

# Adsorption equilibrium modeling and solution chemistry dependence of fluoride removal from water by trivalent-cation-exchanged zeolite F-9

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## Abstract

Fluoride in drinking water above permissible levels is responsible for human dental and skeletal fluorosis. In this study, therefore, the large internal surface area of zeolite was utilized to create active sites for fluoride sorption by exchanging  $\text{Na}^+$ -bound zeolite with  $\text{Al}^{3+}$  or  $\text{La}^{3+}$  ions. Fluoride removal from water using  $\text{Al}^{3+}$ - and  $\text{La}^{3+}$ -exchanged zeolite F-9 particles was subsequently investigated to evaluate the fluoride sorption characteristics of the sorbents. Equilibrium isotherms such as the two-site Langmuir (L), Freundlich (F), Langmuir–Freundlich (LF), Redlich–Peterson (RP), Tóth (T), and Dubinin–Radushkevitch (DR) were successfully used to model the experimental data. Modeling results showed that the isotherm parameters weakly depended on the solution temperature. From the DR isotherm parameters, it was considered that the uptake of fluoride by  $\text{Al}^{3+}$ -exchanged zeolite proceeded by an ion-exchange mechanism ( $E = 11.32 - 12.13$  kJ/mol), while fluoride– $\text{La}^{3+}$ -exchanged zeolite interaction proceeded by physical adsorption ( $E = 7.41 - 7.72$  kJ/mol). Factors from the solution chemistry that affected fluoride removal from water were the solution pH and bicarbonate content. The latter factor buffered the system pH at higher values and thus diminished the affinity of the active sites for fluoride. Natural groundwater samples from two Kenyan tube wells were tested and results are discussed in relation to solution chemistry. In overall,  $\text{Al}^{3+}$ -exchanged zeolite was found to be superior to  $\text{La}^{3+}$ -exchanged zeolite in fluoride uptake within the tested concentration range.

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**Keywords:** Fluoride; Equilibrium modeling; Solution chemistry;  $\text{Al}^{3+}$ - or  $\text{La}^{3+}$ -exchanged zeolite

## 1. Introduction

A lot of work has been done geared toward removing health-hazardous anions from drinking water and waste water by different techniques [1–5]. Each of the techniques has advantages and disadvantages that limit its use. As an example, trivalent metals such as aluminum, iron, and lanthanum and divalent metals such as calcium and magnesium have been widely used to precipitate fluoride and arsenic in water streams [3,4,6–8]. The precipitation method is simple and

economical. However, the method may not be a viable option for certain end-users since it is not versatile, it produces large amounts of sludge that may pose handling problems, and achieving allowable concentrations is in most cases difficult. Furthermore, most countries have in recent times adopted strict environmental policies for waste disposal. This implies that the cost for environmental management must be considered in water facility design. For part or all of the above reasons, an environmentally benign, robust, and low-cost a technique that is applicable to diverse end-uses is desired.

Proponents of adsorption technology argue that the technique is economical and efficient and produces high quality (waste) water [9,10]. The removal of fluoride by adsorption methods has been widely studied in recent years [11–14]. In-

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terest is growing in the use of high-valency metals to dope sorbents [12,15]. Very little, if any, work has been reported on fluoride–zeolite interaction in aqueous solution. Zeolite is a highly porous material. The skeletal framework of zeolite is made of alumina and silica tetrahedra and has a high concentration of negative charges induced by oxygen atoms. The alumina tetrahedron, too, is negatively charged, but the charges are balanced by the loosely bound cations.

In order to develop a sorption facility, preliminary tests must first be performed to approximate the design parameters. The latter are obtained from modeling results. Usually, equilibrium results are coupled into reaction and transport models. The equilibrium relation depends on the nature of the adsorptive–sorbent interaction. The aim of this study was, therefore, to investigate the fluoride sorption characteristics of zeolite F-9 containing surface-active sites created by exchanging Na<sup>+</sup>-bound zeolite with Al<sup>3+</sup> or La<sup>3+</sup> ions. Surface modification was done in accordance with a similar procedure presented in another work [16] but this time using Al<sup>3+</sup> or La<sup>3+</sup> ions because they show good affinity for fluoride. Guided partly by the shape of the equilibrium curves (Freundlich type) and partly by the expected sorbent surface properties (surface heterogeneity), results are modeled using simple isotherms such as two-site Langmuir (L), Freundlich (F), Redlich–Peterson (RP), Tóth (T), Langmuir–Freundlich (LF), and Dubinin–Radushkevitch (DR) in a single-ion solution in the temperature range 20–40 °C. The details of the above isotherms are available in the literature [17–22]. For completeness, however, a brief description is given in the subsequent section. The fluoride problem is persistent mainly in the Rift Valley of Africa, China, and India. Subsequently, fluoride removal from two groundwater samples from Kenya is tested in this work. Since the solution chemistry of groundwater varies from point to point, the effects of pH and electrolytes such as chloride, sulfate, bicarbonate, nitrate and phosphate on fluoride uptake are studied too.

## 2. Theory

In this work, six simple isotherm models applicable to heterogeneous surfaces are used. These are the two-site Langmuir (L), Freundlich (F), Redlich–Peterson (RP), Langmuir–Freundlich (LF), Tóth (T), and Dubinin–Radushkevitch (DR) isotherms. The isotherm models and their linear forms, where applicable, are summarized in Table 1.

