

## Experimental Evaluation of Activated Termite Mound for Fluoride Adsorption

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**Abstract:** The main objective of this study was to examine fluoride adsorption potential of thermally activated termite mound (TTM) under batch adsorption experimental setup. Thermal activation of the mound in between 100 to 500°C increased the adsorption efficiency (~ 50 to ~ 79%), whereas activation above 500°C decreased the efficiency. The removal of fluoride was optimal (~ 91%) in the pH ranging from 3 to 10. Adsorption kinetics data followed pseudo-second order equation ( $R^2 > 0.99$ ). Freundlich and Dubinin-Radushkevich isotherms satisfactorily described the equilibrium isotherm data ( $R^2 > 0.98$ ,  $\chi^2 < 0.25$ ). The obtained mean sorption energy,  $E_{DR}$ , was 11.12 kJ/mol suggesting chemisorption as the predominant sorption mechanism. Fluoride adsorption was significantly decreased in the presence of  $CO_3^{2-}$  and  $PO_4^{3-}$  at a higher concentration range. TTM effectively reduced 7.56 mg/L fluoride in groundwater to below 1.5 mg/L. Fluoride loaded adsorbent was successfully regenerated with NaOH solution for effective reuse. The results of this study demonstrated that TTM could be a promising defluoridation material requiring further investigation for practical applicability.

**Keywords:** Sorption energy, TTM; Thermal activation; Equilibrium; Termite mound

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### I. Introduction

Fluoride in drinking water may be useful or harmful depending on the amount ingested. A small concentration (1-1.5 mg/L) is believed to strengthen the enamel. However, the debate over the health benefits of fluoride even at low concentrations is rising [1]. Fluoride levels in the range of 1.5-4 mg/L can cause dental fluorosis, whereas with prolonged consumption of higher fluoride concentrations (> 4 mg/L) dental fluorosis develops to skeletal fluorosis. Excess fluoride concentrations in groundwater, up to 20 mg/L, occur widely in many parts of the world [2] including Ethiopia [3, 4]. The Main Ethiopian Rift Valley region is one of the fluorosis endemic regions of the world [5], where more than 8 million populations are exposed to high fluoride levels in the drinking groundwater [3, 4]. Consequently, the World Health Organization (WHO) as well as the Ethiopian Quality and Standard Authority set a guideline value of 1.5 mg/L for fluoride in drinking water [5, 6]. However, the Ministry of Water Resources of Ethiopia, for many reasons, suggested the fluoride level in the drinking water at 3.0 mg/L [7]. Therefore, the search for simple, low-cost, efficient locally available adsorbent materials is an important in the development of defluoridation technique to reduce excess fluoride in the drinking groundwater to acceptable levels.

There are several methods of fluoride removal, such as ion exchange, reverse osmosis, nanofiltration, electro dialysis and dialysis that effectively reduce fluoride concentrations to below acceptable level [2, 8-12]. However, these membrane techniques have inherent disadvantages for the practical application in the fluorosis endemic regions of the developing countries like Ethiopia. Although membrane methods are efficient, adsorption has been given priority in the defluoridation research and practice for easier accessibility, cost-effectiveness, and simplicity of design and operation [2]. Various investigations have been thus carried out to remove fluoride by adsorption technique using locally available materials, such as solid waste residue from alum factory [13], laterite [14], bauxite [15], allophanes [16], bone char [17], ceramics [18], gypsum [19] and many others.

Nevertheless, the practical applicability of locally available materials is limited due to their low sorption capacity, need for pH adjustment and dissolution problem. Hence, several studies have been conducted to enhance the sorption capacity through thermal activation. In this regard, researchers have observed improvement of the sorption capacity of various materials after thermal activation [15, 19-21]. As such, the sample of termite mound, containing mainly oxides of Si, Fe, Al and Ti, was thermally activated at different temperatures before the adsorption experiments. Therefore, this study focused (1) to evaluate fluoride sorption capacity of activated termite mound under batch adsorption conditions; (2) to examine the trend of fluoride adsorption with respect to variation of activation temperature, solution pH, adsorbent dose, initial fluoride concentration, and initial concentration of competing anions; and (3) to investigate the reusability of fluoride loaded adsorbent.

## **II. Materials and Methodology**

### **Adsorbent:**

In Ethiopia termite mounds are abundantly found. Particularly, in 8 districts of east and west Wallaga Zones in Oromia Regional National State infestation of mound building termites is has become serious problem for the local farmers [22]. In the southern and western parts of Ethiopia, average mound abundance was found to be 12 mound hills/ha [23, 24], and the estimated mound soil mass is 58.9 t/ha [23]. Six samples of mound soil were collected from 6 termite mounds in the surroundings of Gimbi, (36 P 1036902E 815766N), west Wallaga Zone, Oromia Regional National State, western Ethiopia. A composite sample was made mixing thoroughly the six samples in an equal proportion, and dried afterwards at room temperature. Particle size analysis of the composite sample was performed according to the American Society for Testing and Materials (ASTM D 422) and soil textural classification system [25]. The moisture content was determined heating in an oven at 105<sup>o</sup>C for 24 h. The pH of the adsorbent was measured using a Microprocessor pH 196 meter (pH 196, WTW, Germany) in a 1:10 soil/water ratio according to the standard method [26]. The pH of the point of zero charge (pH<sub>PZC</sub>) of untreated mound soil was determined by the potentiometric titration method [27]. Oxides and elemental compositions were analyzed using X-Ray Fluorescence (XRF) spectrometry and inductively coupled plasma spectrometer (ICP, Thermo Scientific iCAP 6300 Inductively Coupled Plasma Spectrometer), respectively. Total carbon, total nitrogen and total sulfur contents were determined using Elementar Vario EL analyser (Elementar Analysensysteme GmbH, Hanau, Germany) according to DIN ISO 10694 and 13878 [28, 29]. Surface area of untreated and heat treated mound soil of particle size < 0.075 mm were determined by BET method using Micromeritics (ASAP 2010, USA) after degassing.

### **Thermal Activation:**

Earlier investigations [15, 19-21] show that thermal activation influences fluoride adsorbing capacity of adsorbents. As such, a weighed amount of air dried composite sample of raw termite mound was thermally heated in between 100 and 800<sup>o</sup>C for 4 h in a preheated furnace. The calcined sample was crushed, sieved to particle size < 0.075 mm and stored in airtight plastic bottles before adsorption experiments. The weight after calcination was taken to calculate the loss of water and other volatile substances.

