2} K_2 t / 1 + Q_e K_2 t \qquad (13)$$

And linearly represented as

$$\frac{t}{Q_t} = {}^{1}\!/_{h_o} + {}^{1}\!/_{Q_e t} \qquad (14)$$

$$h_o = K_2 Q_{e^2} \qquad (15)$$

$$t_{1/2} = {}^{1}\!/_{K_2 Q_{e^2}} \qquad (16)$$

Where Q_e and Q_t represent the amount of fluoride absorbed (mg/g) at any time t (h) and at equilibrium respectively. $K_2(gmg^{-1}h^{-1})$ is the 2nd order adsorption constant, h_o is the initial adsorption rate at t=0, $t_{1/2}$ is the time required for the adsorbent to take up half as much fluoride as its equilibrium value. The rate constant K_2 and calculated Q_e (Cal) were determined from the slope of the linear plot of t/qt vrs t. from equation (14). When the values of experimental Q_e (Exp) are close to that of calculated Q_e (Cal) it portrays the applicability of the model (which assumes that the fluoride adsorption process follows a second-order chemisorption) to describe the adsorption process of fluoride unto AMZL. The Ho and $t_{1/2}$ values will be calculated from K_2, Q_e.

2.2.3 Elovich model

The Elovich Model has been used appropriately for the description of chemisorption on heterogeneous materials (Cortes et al., 2004). It is represented as below

$$\frac{dQ_e}{dt} = \alpha\, e^{-\beta Qt} \qquad (17)$$

With the same boundary conditions as in pseudo 1st and 2nd order kinetic models, equation (17) can be linearly written as

$$Q_t = \frac{1}{\beta In(\alpha\beta)} + \frac{1}{\beta In}\, t \qquad (18)$$

Where α and β are constants during a specific experiment. To test the validity of the Elovich equation, Q_t is plotted against ln t to yield a straight line with slope 1/β and intercept I/ β ln (αβ). The "α" (mg/gmin) is considered as the initial rate of adsorption and "β" is indicative of the number of sites available for adsorption.

2.2.4 Intra – particle diffusion model

The intra-particle diffusion model describes the movement of adsorbate from the solution phase to the surface of the adsorbent particles through numerous stages. According to Habuda-Stanbic and Ravincic, (2014), the overall adsorption process, maybe controlled by one or more of the stages (pore diffusion, surface diffusion, external diffusion, adsorption on the pore surface or a number of these stages combined.

This kinetic model is represented by the equation below

$$Q_t = K_{id}\, t^{1/2} + C \qquad (19)$$

Where K_{id} is the intraparticle pore diffusion rate constant (mg/gmin) and C represents the intercept. The larger the C, the greater the boundary layer effect (Singh et al., 2012). If intra-particle diffusion is involved, a plot of Q_t vrs. $t^{1/2}$ will be linear. And if the line passes through the origin, then it is likely the rate limiting process is only due to intra-particle rate diffusion (Yosef et al., 2011).

3 MATERIALS AND METHODS

3.1 Materials and Reagents

Bauxite was obtained from Ghana Bauxite Company at Awaso in the Western region of Ghana whilst clay was sampled from Asokwa, a suburb of Adansi East district in the Ashanti Region of Ghana. Sodium hydroxide (Analar grade) from Analar Normapur, UK, was used. The clay and bauxite were ground and sieved with a 0.75µm mesh sieve under dry conditions. Teflon bottles used were obtained from Cowie Technology, Middlesbrough, UK.

3.2 Synthesis, Modification and Characterization of Zeolite Na-LSX and Alum Modified Zeolite LSX

Zeolite Na-LSX was synthesized from solid sodium silicate prepared from clay and sodium aluminate solution prepared from bauxite. The solid sodium silicate was first mixed with water to form a suspension before sodium aluminate solution was added to form a uniform slurry / gel. Zeolite Na-LSX was obtained after crystalizing the uniform slurry at 100^{o}C for 24hrs in a WTC Binder electric oven.

The zeolite synthesized was ground and sieved to obtain particle size of ≤ 250 microns. Aluminium sulphate (alum) solution (0.075M) was used for zeolite modification. Fifty grams (50g) synthesized zeolite Na-LSX was added to 0.075M hydrated aluminum sulphate solutions for the aluminium modification. The mixture was stirred continuously in a flocculator at 90 rpm for 12hrs, filtered with Whatman filter paper No. 1 and washed several times using demineralized water to remove the excess aluminium. The alum modified zeolite (AMZL) was then oven dried at 100^{o}C overnight, cooled, ground, sieved with 250 microns strainer and stored in ziploc bags.

3.3 Characterization of modified and Unmodified zeolite Na-LSX

The characterization of the modified and unmodified zeolite was performed in the laboratories of Faculty of Science and Engineering, University of Wolverhampton, UK. The synthesized and modified zeolites were verified using Scanning Electron Microscopy (SEM), Electron Dispersive X-ray (EDX), and Fourier Transform Infrared Spectroscopy (FTIR). The morphology of the zeolite sample was examined using the ZEISS EVO50 Scanning Electron Microscope equipped with an Energy Dispersive X-ray spectrometer - Zeiss, UK. Samples were prepared by spraying zeolite powder unto aluminium holder supported by double-sided adhesive discs and examined. The following analytical conditions were applied in the use of the electron scanning electroscope: I probe 1 nA, EHT = 20.00 kV, beam current 100 µA, Signal A = SE1, WD = 8.0 mm and 5mm. Samples for EDX analysis were prepared similarly to that of SEM but instead of an aluminium sample holder, a carbon sample holder was utilized to avoid errors in the aluminium content. The FTIR analysis was carried out using a Genesis 2000 Matson FTIR spectrophotometer by taking readings from 400 cm^{-1} to 4000 cm^{-1}. An air background spectrum was collected at the start of the sample analysis. A small sample each of the modified or unmodified zeolite (i.e. zeolite LSX or zeolite Na-LSX) was placed at the center of the Zinc Selenium (ZnSe) plate ensuring the entire crystal surface was covered. Pressure was then introduced using a pressure clamp. Each zeolite sample was analyzed three times. In order to make up for atmospheric conditions around the FTIR, a background spectrum was measured before samples were scanned. Measurements were done using 100 scans at 4 cm^{-1} resolution, units of log (1/R) (absorbance), over the mid-infrared mid- IR region of 1200-400cm^{-1}.

3.4 Adsorption of fluoride unto AMZL

A Stock fluoride solution (1000mg/l) was prepared by dissolving 2.21g sodium fluoride in deionized water. The model fluoride water used for the experiment was prepared by spiking deionized water to the required concentration using the stock fluoride solution. The adsorption experiments were performed using seven 500 mL beakers filled with 200 mL fluoride solutions of varying initial concentrations:3, 5, 7, 9, 11, 13 and 15 mg /L for 72 hours. In each beaker, the experimental reactions were initiated by adding 1g of the AMZL and stirred continuously at 90 revolutions per minute (rpm) to enhance particle transport. A control adsorption experiment using unmodified zeolite Na-LSX was conducted. In addition, a blank fluoride adsorption experiment, without adsorbent, was carried out to evaluate experimental uncertainties.