The L isotherm (Eq. (1)) is a modification of the classical Langmuir isotherm model and is used to describe sorption on two sites with different binding energies. In our case, if it is assumed that protonated and neutral surface sites created during surface modification of zeolite have different binding affinities for fluoride, then the L isotherm may be applicable. However, the implications of energetic heterogeneity of surface sites may not be limited to their number but may also apply to their spatial distribution. At the moment, we do not have direct evidence of site distribution, but assum-

Table 1  
Summary of equilibrium models applicable to heterogeneous surfaces

Isotherm	Equation	Eq. no.
Two-site Langmuir	$q_e = \frac{Q_1 b_1 C_e}{1 + b_1 C_e} + \frac{Q_2 b_2 C_e}{1 + b_2 C_e}$	(1)
Freundlich	$q_e = K_F C_e^{1/n}$	(2)
	$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$	(3)
Redlich–Peterson	$q_e = \frac{K_R C_e}{1 + a_R C_e^\beta}$	(4)
	$\ln \left[ \frac{K_R C_e}{q_e} - 1 \right] = \ln a_R + \beta \ln C_e$	(5)
Langmuir–Freundlich	$q_e = \frac{K_{LF} C_e^{1/n}}{1 + a_{LF} C_e^{1/n}}$	(6)
	$\ln \left[ \frac{1}{q_e} - \frac{a_{LF}}{K_{LF}} \right] = -\ln K_{LF} - \frac{1}{n} \ln C_e$	(7)
Tóth	$q_e = \frac{q_m C_e}{[a_t + C_e^{1/t}]^{1/t}}$	(8)
Dubinin–Radushkevitch	$\frac{q_e}{q_m} = \exp(-K \varepsilon^2)$	(9)
	$\ln q_e = \ln q_m - K \varepsilon^2$	(10)

Note.  $K_F$ ,  $K_{LF}$ ,  $K_R$ : Freundlich, Langmuir–Freundlich, and Redlich–Peterson constants (l/g).  $b_1$ ,  $b_2$ ,  $a_{LF}$ ,  $a_R$ : affinity coefficients (l/mg F).  $1/n$ ,  $\beta$ , and  $t$ : heterogeneity coefficient [—].  $q_e$ ,  $Q_1$ , and  $Q_2$ : uptake at equilibrium (mg F/g). 1,2: high- and low-energy sites.  $\varepsilon$ : Polanyi potential (kJ/mol).  $K$ : constant (mol<sup>2</sup>/kJ<sup>2</sup>).  $C_e$ : equilibrium concentration (mg F/l).  $a_t$ : adsorptive potential constant ((mg F/l)<sup>t</sup>).

ing that the heat of adsorption varies from site to site within the sorbent, the F isotherm (Eq. (2)) and its linear form (Eq. (3)) may be applicable. In order to improve the fitting of the classical Langmuir and Freundlich isotherms, three-parameters sorption isotherms that incorporate the features of these isotherms are often used. Thus, the RP (Eq. (4) and its linear form Eq. (5)) and LF (Eq. (6) and its linear form Eq. (7)) isotherms were tested in this work. Equations (5) and (7) contain three parameters each and therefore plotting them is not possible. However, by use of a minimization procedure similar to that used by Allen et al. [22], in which the linear regression coefficient,  $R^2$ , is maximized by adjusting either  $K_R$  in Eq. (5) or  $a_{LF}/K_{LF}$  in Eq. (7), linear plots are obtainable.

The T isotherm model [21], which simulates adsorbate sorption on energetically heterogeneous surfaces and assumes that most sites have sorption energy lower than the maximum adsorption energy, was also tested. The Tóth correlation in a form applicable to liquid-phase adsorption as presented by Allen et al. [22] is given in Eq. (8). Finally, to distinguish the mechanisms involved in fluoride uptake by metal-ion-exchanged zeolite, we applied the DR isotherm model, which is based on the Polanyi theory. In its widely used form, it relates the fractional coverage to the Polanyi potential ( $\varepsilon$ ) as expressed in Eq. (9) and its linear form Eq. (10).

### 3. Materials and methods

#### 3.1. Surface modification and characterization

Aluminum- and lanthanum-exchanged zeolites were prepared for batch studies by a procedure similar to one used previously [16]. It involved adding, separately, 50 g zeolite to 0.075 M reagent-grade hydrated aluminum sulfate or lanthanum nitrate. The zeolite F-9 shots used in this study (particle size 0.500–1.180 mm Ø) were supplied by Wako Chemicals, Japan. The mixture was stirred for 2 days and then washed several times using demineralized water to lower the electrical conductivity. Finally, the modified zeolite was air-dried at room temperature for 2 days and then milled to a grain fraction of size 0.150–0.300 mm.

The numbers of  $\text{Al}^{3+}$  and  $\text{La}^{3+}$  ions exchanged were determined by measuring the residual concentrations of the metals in solution using ICP-AES (Perkin–Elmer, Optima 3300DV), assuming negligible dissolution of zeolite, and carrying an appropriate material balance. The porosity and density of the zeolite and its Al- and La-forms were determined with a mercury porosimeter (Shimadzu, autopore III 9400). The results are summarized in Table 1.

#### 3.2. Point of zero charge ( $\text{pH}_{\text{PZC}}$ )

In this experiment, unmodified zeolite, Al-modified zeolite, and La-modified zeolite samples were dispersed into NaCl (10 mM) aqueous solution by sonic disintegration. The pH of the dispersed samples were adjusted to 5 and 3 by the addition of HCl (0.1 M) and to 7, 9, and 11 by the addition of NaOH (0.1 M). The zeta potential of each dispersed sample was measured by an electrophoretic light scattering spectrophotometer (ELS-7300K, Otsuka Electronics Co., Japan) at 25 °C. The pHs of the sorbents in  $5 \times 10^{-3}$  M NaCl (initial pH 5.7) were measured too. For this, zeolite suspensions with varying solid content (0.01–10%) were filled in glass bottles, ensuring that air volume above the suspension was minimized. The bottles were intermittently agitated at constant temperature for 24 h. Finally, the suspension pHs at equilibrium were measured and plotted against the solid content. It was considered that the final pH of the suspension with the highest solid content corresponded with the pH of the sorbent.

#### 3.3. Adsorption isotherms

Data for sorption isotherm were generated by contacting a fixed amount (0.1 g) of trivalent-metal-ions-exchanged zeolite with fluoride-containing aqueous solutions. Samples of 50 ml of fluoride ion solutions at concentrations ranging from 10 to 80 mg/l were pipetted into 100-ml plastic bottles. The bottles were placed in a thermostatic shaker and shaken for 1 day at temperatures ranging from 20 to 40 °C. The shaking speed was set at 150 spm. At the end of the experiment, samples were withdrawn from the test bottles and

filtered through a 0.2- $\mu\text{m}$  syringe filter and residual fluoride concentration was measured by a fluoride-ion-selective electrode (Horiba, Japan). The equilibrium sorption capacity was determined from

$$q_e = \frac{C_0 - C_e}{\rho}, \quad (11)$$

where  $C_0$  (mg F/l) is the initial concentration and  $\rho$  (g/l) is the ratio of sorbent mass to sorbent-free solution volume.