### **Preparation of Desorbent Solution:**

The study conducted by Thongthai [30] indicates that egg shell calcined in a preheated furnace at 900<sup>o</sup>C for 3 h contains ~ 97% CaO. To prepare CaO, the egg shell was washed with deionized water, and dried in an oven at 105<sup>o</sup>C for 24 h. The dried egg shell was milled by hand using a mortar for calcination at 900<sup>o</sup>C for 3 h in a preheated furnace [31, 32]. The calcined egg shell was cooled in a desiccator. To prepare an alkaline solution of Ca(OH)<sub>2</sub>, 100 g of the powder of calcined egg shell was stirred in 1 L deionized water and filtered to remove undissolved matter. Then the supernatant solution of Ca(OH)<sub>2</sub> labeled “CES solution” having pH 12.27 was used for fluoride desorption.

### **Chemicals:**

All chemicals used were analytical grade reagent of the Merck product, Damstadt, Germany. A 1000 g/L fluoride stock solution was prepared by dissolving 2.21 g anhydrous NaF in 1 L of deionized water. Working solutions of fluoride were prepared from the stock solution by dilution using deionized water. The solutions of HCO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup> and PO<sub>4</sub><sup>3-</sup> anions were prepared from their respective potassium salts. The pH of the solution was adjusted using 0.1 M NaOH and/or 0.1 M HCl. A 1000 mg/L standard solution of fluoride was used to calibrate the ion chromatography.

### **Adsorption Experimental Procedures:**

Batch adsorption experiments were carried out in acid washed high density polyethylene (HDPE) plastic bottles using a desired fluoride concentration and dose of TTM. All the experiments were conducted in duplicate at room temperature (23.5 to 25.5<sup>o</sup>C). Average data of the duplicate measurements were reported. Blank (only with TTM) and control (only with fluoride) experiments were conducted at every set of the experiments. After shaking 500 mL solution containing known concentration of fluoride and desired dose of adsorbent at 200 rpm on a horizontal shaker for a desired time, the solid matter was separated by filtration with 0.45 µm acetate filter paper. The concentration of fluoride in the filtrate was analyzed using double beam T80 UV-VIS spectrophotometer (PG Instruments, UK).

Experimental parameters, such as varying contact time, dose of TTM, pH of the solution, initial concentration of fluoride and the presence of interfering anions were investigated to assess the effect on fluoride adsorption, and optimize the adsorption process for maximum fluoride removal. The effect of contact time was studied varying the agitation time from 0 to 60 min at pH 7 using 12 g/L TTM in 500 mL solution of 10 mg/L fluoride. The adsorption kinetic was examined varying the concentration of fluoride (5 to 25 mg/L) and the dose

of adsorbent (5 to 30 g/L) while keeping the other conditions constant. The pattern of the efficiency of fluoride removal under different initial solution pHs was investigated in the pH range ~ 3 to ~ 11 using 10 mg/L fluoride and 12 g/L TTM. The efficiency of fluoride adsorption by TTM was examined varying the amount of adsorbent from 1 to 28 g/L under 10 mg/L fluoride at solution pH ~ 7. The effect of varying the level of fluoride concentration on the fluoride removal was studied in the concentration range 3 to 155 mg/L at pH ~ 7 using 12 g/L TTM. To evaluate the influence of the presence of co-existing anions in water, 10 to 500 mg/L anion concentrations were used separately and in a mixture in 500 mL solution of 10 mg/L fluoride at solution pH ~ 7. The fluoride sorption efficiency of 12 g/L TTM was evaluated under identical batch adsorption setup using two samples of groundwater containing 7.56 and 15.93 mg/L fluoride, respectively.

The amount of fluoride adsorbed per unit mass of the adsorbent and the percentage of fluoride adsorbed were computed, respectively using Eq. (1) and Eq. (2) [33] shown below:

$$q_t = \left( \frac{C_0 - C_t}{M} \right) \times V \quad (1) \quad A\% = \left( \frac{C_0 - C_t}{C_0} \right) \times 100 \quad (2)$$

where,  $q_t$  (mg/g) is the amount adsorbed at any time,  $t$  (min),  $A(\%)$  is the percentage of fluoride adsorbed,  $C_0$  (mg/L) and  $C_t$  (mg/L) are the initial concentration of fluoride and the concentration of fluoride in the aqueous phase at any time,  $t$ , respectively,  $V$  (L) is the volume of the aqueous solution, and  $M$  (g) is the mass of TTM used in the experiments.

### Desorption Study

To evaluate the regenerability of the spent TTM, a 10 mg/L of fluoride in the aqueous solution was initially allowed to adsorb on 12 g/L TTM at pH ~ 7 for 60 min by shaking the mixture. After adsorption, the solid was separated by filtration, dried at 105°C for 12 h in an oven, and then used for desorption study. Desorption investigations were conducted shaking at 200 rpm for 60 min the dried fluoride loaded TTM with 500 mL solution of CES, 0.1 and 0.2 M NaOH separately. In addition, the pH of deionized water was adjusted to ~ 5 to assess the release of fluoride ion from fluoride loaded adsorbent for safe disposal of the spent TTM at pH ≤ 5. The amount of fluoride desorbed from the solid into the solution was then determined analyzing the concentration of fluoride in the supernatant solution after desorption experiment.

The regenerated fluoride loaded adsorbent was rinsed with 0.1 M HCl until the pH of the supernatant solution was ~ 5, which is the pH of the fresh mound soil measured in 1:10 adsorbent/water ratio. Then, the dried regenerated TTMS was allowed to adsorb 10 mg/L fluoride for 60 min at solution pH ~ 7 under batch adsorption setup.

### Analysis:

After filtration to separate the solid particles, residual fluoride in the clear supernatant solution was measured using ion chromatography (Metrohm AG, Switzerland) with chemical suppression and a Metrosep Dual 2 column (75 mm). Calibration of the ion chromatography using a standard solution of fluoride was performed prior to each set of the analyses. Fluoride concentration was calculated on the basis of the peak area using a quadratic regression equation derived from the measurements of the standard solutions. The concentrations of elements were analyzed using an inductively coupled plasma spectrometer (ICP, Thermo Scientific iCAP 6300 Inductively Coupled Plasma Spectrometer).