All the adsorption experiments were carried out in triplicate in order to check reproducibility. For all experiments, the solution in each beaker was sampled at pre-determined time intervals (5, 10, 20, 25, 30, 60, 120, 240, 720, 1440, 2880, 4320 minutes) and immediately filtered through a 0.45 μm membrane filter using a polypropylene syringe. Each filtered sample was mixed with a Total Ionic Strength Adjustment Buffer (TISAB) in a ratio of 1:1. The residual fluoride concentration in the sampled solutions was measured using a WTW 3310 pH / ion meter. The equilibrium sorption capacity was determined from

$$Q_e = \frac{(C_o - C_e)}{M} V \qquad (20)$$

Where Q_e is the amount of fluoride adsorbed per unit mass of media at equilibrium, C_o is the initial concentration, C_e is fluoride concentration at equilibrium, m is mass of adsorbent and V is volume of the solution used.

3.4.1 Determination of isotherms and kinetics of fluoride adsorption

The interactions between the AMZL and fluoride at 27°C are presented in the form of equilibrium data (experimental points). From the experimental data, the fitting of four equilibrium models (Langmuir. Freudulich, Dubinin Raduskevich and Temkin) and four kinetic models (as Pseudo 1st and 2nd order, Elovich and intra particle diffusion) were tested using their linear equations). During the fitting error functions such as Chi Square (χ), Sum of Square errors (SSE) and sum of absolute errors (SAE) were used to select the best fitted equilibrium model isotherm that suited the experimental data.

3.4.2 Evaluation of factors affecting adsorption of fluoride onto AMZL

In this section, the effect of modification, adsorbent dosage, pH and co-existing ions on fluoride adsorption were investigated under the same equilibrium experimental conditions.

3.4.2.1 Effect of modification

In evaluating the effect of modification, the modified and unmodified zeolite Na-LSX were employed in a batch experiment. In the experiment 1g of unmodified / modified zeolite was put in 200 ml of 5 mgF-/L aqueous solutions. In addition, a blank fluoride adsorption experiment, without adsorbent, was carried out to evaluate experimental uncertainties.

3.4.2.2 Effect of adsorbent dosage

The effect of varying modified zeolite dosage was investigated using various amounts of the adsorbent (i.e. 0, 2.5, 4, 5, 7.5, 10, and 12.5g/l) and a fixed amount of fluoride concentration 5.0 ± 0.002gF-/L at a pH of 6 at room temperature (27°C) and stirred at 90 rpm for 2 hours. Water samples were picked from the experimental beakers at specified time intervals (5, 10, 20, 30, 60 and 120 minutes) for residual fluoride determination. The samples taken at the predetermined times were filtered using Whatman Paper No1 filter paper. Five ml of the sampled solution was added to TISAB (total ionic strength adjusting buffer) to maintain the ionic strength, pH and eliminate the interference effect of complexing ions. The residual fluoride concentration in the solution was analyzed using a fluoride ion selective electrode (PF-1C, Model 201, China).

3.4.2.3 Effect of pH

The effect of pH on fluoride adsorption using AMZL was examined. These experiments were conducted over a pH range of 3 – 9 using an adsorbent dosage of 5 mg/L. All other parameters (temperature, RPM, and the initial fluoride concentration of the solution) were held constant.

3.4.2.4 Effect of co-existing anions

A number of other anions are usually present in aqueous solutions, and may compete with fluoride ion adsorption onto the AMZL. In order to investigate the effect of interfering ions on the fluoride removal, the experiments were carried out using 5 mgF-/ L solution containing various concentrations of coexisting ions like chloride (50-100 mg/L), nitrate (5-30 mg/L), and bicarbonate (150-500 mg/L) using the same general procedure described in the previous experiments. The adsorbent dosage of 5 g/L and initial of pH 5 were kept constant but the contact time was extended to 8 hours in order to observe well the trends of fluoride adsorption.

4 RESULTS

4.1 Characterization of modified and unmodified zeolites

The characteristic hexagonal shape of the micrograph of zeolite Na-LSX as shown in Plate 1A, is no exception to the traditional micrographs of zeolite Na-LSX. Similar characteristics has been reported by Kwakye-Awuah et al., (2014). The SEM of the modified zeolite shows a change in shape of the crystals of zeolite Na-LSX (Plate 1B), however the EDX spectra (Plates 2 and 3) indicate that it is still the initial zeolite but with a reduced sodium percentage (Plate 3A). This is as a result of the modification of Zeolite Na-LSX with alum (aluminium sulpahte). This is clear evidence of aluminium ions exchanging with sodium ions during the modification and so resulting in high aluminium ions content.

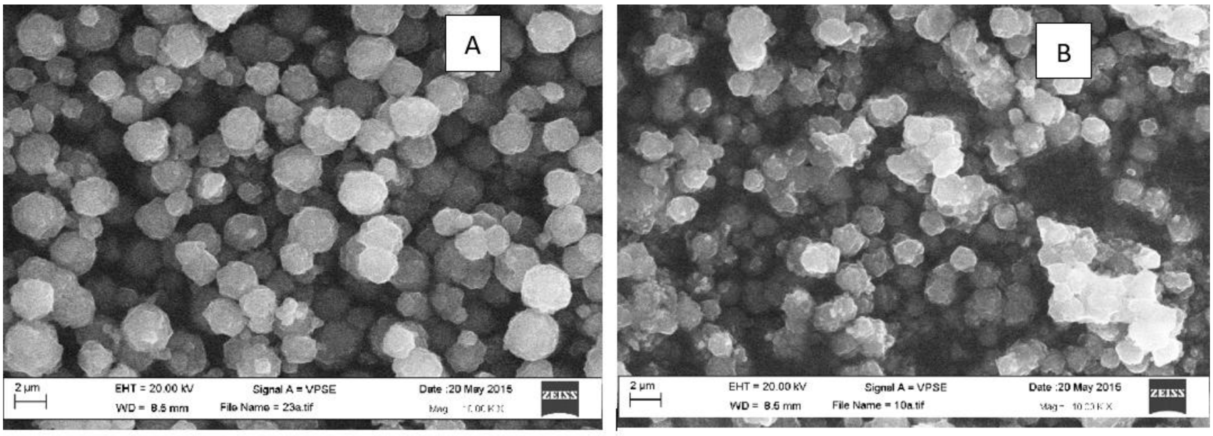

Plate 1. The SEM micrograph of A) Zeolite Na-LSX and B) aluminium modified Zeolite Na- LSX