#### 3.4. Effect of solution chemistry

The effects of solution pH and ions such as chloride, sulfate, bicarbonate, nitrate, and phosphate were studied in a batch mode. Experiments were carried out by taking 50 ml of fluoride-ions-spiked aqueous solution of initial concentration 20 mg F/l and a surface-modified zeolite dose of 2 g/l. In the study of the effect of pH, the values were varied from 4 to 9 while the effects of ions were studied without pH adjustments.

#### 3.5. Test with Kenyan groundwater

The fluoride sorption capabilities of surface-modified zeolites were further tested using two samples of groundwater obtained from the Njoro area of Nakuru district, Kenya. The initial water sample concentrations were 3.3 (Egerton) and 4 mg/l (Kihingo). Table 2 summarizes the content of a few chosen ions in the two groundwater samples. The concentrations of the cations were determined by ICP-AES (Perkin–Elmer, Optima 3300DV), while the anions content was determined by ion chromatography with a column (Tosoh, TSKgel IC-Anion-PW) using an electroconductivity detector (Shimadzu, CDD-10AVP). In this study, the sorbent dose was varied from 1 to 4 g/l. To explore the effects that the groundwater had on the performance of the zeolites, another set of experiments was carried out using distilled-water-spiked fluoride solution at concentration and pH similar to those of the Kihingo water sample.

## 4. Results and discussion

#### 4.1. Surface modification and characterization

The three-dimensional skeletal structure of zeolite has small pores where the exchangeable cations are located and where the ion-exchange reaction takes place [23]. Zeolites have been widely tested in heavy-metal removal from water. In recent work by Madjan et al. [24], zeolite A was used to remove lanthanides from aqueous solution. The authors explained that the mechanism involved ion exchange of the lanthanides for sodium and hydrolysis. Utilizing the preceding facts as a means of producing a novel sorbent for fluoride uptake, we carried out the ion-exchange process at about pH 3.80 for  $\text{Al}^{3+}$  and pH 5.30 for  $\text{La}^{3+}$ . The former value,

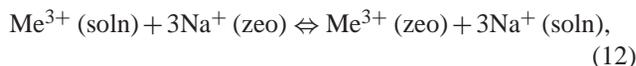
Table 2  
Selected sorbent characteristics and physicochemical composition of groundwater samples

Sorbents	Zeolite F-9	Al <sup>3+</sup> -exchanged zeolite F-9	La <sup>3+</sup> -exchanged zeolite F-9
Bulk density (g/cm <sup>3</sup> )	0.744	0.798	0.945
Skeletal density (g/cm <sup>3</sup> )	0.992	1.181	1.529
Total intrusion volume (cm <sup>3</sup> /g)	0.337	0.407	0.404
Porosity (%)	25	32	38
pH <sub>pzc</sub> (–)	–	8.15	4 and 5.25
pH of sorbent (–)	8.1–8.2	5.2–5.3	7.2
Al <sup>3+</sup> or La <sup>3+</sup> exchanged (mmol/g)	–	1.71	0.97

Groundwater samples	Kihingo	Egerton
F <sup>–</sup> (mg/l)	4.0	3.3
Cl <sup>–</sup> (mg/l)	60.2	9.5
NO <sub>3</sub> <sup>–</sup> (mg/l)	90.9	Not detected
HCO <sub>3</sub> <sup>–</sup> (mg/l)	202.4	285.7
Na <sup>+</sup> (mg/l)	58.5	107.0
pH (–)	7.4	6.9
Conductivity (μS/cm)	770	413

however, may lead to slight dissolution of zeolite particles. The ion-exchange process is controlled by species diffusion within the pore network. Therefore, after several preliminary tests, it was found that 2 days were optimum for the exchange reaction. Using a scheme similar to that presented by Biškup and Subotić [25], the exchange of the trivalent ions Al<sup>3+</sup> and La<sup>3+</sup> for Na<sup>+</sup> ions fixed in the zeolite F-9 (pore size 9 Å, silica/alumina ratio 1.23) can theoretically be written as



where Me<sup>3+</sup> refers to Al<sup>3+</sup> or La<sup>3+</sup>, and (soln) and (zeo) denote the solution and zeolite phases. It was found that a solution initially containing 0.075 M aluminum sulfate or lanthanum nitrate exchanged approximately 1.71 mmol Al<sup>3+</sup>/g-sorbent and 0.97 mmol La<sup>3+</sup>/g-sorbent. However, the processes of hydrolysis and surface precipitation could also have been part and parcel of the uptake mechanism. The higher exchange value for Al<sup>3+</sup> could be due to the fact that a 0.075 M aluminum sulfate solution contains twice as many Al<sup>3+</sup> ions (ionic radius 0.535 Å) as there is La<sup>3+</sup>. Also, because La<sup>3+</sup> is of larger size (ionic radius 1.17 Å), this might have caused steric overcrowding near the pore mouth, leading to a lower exchange with Na<sup>+</sup> ions. The consequence of the ion exchange process was an increase in porosity of the zeolite particles from 25 to 32% (when Al<sup>3+</sup> was loaded into zeolite) and 38% (when La<sup>3+</sup> was loaded into zeolite) as determined in the porosimetric studies. If ion exchange is considered in isolation (though hydrolysis and surface precipitation cannot be assumed), it can be seen in Eq. (12) that for every one mole of trivalent cation, three moles of sodium-bound zeolite are exchanged. This phenomenon opens up the pores, leading to an increase in porosity of the trivalent-cations-exchanged zeolite.