## III. Results and Discussion

### Characterization of Adsorbent:

The chemical compositions, major oxides and some elements, of termite mound are given in Table 1. The Si, Fe, AL and Ti oxides together made up 85.60 wt%, while basic metallic (Na, Ca, Mg and K) oxide contents were negligible (~ 1%). Silicon was the major elemental content of the adsorbent. The composition of Si + Fe + Al + Ti elements amounted to 35.59 wt%. Compositions of the analyzed toxic elements were below detection limit except for Cr, which was 0.01 wt%. The BET surface area of raw termite mound was found to be 28.40 m<sup>2</sup>/g. The pH<sub>PZC</sub> of TM determined by the potentiometric titration method was found to be 7.96. The obtained value of pH<sub>PZC</sub> is within the range of the pH<sub>PZC</sub> of the mixture of Si, Fe, Al, and Ti oxides, 5.5 to 8.3 [34], and comparable to the pH<sub>PZC</sub> of termite mound (pH<sub>PZC</sub> = 7.8) investigated for the removal of Pb(II) [35]. Total carbon, total sulfur and total nitrogen contents together constituted 2.60%. The pH of uncalcined termite mound determined in water was 5.10. The moisture content of the raw mound soil was found to be 3.92%. Particle size analysis showed that the majority of particles were in the range of 0.075-2.00 mm with mean particle size ( $d_{50}$ ) of 0.51 mm.

**Table 1.** Chemical Composition of Raw Termite Mound

Oxides	Wt%	Elements	Wt%
SiO <sub>2</sub>	27.43	Si	15.07

Al <sub>2</sub> O <sub>3</sub>	22.83		Fe	12.67
Fe <sub>2</sub> O <sub>3</sub>	26.08		Al	6.35
TiO <sub>2</sub>	8.86		Ti	1.50
MgO	0.83		Na	< 0.01
Na <sub>2</sub> O	< 0.01		K	< 0.01
K <sub>2</sub> O	0.23		Mg	< 0.01
CaO	< 0.01		Cr	0.01
MnO	0.25		Mn	0.21
P <sub>2</sub> O <sub>3</sub>	0.35		P	0.35
SO <sub>3</sub>	0.33		Hg	bdl
Total C	2.30		Pb	bdl
Total S	0.28		As	bdl
Total N	0.04		Ni	bdl
LOI	11.29		Cd	bdl

bdl-below detection limit, LOI-loss on ignition

### Solubility of TTM

An investigation was carried out to assess the stability of TTM under experimental conditions (shaking speed: 200 rpm, contact time: 60 min and pH: ~ 7). Mineral dissolution was tested via analysis of the concentration of elements in the supernatant solution. The concentrations of the elements in the supernatant solution in wt% were as follows: Si: 0.034, Fe: 0.01, Al: 0.048, As: < 0.01, Ni: < 0.01, Cd: < 0.01, Cr: 0.048, Pb: < 0.01 and F: < 0.01. The analysis results indicated that mineral dissolution was insignificant resulting in < 0.1 wt% of total Si, Fe or Al being dissolved, and the concentrations of elements obtained were significantly lower than the WHO maximum permissible level in drinking water[5]. Therefore, TTM can be used safely as an adsorbent for the removal of fluoride without generating toxic sludge.

### Effect of Thermal Treatment

Investigation of the effect of thermal treatment was carried out using 5 g/L raw and calcined (100 to 800<sup>o</sup>C) termite mound separately in 500 mL of 10 mg/L fluoride solution under identical experimental conditions. The results of the effect of calcination temperature on the adsorption of fluoride are shown in Fig. 1 along with the coefficient of distribution and weight loss upon calcination at different temperatures. It was observed that weight loss progressively increased from 4.67 to 27.67% with the increase in the calcination temperature from 100 to 800<sup>o</sup>C. The increase in the loss of weight upon increasing calcinations temperature could be attributed to the loss of considerable structural water molecules (as the moisture and organic matter contents together contributed 6.54 wt% only) upon increasing calcination temperature [15, 36]. BET and single point surface areas of uncalcined and calcined termite mound are given in Table 2. It is obvious that the untreated termite mound had a lower surface area which gradually increased with the increase of calcination temperature up to 600<sup>o</sup>C. This increase in surface area with temperature is presumably due to loss of structural water molecules, and formation of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and various structural rearrangements which made the material more porous [15, 36].

The results (Fig. 1) also revealed that the efficiency of fluoride adsorption and adsorption capacity progressively increased from ~ 50 to ~ 79% and 0.08 to 0.38 L/g, respectively with the increase in the heating temperature from 100 to 500<sup>o</sup>C. The progressive increase in the percentage of fluoride adsorbed and fluoride binding capacity with the increase of calcination temperature up to 500<sup>o</sup>C could be due to increase in Al, Ti, and Fe content, and increase in the surface area as a result of loss of structural water molecules, and formation of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> which could have a larger surface area [15, 36]. On the contrary, increasing temperature of calcination above 500<sup>o</sup>C resulted in the progressive decrease of percent fluoride adsorbed and fluoride adsorption capacity from ~ 79 to ~62% and 0.38 to 0.17 mg/g, respectively. Although the BET surface area of termite mound calcined at 600<sup>o</sup>C (90.75 m<sup>2</sup>/g) was higher than that of the 500<sup>o</sup>C calcined (87.81 m<sup>2</sup>/g), termite mound calcined 600<sup>o</sup>C demonstrated lower fluoride adsorption efficiency. This could be attributed to a considerable dehydroxylation of oxides which prevail over the effect of increased surface area [15]. The progressive decrease in the adsorption efficiency and binding capacity upon increasing the heating temperature above 500<sup>o</sup>C could be attributed to a significant dehydroxylation of mainly Al and Fe oxides, and sintering effect [15]. Similar observations have been observed earlier for different materials (14, 25).

The 500<sup>o</sup>C calcined termite mound had higher sorption efficiency (~ 79%) compared to the raw termite mound (~44%). Consequently, it can be concluded that TTM could be more effective adsorbent. As a result, further experiments were carried out using TTM for the evaluation of the sorption capacity and optimization of adsorption parameters unless otherwise stated.

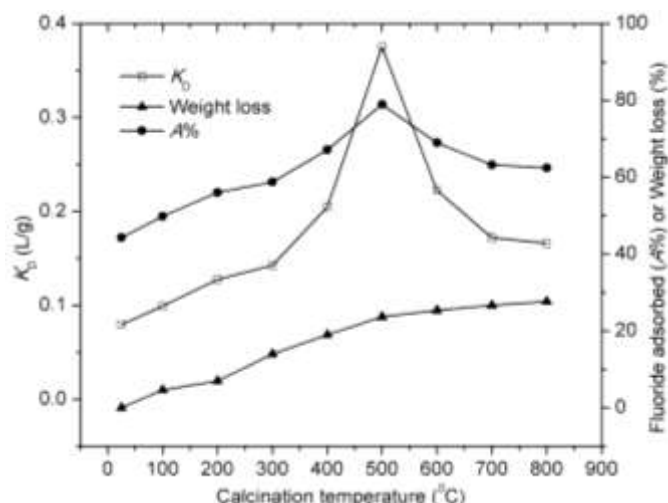


Fig. (1). Effect of heating temperature on weight loss, coefficient of distribution and fluoride adsorption by TTM.