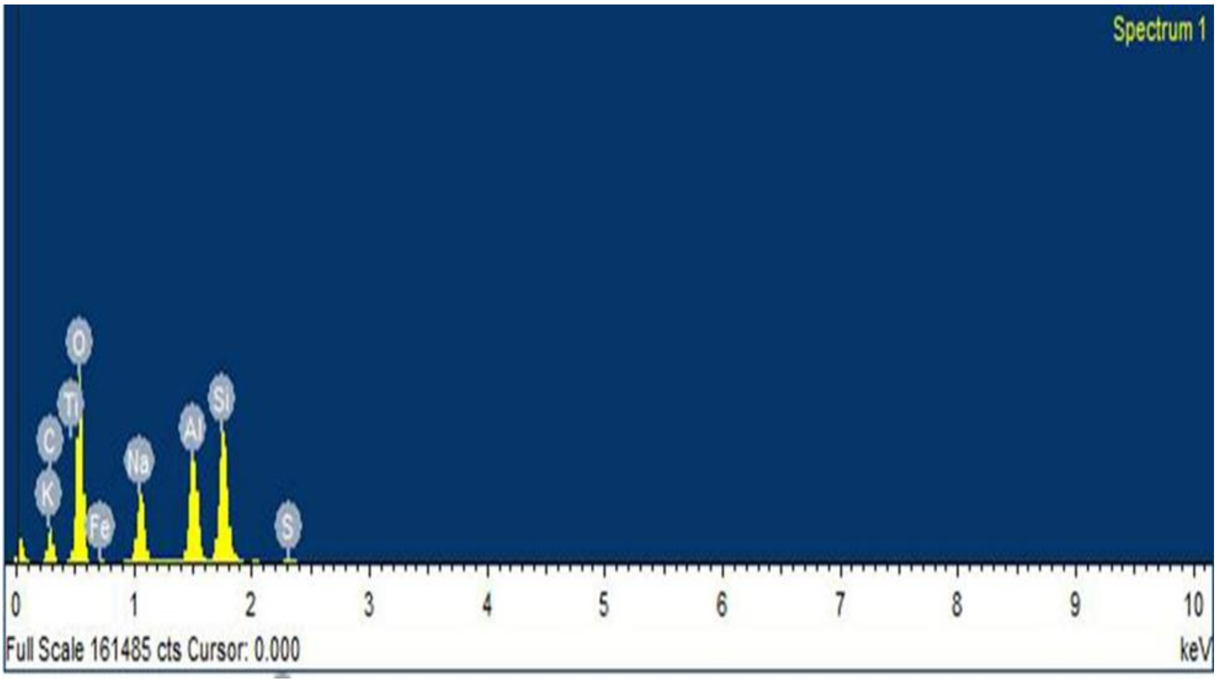

Plate 2. EDX spectrum / Composition of Zeolite Na-LSX.

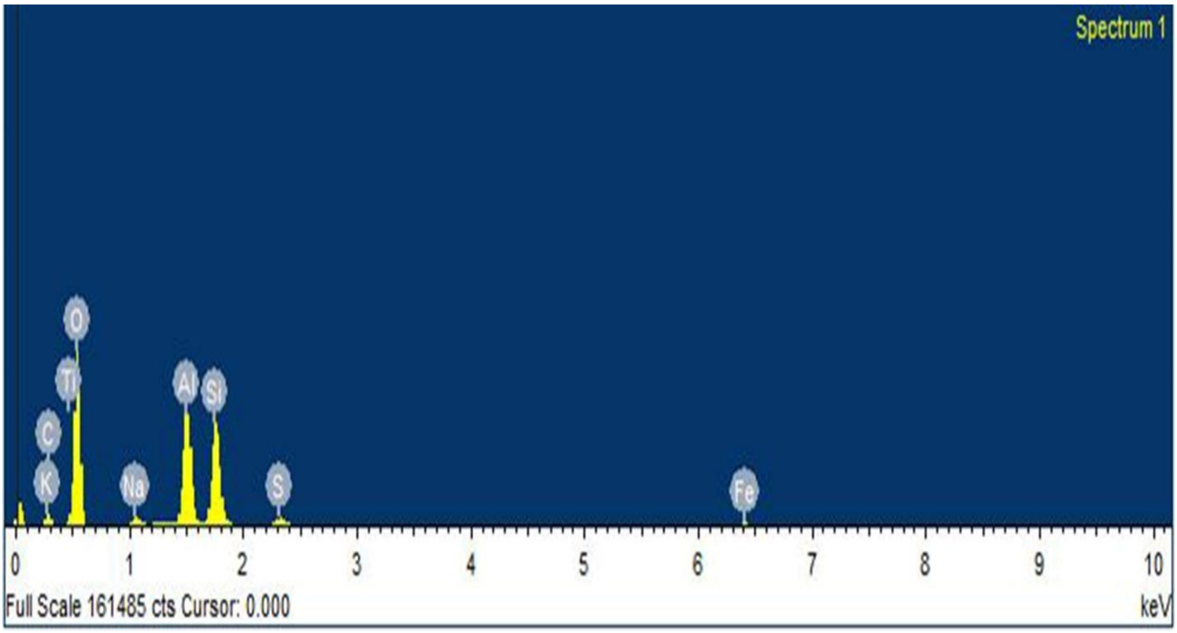

Plate 3. EDX spectrum / Composition of Aluminium modified Zeolite Na-LSX.

From the FTIR spectra, there are certain asymmetric and symmetric peaks occurring at wavelengths typical of tetrahedral oxygen (T-O) bend in the internal structure of the modified zeolite compared to the unmodified spectrum (Plates 4 and 5). The featuring of the T-O bend wavelength which is more pronounced in the modified than the unmodified gives further evidence to the fact that there has been Na-Al ion exchange.