The pH of the point of zero charge, pH<sub>pzc</sub>, of zeolite and its modified forms suspensions in 10 mM NaCl as a background electrolyte was determined from zeta potential

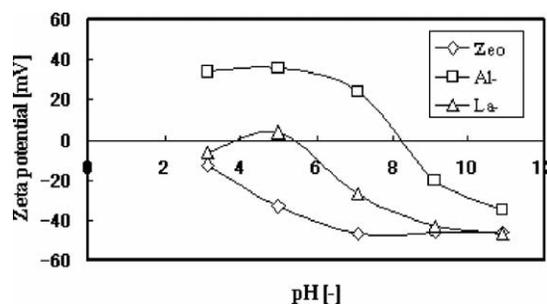


Fig. 1. Determination of pH of point of zero charge of zeolite F-9 and its modified forms. Al-, La-, Zeo, imply Al<sup>3+</sup>-exchanged zeolite, La<sup>3+</sup>-exchanged zeolite, and zeolite, respectively.

measurements. Zeolite F-9 contains sodium oxide, silicon oxide, and aluminum oxide and therefore it is a mixed oxide sorbent. It is shown in Fig. 1 that the material is negatively charged over the whole pH range tested and therefore has no pH<sub>pzc</sub>. By contrast, when Na<sup>+</sup> ions were exchanged for Al<sup>3+</sup> ions, the zeolite particles were charge-reversed and the pH<sub>pzc</sub> was found to be 8.15. At this pH, the positively charged aluminol sites (Zeo-AlOH<sub>2</sub><sup>+</sup>) and those due to un-exchanged sodium, if any, are basically equal to the negatively charged sites mainly from silica and hydroxylized aluminol sites. On the other hand, exchanging Na<sup>+</sup> for La<sup>3+</sup> ions led to La-form zeolite F-9 having a pH<sub>pzc</sub> of 4 and 5.25. The low values could be a result of surface charge properties of lanthanum and extent of ion exchange. A mass titration method was used to determine the pH of the sorbents in 5 × 10<sup>–3</sup> M NaCl solution as shown in Fig. 2. In the presence of zeolite and La-exchanged zeolite, the suspension pH increased from 5.7 to 8.1–8.2 and 7.2, respectively, as the solid content was increased, indicating that the sorbents were negatively charged. The increase in pH is attributed to sorption of H<sup>+</sup> ions on the negative surfaces [26]. Al-exchanged zeolite, however, exhibited a positive surface charge, as seen from a decrease in the suspension pH from 5.7 to 5.2–5.3 as solid content was increased from 0 to 10%. This observation

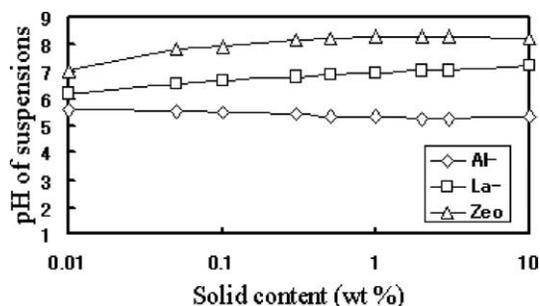


Fig. 2. Determination of sorbent pH. The initial pH at 0% solid content was in all cases 5.7.

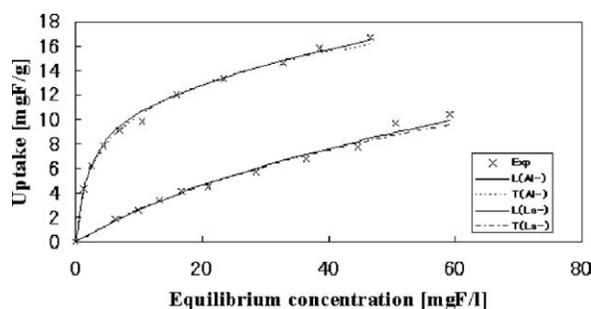


Fig. 3. The two-site Langmuir and Tóth equilibrium modeling results at 30 °C.

gave evidence of charge reversal in zeolite. Other properties of the sorbents are summarized in Table 2.

#### 4.2. Equilibrium modeling

The design and efficient operation of adsorption processes require equilibrium adsorption data to be coupled in kinetic and mass-transfer models [22]. Equilibrium models relate the solid-phase sorption to bulk-phase concentration as a function of solution and sorbent properties such as sorbate concentration, pH, temperature, existence of other ions, and site heterogeneity. Several researchers [27,28] have shown that fluoride sorption takes place through ion exchange and formation of surface complexes with active sites, suggesting a chemisorption mechanism. At near-neutral pHs, the trivalent metals used for surface modification of zeolite form numerous complexes [29], both protonated and nonprotonated. Thus, basically the active sites are heterogeneous. We have, therefore, correlated the experimental and model data using general purpose isotherms such as L, F, L–F, R–P, and T.

When a sorbate occupies sites with varying affinity, the higher affinity sites are first occupied. Fig. 3 illustrates the fitting of the two-site Langmuir model to the experimental data at 30 °C. The model satisfactorily correlated the fluoride sorption data with normalized standard deviations less than 10% in all cases. Table 3 summarizes the isotherm parameters. It was found from the modeling results that the capacity of fluoride ions for the higher energy sites were only 27–29% ( $Q_1/Q^0$ ) and 7–11% of the total sorption capacity for Al<sup>3+</sup>-exchanged zeolite and La<sup>3+</sup>-exchanged zeolite, respectively.

Table 3

Two-site Langmuir and Tóth isotherm parameters for F<sup>-</sup> uptake by Al<sup>3+</sup>- and La<sup>3+</sup>-exchanged zeolites

	Langmuir parameters					
	$Q_1$	$Q_2$	$Q^0$	$b_1$	$b_2$	$\Delta q\%$
Al <sup>3+</sup> -exchanged zeolite						
20 °C	9.21	25.20	34.41	$4.33 \times 10^{-1}$	$8.53 \times 10^{-3}$	5.0
30 °C	10.88	26.39	37.27	$4.55 \times 10^{-1}$	$6.47 \times 10^{-3}$	3.5
40 °C	10.95	28.57	39.52	$3.90 \times 10^{-1}$	$5.81 \times 10^{-3}$	7.0
La <sup>3+</sup> -exchanged zeolite						
20 °C	4.80	40.35	45.15	$4.42 \times 10^{-2}$	$2.64 \times 10^{-3}$	7.3
30 °C	5.20	46.30	51.50	$3.94 \times 10^{-2}$	$2.64 \times 10^{-3}$	5.4
40 °C	3.80	50.48	54.28	$3.86 \times 10^{-2}$	$2.68 \times 10^{-3}$	6.2
Tóth parameters						
	$q_m$	$t$	$a_t$	$\Delta q\%$		
Al <sup>3+</sup> -exchanged zeolite						
20 °C	40.0	0.31	1.09	4.6		
30 °C	40.7	0.30	1.01	3.0		
40 °C	43.0	0.29	1.02	3.2		
La <sup>3+</sup> -exchanged zeolite						
20 °C	42.0	0.48	8.24	6.2		
30 °C	57.2	0.52	12.77	5.4		
40 °C	58.5	0.49	11.25	5.3		