Table 2. Surface Areas of Uncalcined and Calcined Termite Mound

Calcination temperature (°C)	25	100	200	300	400	500	600	700	800
BET surface area (m <sup>2</sup> /g)	28.40	nm	nm	nm	78.36	87.81	90.75	nm	nm
Single point surface area (m <sup>2</sup> /g)	28.34	nm	nm	nm	76.07	88.20	91.13	nm	nm

nm-not measured

### Effect of Contact Time

To determine the equilibrium time for the adsorption of fluoride, an investigation was conducted using 5, 10 and 25 mg/L fluoride concentrations at solution pH ~ 7 under 12 g/L of the adsorbent. The plots of the percentages of fluoride removed versus contact time are given in Fig. 2. Fluoride adsorption was fast within the first 5 min and afterward very slow until the equilibrium time. The rapid removal of fluoride within the first 5 min of agitation time was due to the presence of competent active binding sites on the surface of TTM at the initial stage of the contact time. Equilibrium was achieved within 30 min of the agitation time. However, in order to be sure of the attainment of equilibrium, contact time was maintained at 60 min for further studies. The attainment of the equilibrium time was independent of the initial fluoride concentration 5 to 25 mg/L. Similar results were observed for fluoride removal by activated titanium rich bauxite [15].

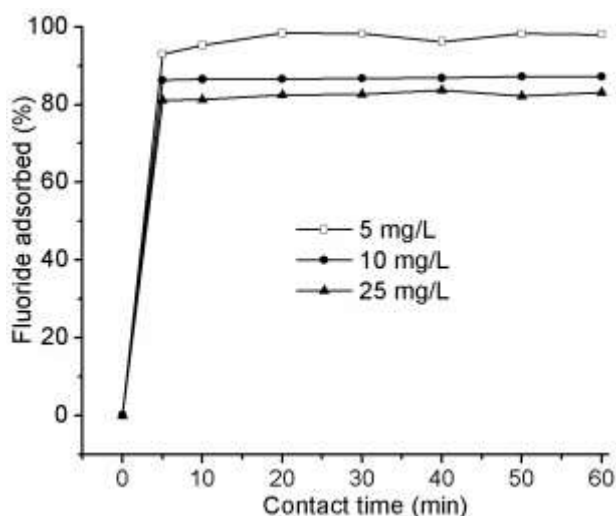


Fig. (2). Effect of contact time on fluoride removal by TTM.

### Kinetics Modeling

The kinetics of fluoride adsorption was studied varying dose of adsorbent (5 to 30 g/L and concentration of fluoride (5 to 25 mg/L) at solution pH ~ 7 keeping the other parameters constant. The adsorption kinetics data followed the pseudo-second-order equation [37] given in Eq. (3):

$$\frac{t}{q_t} = \frac{1}{q_e} (t) + \frac{1}{k_2 q_e^2} \quad (3)$$

where  $q_t$ (mg/g) is the amount of fluoride adsorbed per unit mass of TTM at any time  $t$  (min),  $q_e$ (mg/g) is the modeled equilibrium amount of fluoride adsorbed per unit mass of TTM, and  $k_2$  (g/(mg.min)) is the pseudo-second-order rate constant.

The plots of the kinetics of fluoride adsorption are given in Figs. 3 and 4. The pseudo-second-order rate constant ( $k_2$ ), calculated equilibrium capacity ( $q_{e,cal}$ ) and adsorption affinity ( $V_0 = k_2 q_e^2$ ) were computed from the plots of  $t/q_t$  versus  $t$ . The plots of  $t/q_t$  versus  $t$  were straight lines with correlation coefficients,  $R^2 > 0.99$ . The calculated pseudo-second-order parameters of fluoride adsorption are given Table 3. The obtained results show that the values of modeled equilibrium capacities,  $q_{e,cal}$ , were remarkably comparable to the experimental equilibrium capacities,  $q_{e,exp}$ . Thus, the adsorption of fluoride on TTM could be well described by the pseudo-second-order equation, implying that the rate limiting step may be the chemical adsorption [37]. The values of  $k_2$ ,  $q_{e,cal}$  and  $V_0$  obtained from the slope and intercept data of the plots in Fig. 3 showed the increase in  $k_2$  values (0.818 to 3.938 g/(mg.min)), and the decrease in  $q_{e,cal}$  (1.140 to 0.349 mg/g) and  $V_0$  (1.063 to 0.481 mg/(g.min)) values with an increase in the adsorbent dose. Thus, the rate of adsorption increased with an increase in the TTM dose. Whereas, the values of  $k_2$ ,  $q_{e,cal}$  and  $V_0$  computed from the slope and intercept data of the plots in Fig. 4 depicted the decrease in  $k_2$  values (8.749 to 1.568 g/(mg.min)), and the increase in  $q_{e,cal}$  (0.477 to 3.748 mg/g) and  $V_0$  (1.990 to 22.026 mg/(g.min)) values with an increase in the concentration of fluoride. Thus, the rate of adsorption decreased with an increase in the solute concentration, which is similar to the results observed for the removal of fluoride using hydrous iron(III)–tin(IV) bimetal mixed oxide[38].

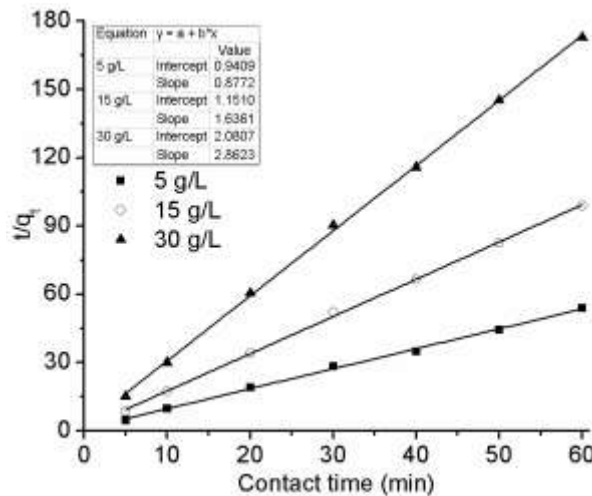


Fig. (3). Pseudo-second order plots related to the effect of adsorbent dose.