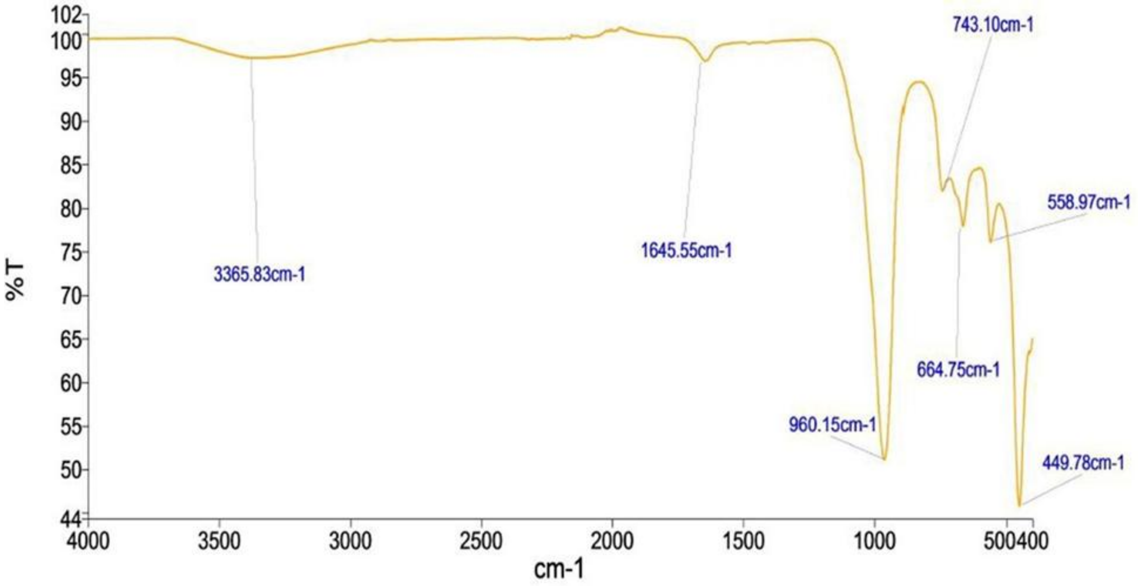

Plate 4: FTIR spectrum of Zeolite Na-LSX

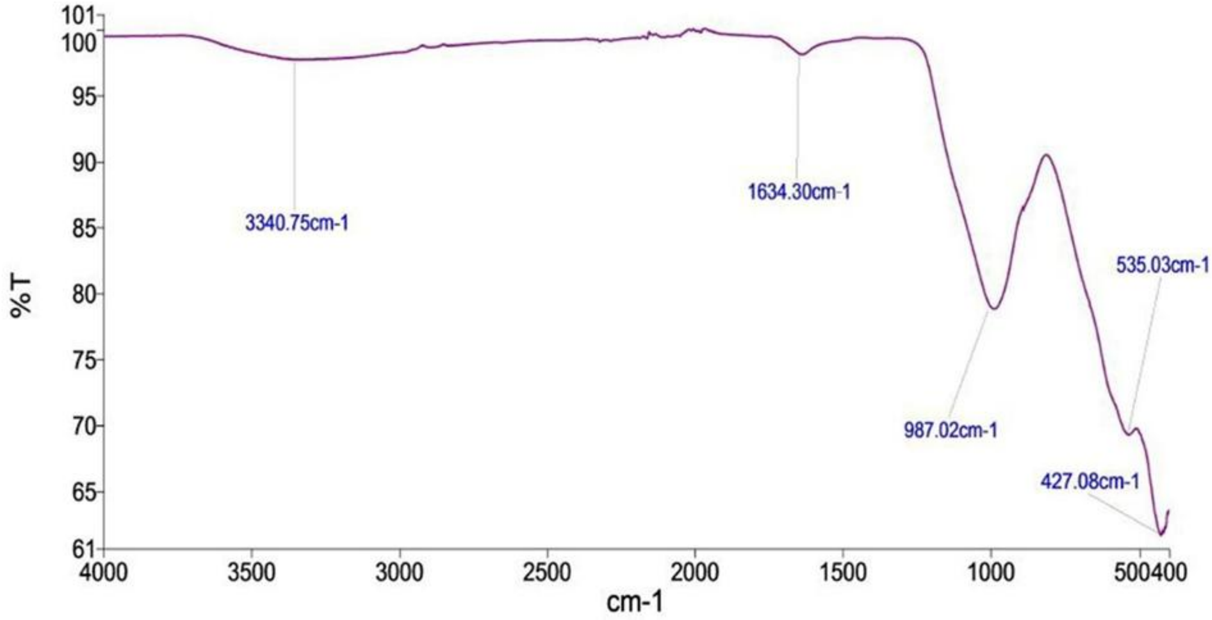

Plate 5: FTIR spectrum of Aluminium modified Zeolite Na-LSX

4.2 Potency of AMZL in fluoride adsorption

In order to ascertain the potential of the AMZL, several tests with unmodified and modified zeolites were conducted separately for fluoride adsorption. at constant temperature (25^{o}C) and pH of 6 for 2 hours. The results indicated that the unmodified zeolite could remove about 46% of the fluoride whiles the AMZL removed about 76% of fluoride (i.e. from initial fluoride concentration of 5.0 ± 0.1.mg/L to 1.4mg/L) within an hour of contact time (Figure 1A). In both experiments a 5mg/l dosage of the zeolites were used. AMZL was able to effectively adsorb a high percentage of fluoride probably because of the modification that might have overcome the columbic forces and eventually created adsorptive sites that aided in the adsorption of anions (Onyango et al., 2006; Bansiwal et al., 2006; Samatya et al., 2007).

4.3 Effect of Dosage

The effect of zeolite dosage on fluoride removal from aqueous solutions was examined using various amounts of zeolite dosages (0, 2.5, 4.0, 5.0, 7.5, 10.0, 12 g / L). In general, it was observed that an increase in zeolite dosage resulted in increased fluoride removal of up to 92% (Figure 1B). This is due to increased availability of more adsorptive sites for fluoride binding and hence adsorption. The increase in the % fluoride removal was however found to be negligible after an adsorbent dosage of 5g/L. This dosage (5mg/L) can therefore be considered as the optimum at pH 6 and a temperature of 25% within the period of 2 hours (Figure 1B).