Similarly, in an earlier study (submitted for publication), we found that the kinetics of fluoride sorption onto Al<sup>3+</sup>-exchanged zeolite followed a two-stage mechanism with the first stage lasting a few minutes and accounting for a lesser uptake. On the other hand, the higher energy sites had a significantly higher affinity for fluoride ( $b_1/b_2 \approx 51$ –70 for Al<sup>3+</sup>- and 15–17 for La<sup>3+</sup>-exchanged zeolite). The Langmuir fluoride sorption capacities  $Q^0$  ( $Q^0 = Q_1 + Q_2$ ) for La<sup>3+</sup>-exchanged zeolite were higher than those of Al<sup>3+</sup>-exchanged zeolite in the temperature range studied. However, within the concentration range considered in this work, Al<sup>3+</sup>-exchanged zeolite had twice as much fluoride carrying capacity as La<sup>3+</sup>-exchanged zeolite. When compared with fluoride sorption capacities of various sorbents reported in the literature [7,10,11,13–15,27,28], the materials used in the present study are highly competitive.

Experimental data of fluoride sorption onto Al<sup>3+</sup>- and La<sup>3+</sup>-exchanged zeolites at 30 °C were further fitted to the Freundlich model (Eq. (2)) by a linear regression technique as shown in Fig. 4 to determine the isotherm parameters. It can be seen that the data sets fit this isotherm reasonably well. The Freundlich constant,  $K_F$ , for the Al<sup>3+</sup>- and La<sup>3+</sup>-exchanged zeolites was 4.39 and 0.49, respectively, indicating that surface modification with aluminum would give a higher capacity. However, the adsorption intensity constant or heterogeneity constant,  $1/n$ , was higher for La<sup>3+</sup>-exchanged zeolite than for Al<sup>3+</sup>-exchanged zeolite. Higher values imply lesser heterogeneity. Model parameters are further summarized in Tables 4 and 5 for the temperatures 20, 30, and 40 °C. It is observed that temperature did not significantly affect the fluoride–sorbent interaction. In a study of fluoride uptake by acid treated spent bleaching earth in

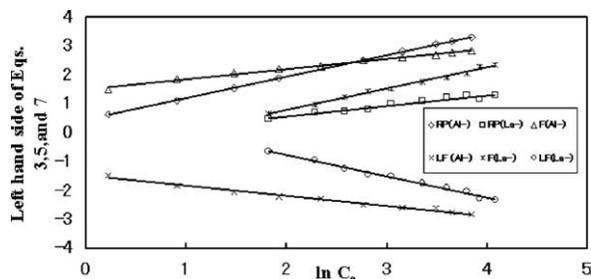


Fig. 4. Linear regression analysis of fluoride uptake by Al<sup>3+</sup>- and La<sup>3+</sup>-exchanged zeolite for F, RP, and LF isotherms.

Table 4  
The F, LF, and RP isotherms parameters for Al<sup>3+</sup>-exchanged zeolite

Isotherm	Parameters				
	$K_{F,LF,RP}$	$1/n$ or $\beta$	$a_{L,LF,RP}$	$R^2$	$\Delta q\%$
Freundlich					
20 °C	4.03	0.36	–	0.987	4.6
30 °C	4.42	0.35	–	0.985	4.1
40 °C	4.16	0.36	–	0.990	4.1
Langmuir–Freundlich					
20 °C	4.03	0.36	$4.03 \times 10^{-4}$	0.987	4.6
30 °C	4.42	0.35	$4.42 \times 10^{-4}$	0.985	4.2
40 °C	4.16	0.36	$4.16 \times 10^{-4}$	0.990	4.1
Redlich–Peterson					
20 °C	10.0	0.72	1.79	0.997	4.0
30 °C	10.0	0.75	1.56	0.999	2.5
40 °C	10.0	0.74	1.67	0.996	4.5
Dubinin–Radushkevitch					
	$q_m$	$E$ (kJ/mol)	$R^2$	$\Delta q\%$	
20 °C	36.18	11.32(ion exchange)	0.989	4.7	
30 °C	37.54	11.78(ion exchange)	0.995	2.8	
40 °C	37.00	12.13(ion exchange)	0.990	4.5	

a similar concentration range, Mahramanlioglu et al. [11] found  $K_F$  and  $1/n$  values of 0.943 and 0.461. In their work, the sorbent had a lower capacity for fluoride than in our results.

The fitting validity of three-parameter models, Redlich–Peterson and Langmuir–Freundlich (Sips isotherm), was tested in linearized forms according to Eqs. (5) and (7), respectively, and plotted as shown in Fig. 4. For the Redlich–Peterson model, the parameters  $a_R$  and  $\beta$  (equivalent to  $1-1/n$  in the LF isotherm) were determined from the intercepts (extrapolated to  $\ln C_e = 0$ ) and slopes of the linear curves shown in the figure. At 30 °C, for example, the  $K_R$ ,  $a_R$ , and  $\beta$  values for Al<sup>3+</sup>-exchanged zeolite, were 10, 1.56, and 0.75, respectively. These parameters deviated only slightly at the other temperatures tested, suggesting that increasing solution temperature did not significantly change the sorption capacity of the sorbent and neither the energetic heterogeneity of the active sites. The parameters obtained from linear regression analysis were further used to compute the model uptake data as shown in Fig. 5.