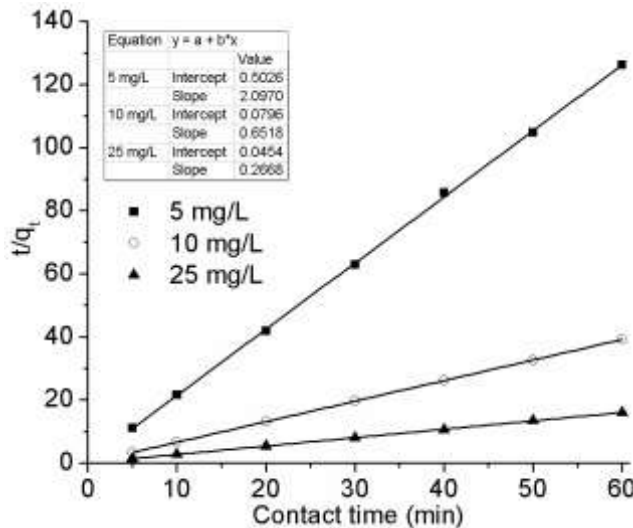


Fig. (4). Pseudo-second order plots related to the effect of initial fluoride concentration.

Table 3. Pseudo-Second-Order Parameters of Adsorption of Fluoride on TTM

Parameters	TTM dose (g/L)			Fluoride concentration (mg/L)		
	5	15	30	5	10	25
$q_{e,exp}$ (mg/g)	1.114	0.607	0.347	0.475	1.532	3.746
$q_{e,cal}$ (mg/g)	1.140	0.611	0.349	0.477	1.534	3.748
$k_2$ (g/(mg.min))	0.818	2.326	3.938	8.749	5.337	1.568
$V_0$ (mg/(g.min))	1.063	0.869	0.481	1.990	12.563	22.026
$R^2$	0.997	0.999	0.999	0.998	0.999	0.999

### Effect of Solution pH

The investigation of the effect of pH on the fluoride adsorption was conducted in between initial solution pH ~ 3 and ~ 11 using 10 mg/L fluoride solution and 12 g/L TTM. Graphical presentation of the results is given in Fig. 5. It was observed that the percentage of fluoride adsorption was optimal (~ 91%) in between the initial solution pH range ~ 3 to ~ 10, while the percentage significantly decreased from ~ 90 to ~ 45% with the increase in the solution pH from ~10 to ~11. In the same way, the adsorption capacity was almost constant (~ 0.765 mg/g) in the pH range ~ 3 to ~ 10. The high percentage of fluoride removal in the range of pH ~ 3 to ~ 10 could be attributed to the amphoteric nature of Al and Fe oxides content of the adsorbent [39-42]. The pH dependency of fluoride removal can also be explained considering the  $pH_{PZC}$  of the adsorbent. The  $pH_{PZC}$  of termite mound used in the present study determined by the potentiometric titration method was found to be 7.96. The observed value of  $pH_{PZC}$  is within the range of the  $pH_{PZC}$ , 5.5 to 8.3, of the mixture of oxides of Si, Fe, Al, and Ti [34] and is also comparable to the  $pH_{PZC}$  determined for the termite mound ( $pH_{PZC} = 7.8$ ) evaluated for the removal of Pb(II) [35]. Consequently, when the  $pH < pH_{PZC}$ , the columbic attraction would be responsible for the adsorption of fluoride ions onto the surface of adsorbent (Eq. (4)), and when the  $pH > pH_{PZC}$ , the fluoride ions would be adsorbed through a ligand exchange process (Eqs. (5) and (6)) [43].



where M represents Si, Al, Fe and Ti etc. Importantly, the high percentage of fluoride removal in the basic medium up to pH ~10 is of a great interest in the practical application. The decrease in the percentage of fluoride adsorbed at  $pH > 10$  could be due to the competition of hydroxyl ions or electrostatic repulsion of fluoride ion by the negatively charged surface [44]. The slight fluctuation of adsorption of fluoride in the pH range from ~ 3 to ~10 may be due to both specific and nonspecific adsorptions of fluoride on the adsorbent [44].

Furthermore, when the initial solution pH was in the range of ~ 4 to ~ 10, the pH values after adsorption were ~ 6.64 (data not shown). This implies that TTM had the capacity of maintaining a neutral pH after adsorption. The capacity of maintaining a neutral solution pH may result from the amphoteric nature of oxides of Al and Fe [39, 40], and the negligible compositional content of basic ionic metallic oxides of termite mound (Table 1). Consequently, the effect of the basic metallic oxides to increase the pH of the solution was negligible and overshadowed by the effect of the oxides of Al and Fe. The result is similar to previous defluoridation studies [13, 45, 46].

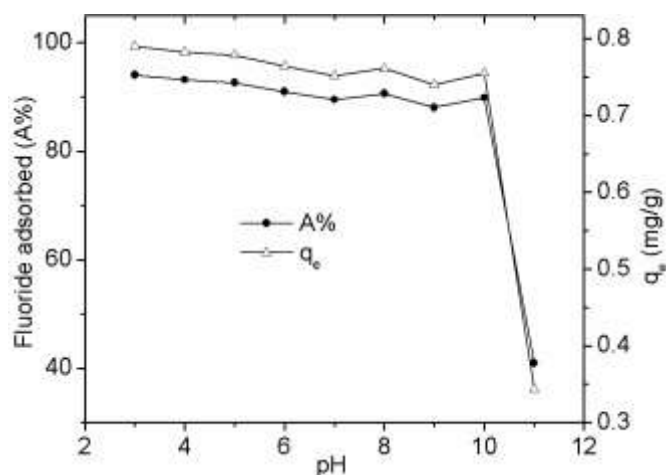


Fig. (5). Effect of pH on fluoride removal by TTM.

### Adsorbent Dose

To determine the required minimum dose for maximum fluoride adsorption, an experiment was conducted varying the amount of TTM from 5 to 28 g/L. The plots of the percentage of fluoride adsorbed and loading capacity versus adsorbent dose are given in Fig. 6. Fluoride loading capacity (amount of fluoride loaded

per unit weight of adsorbent) decreased from ~ 1.76 to ~ 0.39 mg/g with the increase in the dose from 5 to 28 g/L. This decrease in the amount adsorbed could be due to the decrease in the fluoride/active binding sites ratio [20]. In contrast, with increase in the dose of the adsorbent from 5 to 28 g/L percent fluoride removal increased from ~ 79 to ~ 99%. This increase in the percentage of removal can be attributed to the availability of more adsorption sites at a higher adsorbent dose [20, 47]. In the present study, the permissible limit of fluoride in drinking water according to WHO, 1.5 mg/L, was attained at TTM dose of 12 g/L, which reduced 10 mg/L fluoride to 1.37 mg/L. Hence, 12 g/L TTM was considered as the optimal dose for further studies unless otherwise stated.

The coefficient of distribution,  $K_D$  (L/g), which shows the binding ability of adsorbent surface, was computed using  $K_D = q_e/C_e$ [48], where  $q_e$  and  $C_e$  are described elsewhere. The value of  $K_D$  increased from 0.74 to 2.92 L/g as a function of the adsorbent amount at pH ~ 7 (plot not shown). The increase in  $K_D$  value at a given pH indicates the heterogeneity of the surface of the adsorbent [48].