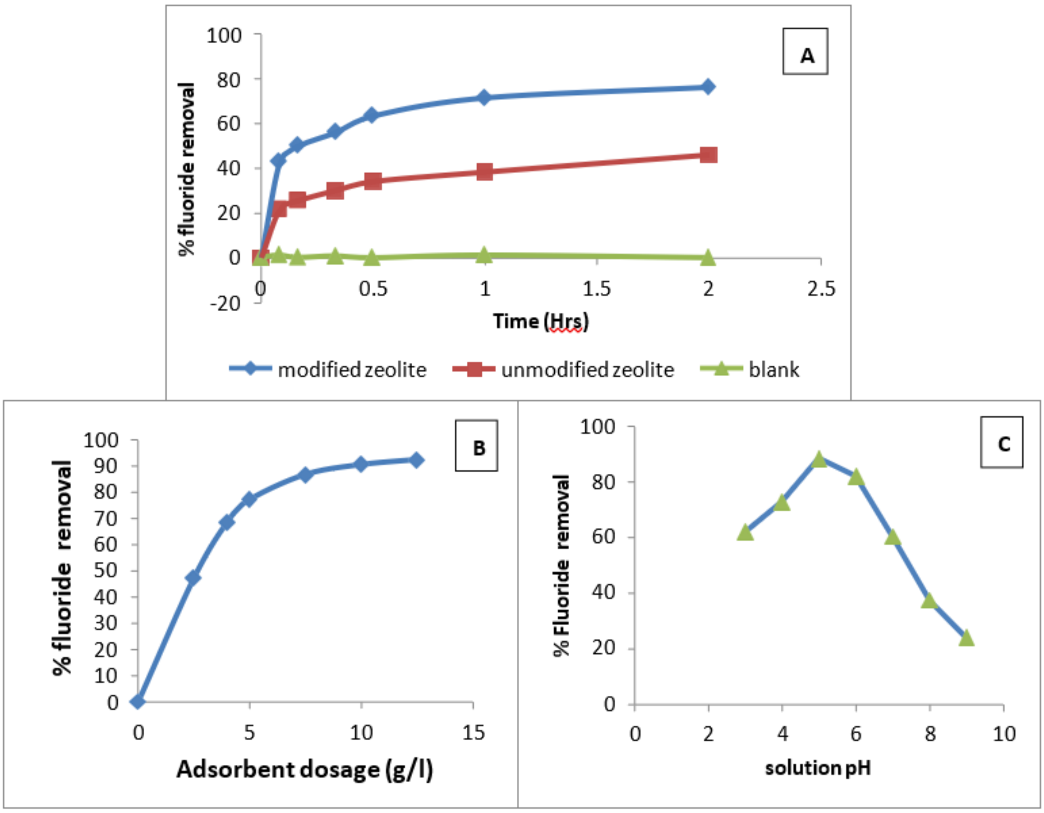

Figure 1: The potency of the modified and unmodified zeolite Na-LSX. A) Fluoride removal trend for the modified and unmodified zeolite LSX B) Effect of modified zeolite dosage on fluoride removal capacity C) Effect of pH on the fluoride removal potential of the modified zeolite Na-LSX (AMZL).

4.4 Effect of pH

The effect of pH on fluoride adsorption was studied using seven pH values i.e. within the range of pH 3 - 9. Using an initial fluoride concentration of 5mg/l; adsorbent dosage of 5g/l and contact time of 2 hours the tests were done to determine the effect of pH on the fluoride adsorption onto AMZL. The pH changes were done using small additions of 1M of NaOH or HCl to increase or decrease pH as and when needed. Figure 1C depicts the effect of pH on fluoride adsorption onto AMZL.

From Figure 1C maximum fluoride adsorption occurred at pH 5. As pH increased above 5 the % fluoride removal decreased. Similar trend is observed with pHs below 5. This phenomenon has been reported by a number of researchers: Ayoob and Gupta (2006), Onyango et al. (2006), Mondal and George, (2014) and Habuda-Stanić et al. (2014). This can be explained from the concept of protonation and deprotonation of active sites on the surface of the adsorbent. When pH decreases below 5, there is the formation of neutral hydrogen fluoride that is less soluble in solution and hence a decrease in fluoride adsorption. On the other hand, deprotonating occurs at higher pH values causing fluoride binding to AMZL to reduce drastically.

4.5 Effect of coexisting anions

Figure 2 illustrates the effect of co-existing anions on the fluoride removal efficiency of AMZL. It was observed that NO_3^- and Cl^- ions at all the concentrations studied did not affect the fluoride removal efficiency of AMZL, however, there was substantial drop of 30-50% in the fluoride removal efficiency in the presence of HCO_3^{2-} ion. The decrease in the fluoride removal efficiency was mainly due to the competitive effect of HCO_3^{2-} on AMZL for active sites on adsorbent surface in addition to the change in pH of solution. Similar results have been reported by Zhang et al., (2011) and Waghmare et al., (2015) about the behavior of HCO_3^{2-} ion during fluoride removal or adsorption.

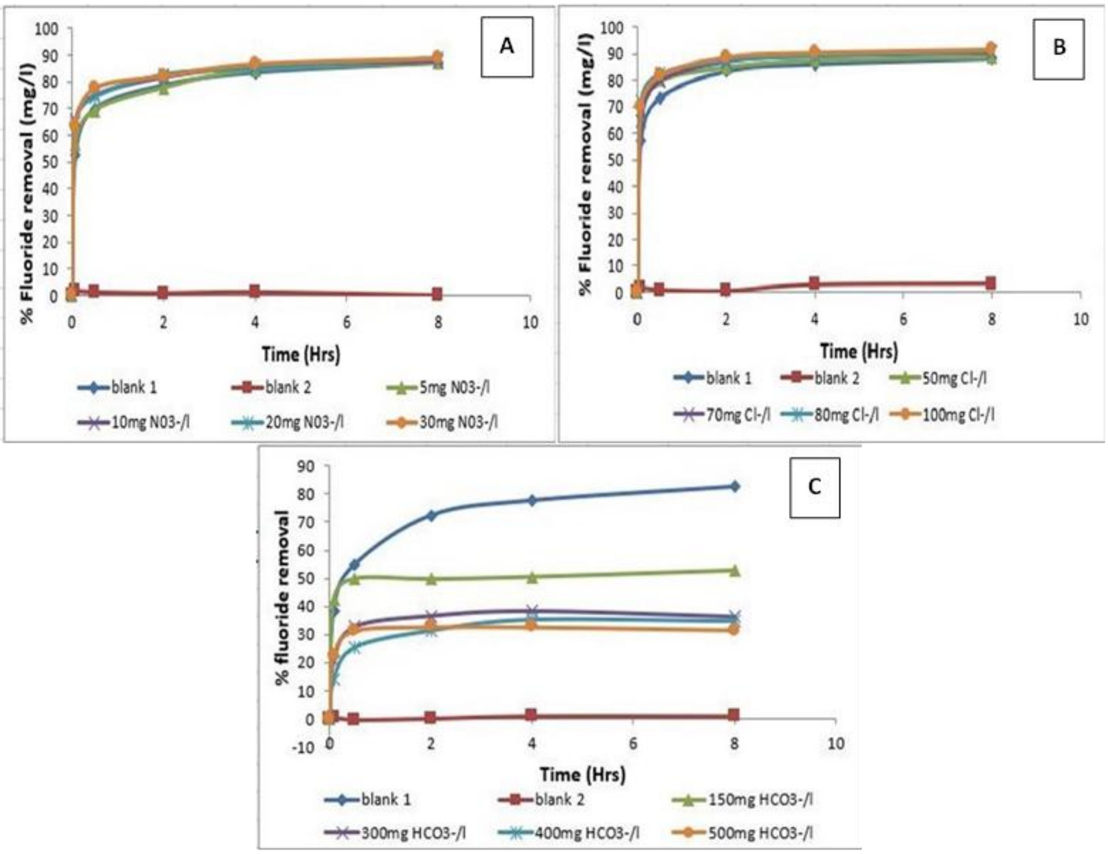

Figure 2: Effects of various anions on fluoride removal using AMZL a) nitrates b) chlorides c) bicarbonate.

4.6 Equilibrium isotherms

Langmuir, Freundlich, Dubinin-Radushkevitch and Temkin were the isotherms used in studying the adsorption capacities of the AMZL at pH 5.5.