Tóth developed an isotherm, now known as the Tóth isotherm, to improve the fitting of the Langmuir isotherm

Table 5  
The F, LF, and RP isotherms parameters for La<sup>3+</sup>-exchanged zeolite

Isotherm	Parameters				
	$K_{F,LF,RP}$	$1/n$ or $\beta$	$a_{L,LF,RP}$	$R^2$	$\Delta q\%$
Freundlich					
20 °C	0.55	0.68	–	0.993	4.2
30 °C	0.49	0.74	–	0.993	4.3
40 °C	0.45	0.74	–	0.996	3.3
Langmuir–Freundlich					
20 °C	0.55	0.68	$5.48 \times 10^{-6}$	0.993	4.2
30 °C	0.49	0.74	$4.16 \times 10^{-5}$	0.993	4.3
40 °C	0.45	0.74	$4.55 \times 10^{-5}$	0.996	3.3
Redlich–Peterson					
20 °C	100	0.32	181.6	0.968	4.2
30 °C	100	0.26	203.0	0.947	4.3
40 °C	100	0.26	219.0	0.967	3.3
Dubinin–Radushkevitch					
	$q_m$	$E$ (kJ/mol)	$R^2$	$\Delta q\%$	
20 °C	45.02	7.72 (physical adsorption)	0.985	6.1	
30 °C	59.12	7.67 (physical adsorption)	0.989	5.4	
40 °C	54.87	7.41 (physical adsorption)	0.989	5.4	

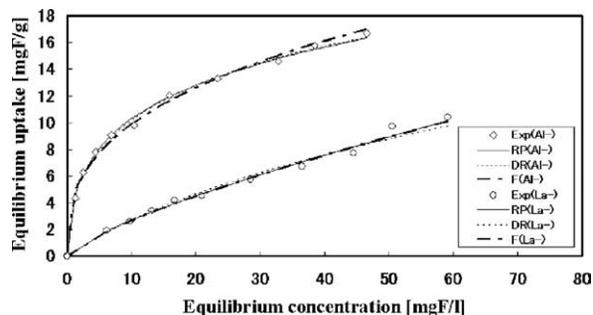


Fig. 5. The F, RP, and DR equilibrium modeling results at 30 °C. The LF modeling results are not shown since they overlapped those of F.

to experimental data based on the premise that there exists site heterogeneity on the sorbent. The Tóth isotherm was applied in the nonlinear form as given in Eq. (8) and plotted in Fig. 3, from which the isotherm parameters were determined and summarized in Table 3. Error analysis shows that this isotherm satisfactorily modeled the experimental data. It can be seen that the predicted sorption capacities were reasonably in the same magnitude (40–43 mg F/g for Al<sup>3+</sup>-exchanged zeolite and 42.0–58.5 mg F/g for La<sup>3+</sup>-exchanged zeolite) as those predicted by the two-site Langmuir and Dubinin–Radushkevitch isotherms. Furthermore, the model, too, confirmed that Al<sup>3+</sup>-exchanged zeolite (heterogeneity constant,  $t = 0.29-0.31$ ) was more heterogeneous than La<sup>3+</sup>-exchanged zeolite (heterogeneity constant,  $t = 0.48-0.52$ ). Parameters characterizing the adsorptive potential, on the other hand, were close to unity for Al<sup>3+</sup>-exchanged zeolite but ranged from 8.24 to 12.77 for La<sup>3+</sup>-exchanged zeolite.

To distinguish the mechanisms involved in fluoride uptake by metal-ion-exchanged zeolite, we applied the Dubinin–Radushkevitch (DR) isotherm model, which is

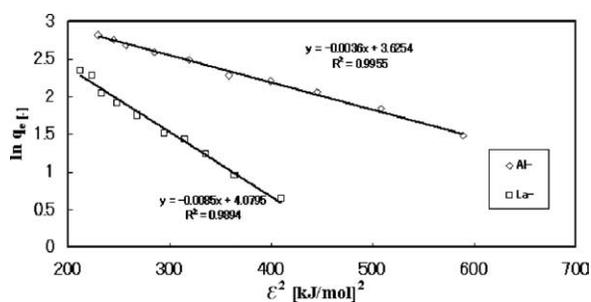


Fig. 6. Fitting experimental data according to Eq. (10) to determine the DR model parameters for fluoride uptake by  $\text{Al}^{3+}$ - and  $\text{La}^{3+}$ -exchanged zeolites at 30 °C.

based on the Polanyi theory. In its widely used form, it relates the fractional coverage to the Polanyi potential ( $\varepsilon$ ) as given in Eq. (9) and its linear form Eq. (10) [20]. For liquid-phase adsorption,  $\varepsilon = RT \ln[1 + (1/C_e)]$ , where  $R$  is the universal gas constant and  $T$  the absolute temperature.

Fig. 6 shows the plot of  $\ln q_e$  vs  $\varepsilon^2$ , from Eq. (10), for the uptake of fluoride by  $\text{Al}^{3+}$ - and  $\text{La}^{3+}$ -exchanged zeolite at 30 °C. Linear curves were obtained whose negative slopes ( $K$ ) and intercepts ( $\ln q_m$ ) are, respectively, 0.0036  $\text{mol}^2/\text{kJ}^2$  and 3.625 for  $\text{Al}^{3+}$ -exchanged zeolite and 0.0085  $\text{mol}^2/\text{kJ}^2$  and 4.079 for  $\text{La}^{3+}$ -exchanged zeolite. From the preceding values, the maximum fluoride sorption capacities,  $q_m$ , for  $\text{Al}^{3+}$ -exchanged zeolite and  $\text{La}^{3+}$ -exchanged zeolite were 37.54 and 59.11 mg F/g, respectively. To evaluate the nature of interaction between fluoride and the binding sites, mean free energy of sorption ( $E = (2K)^{-0.5}$ ) per mole of the sorbate, which is the energy required to transfer one mole of a sorbate to the surface from infinity in solution, was determined. If the magnitude of  $E$  is between 8 and 16 kJ/mol, the adsorption process proceeds by ion exchange, while for values of  $E < 8$  kJ/mol, the adsorption process is of a physical nature [11]. The free energies of sorption of fluoride onto  $\text{Al}^{3+}$ -exchanged zeolite and  $\text{La}^{3+}$ -exchanged zeolite at 30 °C were 11.78 and 7.67 kJ/mol, respectively, suggesting that the former proceeded by ion exchange while the latter proceeded by physical adsorption. For all other solution temperatures, the DR isotherm parameters are summarized in Tables 4 and 5. Basically, these parameters show very weak dependence on solution temperature.