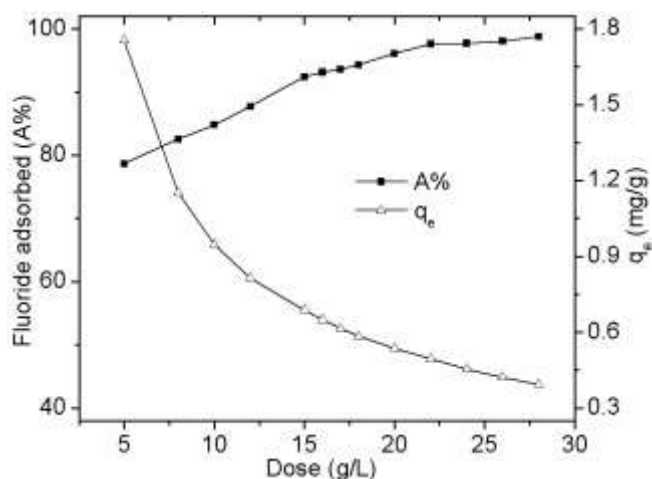


Fig. (6). Effect of adsorbent dose on adsorption of fluoride by TTM.

**Effect of Initial Fluoride Concentration**

The effect of varying the level of concentration of fluoride from 3 to 155 mg/L on the adsorption of fluoride was assessed at solution pH ~ 7 using 12 g/L TTM. The plots of the amount of fluoride removed and percentage of fluoride adsorbed against the initial concentration of fluoride are given in Fig. 7. It was observed that the fluoride adsorption capacity gradually increased from ~ 0.19 to ~ 5.53 mg/g with the increase in the concentration of fluoride from 3 to 155 mg/L, which could be attributed to the availability of more fluoride ions for adsorption at higher concentration [49]. In contrast, the percentage of fluoride removal showed a progressive decreasing trend from ~ 98 to ~ 43% with the increase in the concentration of fluoride from 3 to 155 mg/L. Most fluoride ions adsorbed to the binding sites at low initial concentration, resulting in a high percentage of fluoride adsorbed, while only part of the fluoride combined with the limited binding sites at high initial concentration, resulting in a relatively low removal percentage [42]. Similar observations have been made earlier [46, 47].

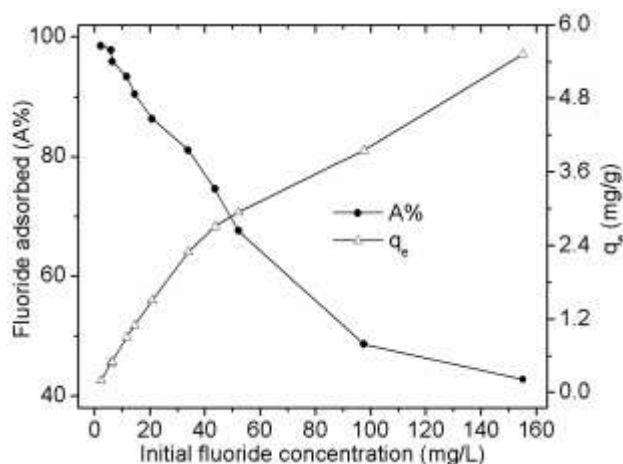


Fig. (7). Effect of initial fluoride concentration on fluoride removal by TTM.

**Analysis of Equilibrium Isotherm Data**



Nonlinear forms [48, 50-52] of the Langmuir (Eq. (7)), Freundlich (Eq. (8)) and Dubinin-Radushkevich (D-R) (Eq. (9)) were applied to analyze the fluoride adsorption capacity of TTM at equilibrium, and the mathematical equations of the isotherm models are given below:

$$q_e = \frac{Q_{max} b C_e}{1 + b C_e} \quad (7)$$

$$q_e = K_F C_e^{1/n} \quad (8)$$

$$q_e = q_m \exp(-K_{DR} \varepsilon^2) \quad (9)$$

$$\varepsilon = RT \ln \left( 1 + \frac{1}{C_e} \right) \quad (70)$$

where  $C_e$ (mg/L) is the concentration of fluoride in the aqueous phase at equilibrium,  $q_e$ (mg/g) is the amount of fluoride adsorbed at equilibrium per unit mass of TTM,  $Q_{max}$  (mg/g) is the adsorption capacity based on the Langmuir equation, and  $b$  (L/mg) is the Langmuir constant,  $K_F$ [(mg<sup>1-1/n</sup>L<sup>1/n</sup>)/g] is Freundlich coefficient of adsorption,  $1/n$  is the adsorption intensity based on the Freundlich equation,  $q_m$  (mol g<sup>-1</sup>) is the molar adsorption capacity based on the D-R equation,  $K_{DR}$ (mol<sup>2</sup>/kJ<sup>2</sup>) is the activity coefficient related to the mean sorption energy,  $\varepsilon$  (mol<sup>2</sup>/kJ<sup>2</sup>) is the Polanyi potential,  $R$  (kJ/(mol.K)) is the gas constant, and  $T$ (K) is the temperature of the equilibrium experiment.

The chi-squared test,  $\chi^2$ , which is given by Eq. (11), was carried out to identify the most suitable isotherm model that well describes the sorption system, and the less the difference between the experimental and modeled equilibrium capacities, the less the value of  $\chi^2$ [53].

$$\chi^2 = \sum \frac{(q_e - q_{e,cal})^2}{q_{e,cal}} \quad (11)$$

where  $q_{e,cal}$ (mg/g) is the equilibrium capacity obtained by calculating from the model and  $q_e$  (mg/g) is the experimental data on the equilibrium capacity.

The plots of the equilibrium adsorption isotherms of fluoride on TTM are given in Fig. 8. Values of the equilibrium constants obtained from their respective nonlinear forms of the isotherm are given in Table 4. The Freundlich and D-R isotherms demonstrated higher values of determination coefficients,  $R^2 > 0.98$ , and lower values of chi-square,  $\chi^2 \sim 0.20$ . Thus, both isotherm models more satisfactorily described the equilibrium data of fluoride adsorption on TTM.

The essential characteristic of the Langmuir isotherm is expressed in terms of a dimensionless constant separation factor,  $R_L$ , which describes the type of isotherm [54], and was computed by  $R_L = 1 + (1/bC_0)$  where,  $C_0$  (mg/L) is the initial concentration of fluoride. The values of  $R_L$  calculated were 0.06 to 0.79 that are between 0 and 1.0, suggesting favorable adsorption of fluoride on TTM. The nature of adsorption isotherm can also be suggested by the magnitude of adsorption intensity of the Freundlich constant,  $n$ . The value of  $n$  for fluoride removal by TTM was found to be 2.74 that is between 1.0 and 10.0, indicating a favorable adsorption system[15]. A similar observation was made by Solangi et al. [51].