4.6.1 Langmuir and Freundlich models

The adsorption experimental values were fitted to both Langmuir and Freundlich equations. From Figures 2A and 2B, the data fitted slightly better the Langmuir equation with a correlation coefficient (R^2) of 0.9849 and 0.9751 for Freundlich. This implies that the fluoride adsorptive sites for AMZL are more homogeneous than heterogeneous. These sites may have different affinities for fluoride and thus, the heat of adsorption on these sites varies from site to site. Other investigators have also reported R^2 that are high and well fitted to the two models (Gao et al., 2009; Kemer et al., 2009).

Values of Q_{max} and K_L using Langmuir model and K_f and 1/n using Freundlich model have been given in Table 1. The value of 1/n, the adsorption intensity, being less than unity is an indication that the fluoride adsorption intensity is well defined for the AMZL powder (Zhang et al., 2011).

4.6.2 Dubinin-Radushkevitch

To evaluate the nature of interaction between fluoride and the binding sites, mean free energy of adsorption ($E = (2K)^{-0.5}$ per mole of the adsorbate was determined. E is the energy required to transfer one mole of fluoride to the zeolite surface from infinity in solution. Table 1 shows the values of q_s, K_{DR} and E as 2.156, 0.1591 and 1.77kJ/mol, respectively. These values were obtained from the linear plot of the Dubinin-Raduskevitch (DR) graph (Figure 2C). The E value (<8 kJ/mol) obtained suggests that physical adsorption plays a significant role in the fluoride up-take. This could be as a result of long - range weak Van der Waals forces between the fluoride ions and the AMZL.

4.6.3 Temkin isotherm

The constant b_T reflects the bonding energy which in turn indicates the type of interaction between fluoride and AMZL. The b_T value of 2.90 kJ/mol obtained from the Temkin isotherm plot (Figure 2D), suggests the involvement of physisorption process in the interactions between fluoride and AMZL. This value is in the same range (< 20kj/mol for physisorption) as that predicted from the Dubinin-Raduskevitch isotherm.

4.6.4 Adsorption capacity

The amount of fluoride adsorbed per unit of AMZL adsorbent increased with an increase in initial concentration of fluoride (3-15 mg/l) used in the study. The maximum adsorption capacity (Q_e experimental) of AMZL was found to be 4.12 mg/g. The adsorption capacities of other adsorbents for fluoride removal under various conditions can be seen in Table 2. It can be observed from the Table 2 that AMZL has relatively higher adsorption capacity than some of its counterparts ($CaCl_2$ modified natural zeolite and Fe modified stillbite) but a lower capacity compared to aluminium modified F9, zeolite Y-AO and STI-AO. According to Ayoob et al., (2008), when different ranges of fluoride concentration are used the comparison of the effectiveness of the adsorption capacities becomes unsuitable and meaningless. Moreover the effectiveness and efficiency of an adsorbent does not always depend on the adsorptive capacity derived using a batch test but rather on its applicability during column or pilot studies (Ayoob et al., 2008).

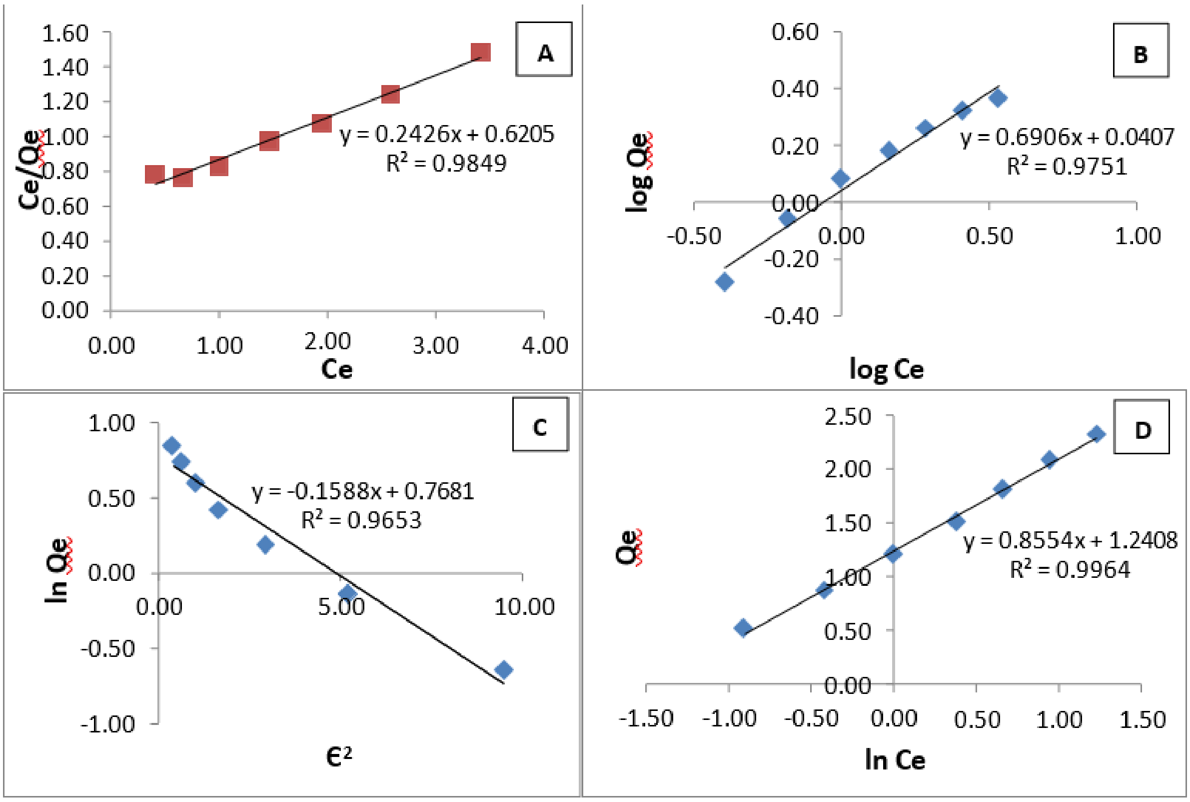

Figure 3: Various Adsorption Isotherms for fluoride removal unto AMZL A) Langmuir plot B) Freundlich plot C) Dubinin-Radushkevitch plot D) Temkin plot

4.6.5 Error analysis

Adsorption data are usually fitted to adsorption isotherms in order to understand and measure the amount of adsorbate associated with the solid adsorbent and liquid phase during adsorption. The experimental Data is fitted to a number of models using their linearized equations. According to Ayoob and Gupta, (2008) and Rhaman et al., (2014), when linearized equations are used they may not give a significant basis to accept or reject a model especially when different range of concentrations are used. Therefore, it is prudent to access the suitability of the adopted models using error analysis. Thus, the adsorption experimental data were fitted to the models adopted and established with error functions such as Chi-square, Sum of squared errors and Sum of Absolute errors, (χ^2, SSE and SAE).