The error function used in this work to quantify the noise produced between the experimental and model data was the normalized standard deviation,  $\Delta q$  (%). All errors were less than 10% for the two sorption systems in the temperature range studied. It was considered that all the models satisfactorily described the data set suggesting sorption on multiplesites. However, experimental data for the fluoride– $\text{La}^{3+}$ -exchanged zeolite interaction were more consistent with the Freundlich isotherm model than with other models.

### 4.3. Effect of solution chemistry

Drinking water contains electrolytes of varying composition and quantity. Factors from solution chemistry that in-

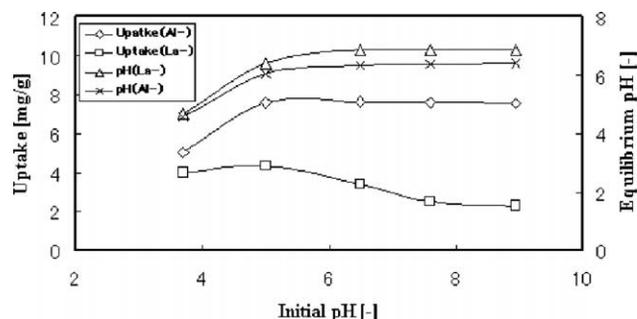


Fig. 7. Effect of initial solution pH on fluoride uptake and equilibrium system pH.

fluence the adsorption process are the solution pH and ionic strength [30]. A study was therefore undertaken to ascertain to what extent these factors affected the sorption of fluoride. Fig. 7 shows the effects of initial solution pH (4–9) on the uptake of fluoride and system (solution–solid) pH at equilibrium. The system pH at equilibrium shows similar trends for both  $\text{Al}^{3+}$ -exchanged zeolite and  $\text{La}^{3+}$ -exchanged zeolite: they rise and reach a plateau at  $\text{pH } 6.36 \pm 0.03$  for  $\text{Al}^{3+}$ -exchanged zeolite and  $\text{pH } 6.86$  for  $\text{La}^{3+}$ -exchanged zeolite. When the effect of fluoride sorption is taken into consideration, the overall changes in solution pH can be explained by the following reactions:



For fluoride sorption on aluminol surface sites (Me = Al),



Interaction of La-exchanged zeolite with fluoride is represented by (Me = La)



where  $\text{Zeo-MeOH}_2^+$ ,  $\text{Zeo-MeOH}$ , and  $\text{Zeo-MeO}^-$  are the protonated, neutral and hydroxylized surface sites, respectively.  $\text{Zeo-Me}$  denotes the zeolite-metal surface and Me represents either Al or La. On charge-reversed zeolite particles, the reaction expressed by Eq. (13) is favored in the forward direction, resulting in consumption of hydroxyl ions and lowering of systems pH, while on negatively charged zeolite particles, the reaction expressed by Eq. (14) is favored. As already determined in Section 4.2, the sorption of fluoride on aluminol sites is mainly by ion exchange (and inner-sphere complexation), expressed by Eqs. (15) and (16). Thus, the observed values of equilibrium pH for the fluoride–Al-exchanged-zeolite system resulted from a complex interplay amongst the various factors including the initial solution pH, reactions expressed by Eqs. (13), (15), and (16), and dissociation of Al from the zeolite structure. In the case of La-exchanged zeolite, fluoride sorption is of a physical nature, leading to the formation of an outer-sphere

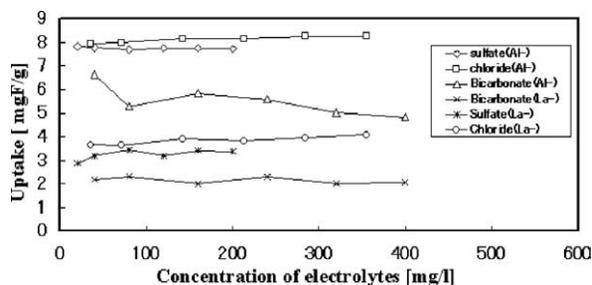


Fig. 8. Effect of solution chemistry on fluoride uptake.

complex, as expressed by Eq. (17). The adsorption of fluoride, therefore, has no effect on the suspension pH of the latter; it is shown in Fig. 2 that at a solid content of 0.2% (2 g/l), the suspension pH was about 6.7, which is nearly the same as the pH 6.86 obtained in the presence of fluoride. It can be concluded that the observed values of equilibrium pH for the fluoride–La-exchanged-zeolite system were dictated only by the initial solution pH, the dissociation of La from the zeolite, and the uptake of hydrogen ions by La-exchanged zeolite expressed by Eq. (14). Meanwhile, the fluoride uptake increased with an increase in initial solution pH, with a plateau forming above initial pH 5, for fluoride–Al<sup>3+</sup>-exchanged-zeolite sorption systems; this could be due to the fact that the system pH was buffered at a nearly fixed point (pH 6.36 ± 0.03). For the fluoride–La<sup>3+</sup>-exchanged-zeolite sorption systems, below and above the initial solution pH 5, fluoride uptake decreased under the present experimental conditions. The pH 5 was found to be the pH of maximum zeta potential (Fig. 1) and hence the highest electrostatic attraction between fluoride and the active sites was expected. On one hand, the low uptake at low pH values, in both systems, could be attributed to the fact that part of the surface-hydroxyl-group-based metals may have been released into the solution as soluble Al<sup>3+</sup> or La<sup>3+</sup> and thus lowered the number of active sites necessary to bind fluoride. Also, at low pH values, fluoride is weakly dissociated. Similar trends have been observed in several fluoride–sorbent sorption systems [1,7,27]. On the other hand, the decrease in equilibrium fluoride uptake by La<sup>3+</sup>-exchanged zeolite with an increase in initial solution pH (from initial solution >pH 5) is attributed to the increase in repulsive forces between fluoride and the negatively charged surfaces and hydroxyl ions.