The D-R equation is used to compute the mean free energy of sorption and assumes the heterogeneity of energies over the binding surface of adsorbent [51]. The mean sorption energy,  $E_{DR}$  (kJ/mol), was computed from D-R isotherm using the equation  $E_{DR} = (-2K_{DR})^{-0.5}$ [55]. The magnitude of  $E_{DR}$  is useful to evaluate the nature of interaction between fluoride ion and the binding sites. The calculated value of  $E_{DR}$  for fluoride adsorption on TTM was 11.12 kJ/mol that is within the energy range of chemical sorption reactions, 8.0 to 16.0 kJ/mol [54]. Thus, the adsorption of fluoride on TTM took place mainly through the chemical sorption process.

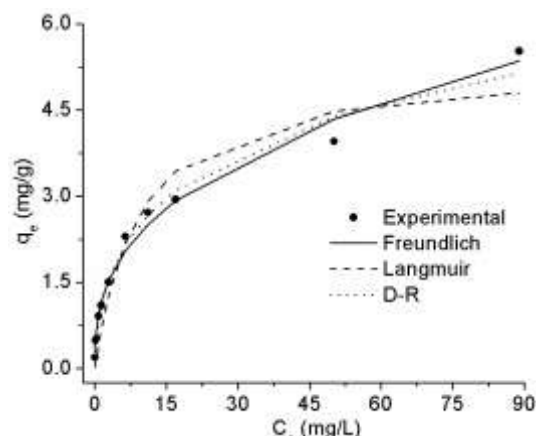


Fig. (8). Isotherm models of fluoride sorption TTM.

Table 4. Isotherm parameters of equilibrium adsorption of fluoride on TTM

Freundlich		Langmuir		Dubinin-Radushkevich	
$K_F[(\text{mg}^{1-1/n}\text{L}^{1/n})/\text{g}]$	1.04	$Q_{max} (\text{mg/g})$	5.29	$K_{DR} (\text{mg/g})$	10.49
$n$	2.74	$b(\text{L/mg})$	0.11	$E_{DR}(\text{kJ/mol})$	11.12
$R^2$	0.989	$R_L$	0.06-0.79	$R^2$	0.985
$\chi^2$	0.163	$R^2$	0.953	$\chi^2$	0.203
		$\chi^2$	5.751		

### Effect of Co-existing Anions

The effects of the presence of co-existing anions in the solution on the efficiency of fluoride removal by TTM were investigated at solution pH ~ 7 varying the concentration of the anions from 10 to 500 mg/L under 10 mg/L fluoride and 12 g/L TTM. Graphical presentation of the efficiency of fluoride removal as a function of the concentration of co-existing anions is given in Fig. 9. The result showed that the adsorption efficiency was significantly decreased in the presence of  $\text{PO}_4^{3-}$  and  $\text{CO}_3^{2-}$  ions in the solution at a higher concentration range of 100 to 500 mg/L. This presumably attributed to the high affinity and capacity of TTM for  $\text{PO}_4^{3-}$  and  $\text{CO}_3^{2-}$  ions [18]. A similar observation has been made by Chen et al [56]. Fortunately, carbonate and phosphate ions are absent or very little in most groundwater sources of the Main Ethiopian Rift [3, 4]. The results also revealed that the adsorption of fluoride was greatly affected in the presence of the mixture of the anions in the solution in the concentration range of 100 to 500 mg/L, indicating that the effect of  $\text{PO}_4^{3-}$  and  $\text{CO}_3^{2-}$  ions overshadowed the influence of the presence of the other anions. The presence of  $\text{HCO}_3^-$  ion in the concentration range of 100 to 500 mg/L slightly decreased the adsorption efficiency. A similar observation of the effect of  $\text{HCO}_3^-$  on the efficiency of fluoride adsorption has been investigated using chemical treated laterite [14].

In contrast, with the increase in the concentration of  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  ions in the solution the percentage of fluoride adsorbed slightly increased suggesting the inner sphere complexation between the fluoride ions and the active binding sites of TTM[14]. Similar results were observed by Meenakish et al. [53]. In general, the results of the effects of co-existing anions on the efficiency of fluoride adsorption on TTM are similar to the observation made by Chen et al. [56] for the removal of fluoride by porous granular ceramic.

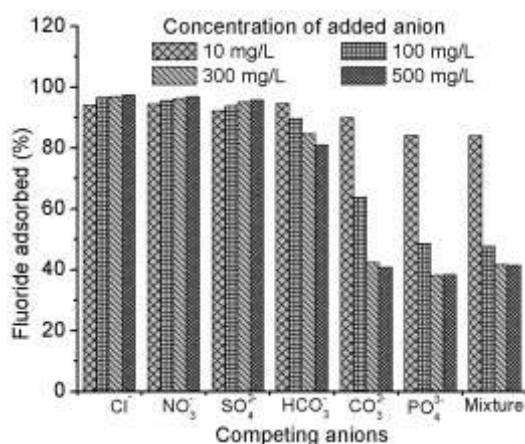


Fig. (9). Effect of co-existing anions on the removal of fluoride by TTM.

### Defluoridation of Natural Groundwater

Two groundwater samples containing 7.56 and 15.93 mg/L fluoride from two wells were collected from the Main Campus of Jimma University, Oromia Regional National State, Ethiopia. The physico-chemical characteristics of the samples are reported in Table 5. The fluoride contaminated water samples were defluoridated using 12 g/L TTM without adjusting the pHs of the samples. Accordingly, the 15.95 mg/L fluoride concentration of Well 1 was reduced to 2.92 mg/L, which is below the fluoride level in drinking water suggested by the Ministry of Water Resources of Ethiopia, 3 mg/L. However, the reduction of 15.95 mg/L fluoride concentration to 2.92 mg/L signified the need for a successive treatment to reduce the fluoride level to the WHO permissible level, 1.5 mg/L. On the other hand, the 7.56 mg/L fluoride content of Well 2 was successfully reduced to 1.06 mg/L, which is below the acceptable value of 1.5 mg/L. Thus TTM could be successfully applied for the treatment of natural groundwater containing excess fluoride.