The R^2 values for all the isotherm models were found to be high (> 0.94). This made the models applicable to the description of the adsorption data (Ayoob and Gupta, 2008). Using the error functions the values of χ^2, SSE and SAE were determined. Values recorded in Table 1 were found to be low for all the adsorption isotherm models used. The experimental data fitted excellently with Langmuir isotherm model followed by Temkin, then Freundlich and Dubinin Radushkevich models. The minimum values of χ^2, SSE and SAE for all models confirm the high values obtained for R^2. This could be due to the use of low concentrations range of fluoride in the fitting of the adsorption isotherm models (Ayoob and Gupta 2008).

Table 1: Values of constants obtained from isotherms and Error analysis used for fluoride adsorption by AMZL

EQUILIBRIUM ISOTHERM MODEL EQUATIONS	**EQUILIBRIUM ISOTHERM MODEL CONSTANTS / ERROR PARAMETERS**	**ISOTHERM PARAMETER VALUES / ERROR VALUES**
Langmuir **$C_e / Q_e = 1/Q_{max}K_l + C_e / Q_{max}$**	Qmax (mg/g) K_L R^2 χ^2 SSE SAE	4.1220 0.3910 0.9850 0.0103 0.0064 0.2042
Freundlich **$\text{Log } Q_e = \text{Log}K_f + 1/n \text{ Log } C_e$**	K_f 1/n R^2 χ^2 SSE SAE	1.0980 0.6910 0.9750 0.0518 0.0919 0.6554
Dubinin – Radushkevich ln **$Q_e = \ln Q_s - K_{DR}Є^2$** **$Є = RT \text{ In } (1 + 1/C_e)$ E** **$= 1/\sqrt{2K_{DR}}$**	Q_s K_D R Energy E R^2 χ^2 SSE	2.1560 0.1590 3.1500 0.9653 0.0915 0.1570 0.8526

	SAE	
Temkin **$Qe = BT\ InAT + BT\ InCe$** **$BT = RT/bT$**	BT bT A T R^2 χ^2 SSE SAE	0.8550 2.9000 4.2700 0.9964 0.0124 0.0166 0.1441

$\chi 2$ – chi square, SSE – sum of square errors, SAE – sum of absolute errors, R2 – correlation coefficient, Qe – equilibrium amount of fluoride, Ce – equilibrium concentration in solution, Qs and Kf – adsorption capacities, Qmax – maximum adsorption capacity, 1/n – adsorption intensity, KL – constant related to affirmity of the binding sites, KDR – constant related to adsorption energy, E –free energy of adsorption, BT – Temkin constant related to heat of sorption, bT – constant that reflects bonding energy. AT is the Temkin isotherm equilibrium binding constant (L/g) that is related to maximum binding energy. R is universal gas constant (8.314J/mol/K) and T is Temperature at 298K.

Table 2: Fluoride removal comparison with other adsorbents

Adsorbents	pH range	Concentration used (mg/L)	Model used	Adsorption capacity (mg/g)	Reference
Aluminium coated Charcoal	7.0	40-60	Langmuir	34.25	Buamah et al., 2015
Activated Alumina	7.0	2.5-14	Langmuir	2.41	Ghorai and Pant, 2005
Hydrous Zinconium Oxide	3.5-2.5	20-900	Freundlich	188.68	Rahman et al., 2014
Aluminium hydroxide pumice	6-9	5	Langmuir	7.89	Salifu et al., 2013
STI-AO (2:1)	6.1	10	Langmuir	12.1	Dessalegne et al., 2017
CaCl2 modified natural zeolite	4-9	100	Langmuir	1.77	Zhang et al., 2011
Fe (III) modified Stillbite	3-11	10	Langmuir	2.31	Sun et al, 2011
Aluminium modified zeolite F9	6.6	10-80	Freundlich	37.5	Onyango et al, 2004

Aluminium sulphate modified zeolite LSX	3-9	1-15	Langmuir	4.12	This study

4.7 Kinetic Models

Largergren Pseudo-first order, Ho‘s pseudo-second order, Elovich and intra-particle diffusion models were used in studying the adsorption mechanism and rate of the adsorption of fluoride by AMZL

4.7.1 Largergren Pseudo first order Model

Fitting the kinetic data to the Largergren model (Figure 3A), it was found out that this kinetic model demonstrated an initial steep slope; subsequently flattened slightly and finally experienced a decreased rate. This might be due to the availability, accessibility and occupation of the adsorptive sites. It could also be explained from the effect of pH on the adsorption of fluoride unto AMZL. The adsorption results in a release of OH- giving rise to an increased pH within the pores of the adsorbent and eventual decrease in adsorption. The kinetic adsorptive parameters Q_e, and K_1 are all shown in Table 2. Moreover, the Largergren pseudo first order kinetic model predicted substantially lower value for the theoretical Q_e (calculated) value (0.333mg/g) than the experimental value of 0.843mg/g. In so far as the calculated and experimental Q_e values are at variance, it implies that the kinetic model does not fit the data well. The R^2 value (Figure 3A) of 0.8424 buttresses the point that the data does not fit so well.