The effect of ionic strength on fluoride–sorbent interaction was evaluated by varying the concentration of certain electrolytes. Our probe ion being fluoride, at the pH values considered (pH > pK<sub>a</sub> = 3.2), it exists as a negative monovalent ion. It is highly probable that only the negatively charged electrolytes in solution may have adverse effects on its uptake characteristics. Therefore, the electrolytes considered included chloride, nitrate, sulfate, bicarbonate, and phosphates, commonly found in groundwater. The dependence of chloride, sulfate, and bicarbonate concentrations on fluoride uptake are shown in Fig. 8. The investigation was limited to allowable ranges of the concentration of elec-

trolytes in drinking water. The presence of chloride and nitrate (not shown) in solution generally enhanced fluoride uptake by Al<sup>3+</sup>-exchanged and La<sup>3+</sup>-exchanged zeolites. Sulfate ions had no effect on fluoride uptake by Al<sup>3+</sup>-exchanged zeolite, whereas a weak increase in uptake was observed with La<sup>3+</sup>-exchanged zeolite. It is expected that the presence of anions in solution would enhance coulombic repulsion forces between the anions and fluoride or would compete with fluoride for the active sites. Though measurement of the extent of uptake of the anions was not part of this study, we can only postulate that in case the anions too were adsorbed on zeolite particles, their preferred surface sites or mechanisms were different from those of fluoride. Genç-Fuhrman et al. [31] note that the weak dependence of the uptake on ionic strength is due to the formation of inner sphere complexes by the target sorbate. It is well documented that fluoride uptake by aluminol sites is due to ion exchange and inner-sphere surface complexation, on one hand [32], while on the other hand, chloride and nitrate ions form outer-sphere but sulfate forms partial inner-sphere complexes with sorbents [33]. Since it has been deduced from the DR model that fluoride–La<sup>3+</sup>-exchanged-zeolite interaction is physical in nature, probably dominated by electrostatic forces, it is not surprising to find an increase in fluoride uptake with increased electrolyte concentration. This is due to shielding effect [30]. By contrast, large effects were observed when bicarbonate was present in solution at increased concentration when Al<sup>3+</sup>-exchanged zeolite was used; however, the uptake of fluoride was fairly constant when La<sup>3+</sup>-exchanged zeolite was used. Bicarbonate is a pH buffering agent. Its presence in solution raised and buffered system pH above neutral values; in our case system was pH 7.3–8.2. This led to reduced uptake of fluoride by aluminol sites since the surface charge density (deduced from Fig. 1) is expected to be lower at above neutral pH. Phosphate (results not shown), tested in the concentration range 0.5–5 mg/l, was found to slightly reduce the fluoride uptake by the sorbents as the concentration was increased.

#### 4.4. Application to Kenyan groundwater

In the recent past, several boreholes were sunk in Kenyan villages as alternatives to surface waters, which were prone to water borne diseases. However, fluoride concentrations in most of the groundwaters used as drinking water are above permissible levels. It is estimated that 61% of boreholes have a fluoride concentration above 1 mg/l and almost 20% above 5 mg/l [34]. Borehole water in Kenya is mostly drunk untreated. Two water samples, for convenience, were randomly taken from two tube wells in and around Egerton University, Njoro, Kenya.

The fluoride uptake from the two groundwater samples and demineralized water by the two sorbents is shown in Fig. 9. First, an increase in sorbent dose resulted in an increased removal of fluoride from the groundwater samples. However, in all cases, Al<sup>3+</sup>-exchanged zeolite outperformed

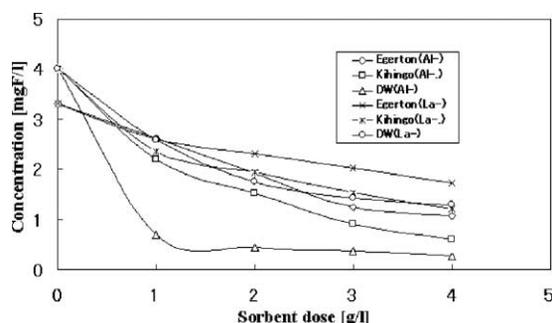


Fig. 9. Effect of sorbent dose on fluoride removal from Kenyan groundwaters and deionized water.

La<sup>3+</sup>-exchanged zeolite. The latter could be attributed to a difference in surface chemistry of the modified zeolites and sorption mechanisms, among others. Second, sample Egerton, though it contained a lower initial fluoride concentration and pH, showed a higher difficulty of fluoride removal than sample Kihingo. We attribute this to the difference in solution chemistry of the samples. It is observed in Table 1 that sample Kihingo contained higher concentrations of anions, which could have caused a shielding effect on otherwise highly negative sites or sites with reduced affinity for fluoride, leading to higher uptake. Also, in the presence of the sorbents, the sample Egerton pH rose above the initial value and remained higher than that of sample Kihingo. The reason for this observation is unclear. Since solution pH significantly affects sorption systems by lowering the total charge density on the sorbent, it could have been an additional factor contributing to the lower fluoride removal from sample Egerton. Finally, La<sup>3+</sup>-exchanged zeolite was less affected by test samples. It was observed that La<sup>3+</sup>-exchanged zeolite has the same fluoride-removal characteristics for demineralized water (spiked with fluoride at the concentration and pH of the sample Kihingo) and sample Kihingo.

## 5. Conclusion

Modeling of batch equilibrium data for the fluoride-trivalent-cation-exchanged zeolite interaction has been successfully done and the sensitivity of isotherm parameters to solution temperature evaluated. The isotherm parameters were weakly dependent on the solution temperature. Error analysis was done and it was found that all the isotherms tested simulated the experimental data of the current sorption systems, suggesting sorption on heterogeneous sites. Moreover, from the two-site Langmuir, Tóth, and Dubinin–Radushkevitch isotherms, the sorption capacities of the sorbents were determined. The capacity values were highly competitive compared to those reported in literature. Sorption on Al<sup>3+</sup>-exchanged zeolite was consistent with an ion-exchange mechanism, while sorption on La<sup>3+</sup>-exchanged zeolite was of a physical nature probably involving electrostatic interaction. It was found that factors from solution

chemistry that affected the fluoride sorption characteristics were the solution pH and bicarbonate content and, to a lesser extent, the phosphate content. Whereas removal of fluoride from the Kenyan groundwaters was possible, there was a reduction in performance compared with results obtained with demineralized water. However, the modified forms of zeolite were highly competitive in performance compared with other sorbents used in fluoride removal from water. Since zeolite used in this work is synthetic, cost may be an inhibiting factor in its use. In that case, studies should be done to determine the possibility of regenerating or recoating the material to reduce the environmental and economic impacts.

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