**Table 5.** Physico-chemical Characteristics of Groundwater Samples

Characteristic parameter	Well 1	Well 2
Conductivity ( $\mu\text{S cm}^{-1}$ )	1217.00	1215.00
Total hardness ( $\text{mg L}^{-1}$ ) as $\text{CaCO}_3$	645.56	738.00
Carbonate ( $\text{mg L}^{-1}$ ) as $\text{CO}_3^{2-}$	Nil	Nil
Bicarbonate ( $\text{mg L}^{-1}$ ) as $\text{HCO}_3^-$	623.45	764.94
Chloride ( $\text{mg L}^{-1}$ ) as $\text{Cl}^-$	12.04	3.41
Nitrate ( $\text{mg L}^{-1}$ ) as $\text{NO}_3^-$	17.12	0.20
Sulfate ( $\text{mg L}^{-1}$ ) as $\text{SO}_4^{2-}$	1.22	3.94
Phosphate ( $\text{mg L}^{-1}$ ) as $\text{PO}_4^{3-}$	Nil	0.12
Fluoride ( $\text{mg L}^{-1}$ ) as $\text{F}^-$	15.93	7.56
Calcium ( $\text{mg L}^{-1}$ ) as $\text{Ca}^{2+}$	24.00	10.64
Magnesium ( $\text{mg L}^{-1}$ ) as $\text{Mg}^{2+}$	7.89	3.65
Sodium ( $\text{mg L}^{-1}$ ) as $\text{Na}^{1+}$	289.12	278.00
pH	7.94	7.87

### Adsorption Efficiency of Regenerated TTM

The reusability of an adsorbent is mainly based on the ease with which an adsorbate is released from the spent adsorbent and the adsorption efficiency of the regenerated spent adsorbent. The effect of pH on fluoride removal by TTM showed (Fig. 5) that fluoride adsorption capacity was very low at  $\text{pH} > 10$ , suggesting the possibility of desorbing adsorbed fluoride from the spent adsorbent using alkaline solution of  $\text{pH} > 10$ . Based on this, batch desorption of  $\sim 87\%$  fluoride adsorbed was carried out under identical experimental conditions of the batch sorption studies (subsection 2.4) using 500 mL of CES, 0.1 M and 0.2 M NaOH solution, separately. The percentages of fluoride desorbed at  $\text{pH} > 12$  using CES, 0.1 M and 0.2 M NaOH solutions were 66.75, 80.64 and 96.60%, respectively (Fig. 10). Consequently, fluoride loaded TTM could be successfully regenerated using NaOH solution. The mechanism of fluoride desorption from the exhausted TTM can be interpreted in terms of the ligand exchange mechanism as depicted in Eq. (12).

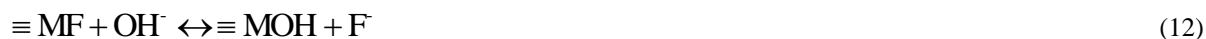


Figure 10 shows that adsorption efficiency of 89.79, 92.09 and 97.43% were achieved respectively with CES, 0.1 and 0.2 M NaOH solutions regenerated and rinsed with 0.1 M HCl spent TTM. The performances of fluoride loaded TTM regenerated using CES, 0.1 M and 0.2 M NaOH solution were found to be superior to that of the fresh TTM. Thus, the regenerated adsorbent rinsed with 0.1 M HCl was more efficient than the fresh TTM that could be due to the effect of HCl that could make the adsorbent more porous. It is important to notice that the spent TM regenerated by any of the desorbent solution was competent to reduce 10 mg/L fluoride to below 1.5 mg/L, the maximum allowed fluoride concentration in drinking water.

The loss of Fe and Al from TTM during desorption was investigated by analyzing their respective concentrations in the supernatant solution after shaking the adsorbent at 200 rpm for 60 min at  $\text{pH} 12.81$ . It was found that 0.01% Fe and 0.70% Al, which is together  $< 1\%$ , were released from the adsorbent, indicating that TTM was stable under regeneration conditions. It was also observed that of  $\sim 87\%$  fluoride adsorbed, only 3.67% fluoride was released from fluoride loaded TTM at  $\text{pH} \sim 5.0$ . The results of adsorption-desorption-adsorption cycle showed that fluoride loaded TM can be regenerated using CES or NaOH solution for effective reuse with insignificant loss of metals, or spent TTM could be safely disposed at  $\text{pH} \leq 5.0$ . However, further investigation will be required to determine the exact life cycle of the regenerated TM.

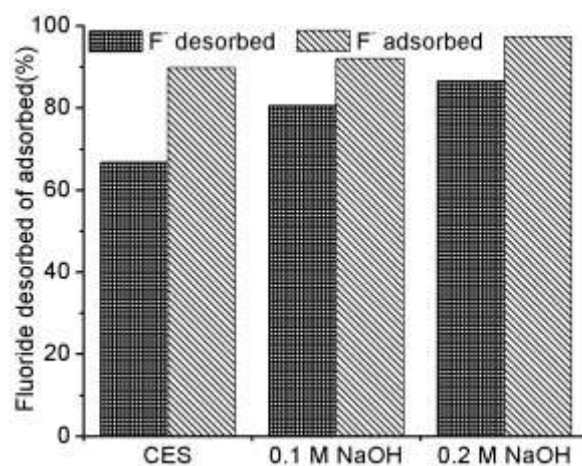


Fig. (10) Fluoride desorbed and adsorbed during an adsorption-desorption-adsorption cycle.

#### IV. Conclusions

The present study showed that the fluoride adsorption capacity of termite mound, containing mainly Al, Fe, Ti and Si oxides could be enhanced by thermally activation. Although the adsorption of fluoride is dependent on contact time, adsorbent dose, solution pH, interfering anions, and concentration of fluoride, the presence of carbonate and phosphate ions at high concentration levels remains the most important factor. The fluoride adsorption efficiency is high over the pH of the natural groundwater overcoming the need for pH adjustment. The fitting of pseudo-second order rate equation to the adsorption kinetics data and the computed value of sorption energy signify the dominance of chemisorption mechanism in the removal fluoride. TTM could be effectively applied for the defluoridation of moderately contaminated groundwater. Successful desorption of fluoride from loaded TTM and high adsorption efficiency of the regenerated spent adsorbent signify the stability and suitability of TTM for defluoridation. In general, the results of this study provides valuable data of the process of fluoride adsorption on TTM warranting further investigations for the practical applicability of the adsorbent to develop household defluoridation technique.

#### Acknowledgements

The author is thankful to the University of Rostock for permitting me the Soil Physics Laboratory for the characterizing the adsorbent. The help from Mr. Reinhard Eckelt of Leibniz-Istitut für Katalyse der Universität Rostock e.v in determining the specific surface area and chemical compositions of the adsorbent is immense. Finally, I would like to thank the laboratory technicians at Biology Department, Jimma University for allowing me to use the analytical instrument.

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