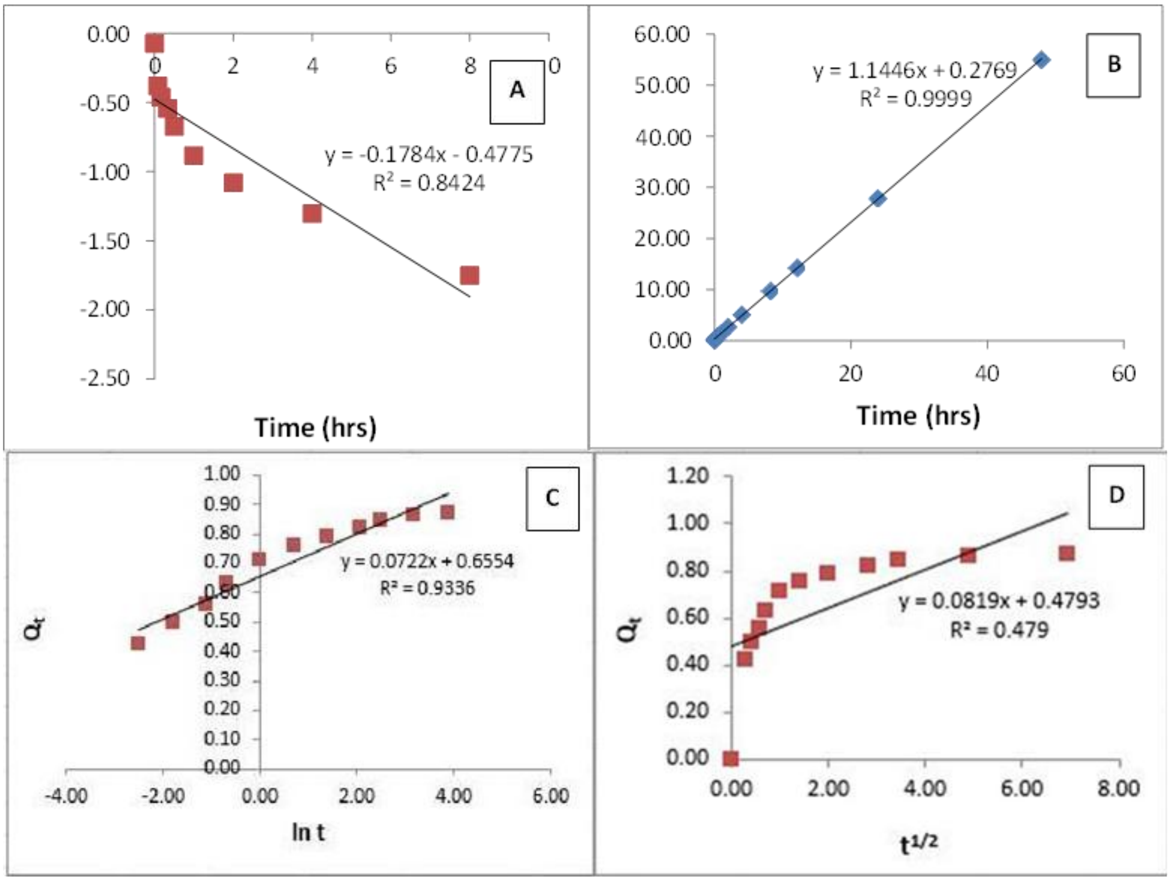

Figure 3: Graphical presentation of the Kinetic models applied to the fluoride removal unto the AMZL. A) Largergren Pseudo first order kinetic model B) Ho's Pseudo second order kinetic model C) Elovich kinetic model D) Intra-particle diffusivity analysis kinetic model.

4.7.2 Ho's Pseudo second order kinetic model

The value of the R^2 (0.9999) from the graph in Figure 3B indicates that the result fitted excellently well to this model. Moreover, the theoretical Q_e (calculated) value was in close agreement with the experimental value Q_e (Table 2). This model assumes that the fluoride adsorption process follows a second-order chemisorption unto AMZL. The half adsorption time, $t_{1/2}$ calculated (0.211) is also close to the experimental value (0.120).

4.7.3 Elovich kinetic model

The linear plots (figure 3C) are highly significant with regression coefficients 0.934, indicating that the data fits well with the Elovich model. The large value of β (13.85) shown in Table 4 is an indication of the high number of adsorption sites available and perhaps the extent of coverage of the adsorbent (larger surface area).

Table 3: Values of constants from the kinetic models used for fluoride adsorption by AMZL

Kinetic adsorptive models linear equations	**Kinetic adsorptive models constants**	**Isotherm parameter value**
Largergren pseudo 1^{st} order **log (Qe-Qt) = log Qe – K1t**	Qe (Exp)* Qe (Cal)** K1 R^2	0.843 0.333 0.178 0.848
Ho's pseudo 2^{nd} order model **t/Qt = 1/ho +1/Qet** **Ho = $k2Qe^2$** **T 1/2 =1/ $k2Qe^2$**	Qe (Exp)* Qe (Cal)** K2 Ho T 1/2 R^2	0.843 0.874 3.611 3.611 0.211 0.999
Elovich **Qt = 1/β ln(αβ) +1/ βln t**	A β R 2	632.23 13.85 0.934
Intra-particle diffusion **Qt = Kid $t^{1/2}$ + C**	K_{id} C R^2	0.082 0.4793 0.479

Qe(Exp)*– experimental adsorptive capacity, Qe(Cal)** – calculated adsorption capacity, R2 – coefficient of correlation, K1is the adsorption rate constant, α (mg/gmin) is considered as the initial rate of adsorption, β is indicative of the number of sites available for absorption, K2(gmg-1h-1) is the 2nd order adsorption constant, ho is the initial adsorption rate at t=0 , t1/2 is the time required for the adsorbent to take up half as much fluoride as its equilibrium value, Where Kid is the intraparticle pore diffusion rate constant (mg/gmin) and C represents the intercept that is proportional to the boundary layer thickness K1(h-1) is the absorption rate constant.

4.7.4 Intra particle diffusivity analysis kinetic model

Figure 3D shows the plot of Q_t verses. $t^{1/2}$ with a low R^2 value of 0.479 indicative of the fact that the data does not fit the model. However, the high values of the constants K_{id} and C in Table 2 which are 0.0819mg/g min and 0.479 indicate adsorption might occur in the pores of the adsorbent. High values of these constants are usually an indication of intra-particle diffusion.

From both isotherm and kinetic analysis, the adsorption mechanism of fluoride onto the AMZL was found to be complex, potraying more of physisorption than chemisorption. This may be due to the nature of the geological raw materials (clay and bauxite) used to synthesize zeolite Na-LSX, which impacted both homogeneity and heterogeneity onto the surface of the adsorbent. This trend has been observed by many researchers in their work during defluoridation of aqueous solutions using similar or other geomaterials as adsorbents. Zhang et al., (2011) reported similar behavioral trend after using calcium modified natural China zeolite for fluoride adsorption. Results indicated that their experimental data fitted well to both Langmuir and Freundlich isotherm models. Salifu et al., (2016) modified bauxite with alum for fluoride removal from synthetic water and their experimental Data also fitted well to both Langmuir and Freundlich isotherm models.

5 CONCLUSIONS

The results indicated that fluoride uptake from water by AMZL is dependent on the pH, contact time, initial fluoride concentration and dosage of the adsorbent. The highest fluoride removals were obtained at pH = 5. Initial fluoride concentration had strong influence on the fluoride adsorption process; higher adsorption capacities were recorded for higher initial fluoride concentration.

Occurrence of nitrate and chloride ions did not affect the fluoride removal efficiency. A significant decrease in Fluoride adsorption was noted in the presence of bicarbonate ions probably due to its competition for active sites on the adsorbent surface of the zeolite.

Considering only the coefficient of correlation (R^2) values, the fluoride adsorption data fitted best the Temkin isotherm model, however applying the error functions the following order of best fit was obtained: Langmuir > Temkin > Freundlich > Dubinin- Radushkevich.

The maximum fluoride adsorption capacity of the AMZL was found to be 4.122 mg/g.

The kinetic study results indicated that the adsorption process followed Ho‘s Pseudo-second order kinetic model and the adsorption mechanism was predominantly physisorption than chemisorption.

The AMZL is a viable adsorbent for fluoride removal from drinking water.

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