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# Modeling sorption of fluoride on to iron rich laterite

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## ABSTRACT

The efficacy and the interface interactions of fluoride on laterite were investigated using batch methods; under various ionic strengths, pH, fluoride loading and diverse spectroscopy along with surface complexation modeling. The laterite used in this study was rich in iron (40%) and aluminum (30%). Proton binding sites were characterized by potentiometric titrations yielding  $PH_{ZPC}$  around pH 8.72. Adsorption of fluoride on laterite is strongly pH dependent showing a maximum adsorption at pH <5, though not affected by the electrolyte concentration. Experimental data were quantified with a 2pK generalized diffused layer model considering two different surface binding sites for both protons and anions, using reaction stoichiometries. Surface complexation modeling showed that both Fe and Al sites of the laterite surface contributes to fluoride adsorption via inner-sphere complexation forming monodentate mononuclear interaction with laterite. Fluoride adsorption followed the Freundlich isotherm, indicating multi-site complexation on the laterite surface. FT-IR spectroscopic data provides an evidence for increased hydrogen bonding, indicated by the broadening of the OH stretch features around 3300 cm<sup>-1</sup>. © 2012 Elsevier B.V. All rights reserved.

# 1. Introduction

In the natural environment, fluoride occurs as the fluoride ion,  $F^-$ , which is considered as the most reactive electronegative ion. Weathering, dissolution and other pedogenic processes can release fluoride into groundwater. Fluoride contamination problem is being recorded in several countries of the world such as Pakistan, India, Sri Lanka, Germany, Sweden, Netherlands and Japan [1–6]. Although the maximum World Health Organization (WHO) recommended level is 1.5 mg/L in drinking water, recent reports showed very high concentrations of fluoride around 5–10 mg/L around some localized areas in the Dry Zone of Sri Lanka [7]. Though fluoride is considered as an essential element for human health, especially for the strengthening of tooth enamel, excessive doses can be harmful [8,9]. Presence of fluoride in water does not impart any colour, odor or taste. Therefore it acts as a dose-dependent invisible poison such as arsenic in groundwater.

Among various technologies used for fluoride removal [10–13], adsorption is considered as the most convenient, effective, and economical. Iron-based sorbents such as hydrous ferric oxide [14], brick powder [15], laterite [16], goethite [17] and aluminum based sorbents such as alumina [18], activated alumina [19], bauxite [20] have been found to be an effective and environmentally friendly

sorbent for the removal of fluoride. Later, iron and aluminum based mixed hydroxides showed good adsorption capacities for fluoride removal [21].

Long lasting weathering, intensified by high temperature and rainfall in the tropics produces laterite from many diverse rocks such as schists, gneisses, migmatites, granites through the laterization process where iron is enriched with highly soluble alkali and alkaline earths and less silica. The chemical composition may vary from conakryte (Fe<sub>2</sub>O<sub>3</sub>·H<sub>2</sub>O·Al<sub>2</sub>O<sub>3</sub>), ferricrete (Fe<sub>2</sub>O<sub>3</sub>·SiO<sub>2</sub>·Al<sub>2</sub>O<sub>3</sub>·H<sub>2</sub>O), ortho-meta bauxite (H<sub>2</sub>O·Al<sub>2</sub>O<sub>3</sub>·Fe<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub>·Fe<sub>2</sub>O<sub>3</sub>) to latosols  $(SiO_2 \cdot Al_2O_3 \cdot H_2O \cdot Fe_2O_3)$  [22]. However, based on the parental rock composition, depth and climatic conditions, laterites show divergent chemical compositions [23]. Mineralogically, laterite is essentially a mixture of varying proportions of goethite, hematite, kaolin and gibbsite due to chemical alterations in weathering [22,23]. Being abundant in the tropics, laterite is commonly found in Sri Lanka and consists of higher concentrations of iron than in the Indian laterites [24].

Understanding the interactions between fluoride and laterite, will assist in predicting its adsorptive properties and provide an accurate description of fluoride mobility in the environment. Sarkar et al. [16] has studied the capability of laterite on fluoride adsorption. However, the surface complexation or mechanisms of adsorption have not been considered in any detail [16]. Also very few studies have attempted surface complexation modeling of the fluoride interaction with clay [25] but restricted to kaolinite and no

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involvement of IR methods in describing the fluoride adsorption behavior that are important environmentally. No effort has been made to study the sorption mechanism of fluoride on laterite along with the experimental investigations, which enables prediction of fluoride adsorption outside the range of calibration. Therefore, the objective of this study was to characterize the fluoride–laterite interface using experiments and surface complexation modeling in order to quantify the plausible laterite–fluoride surface complexes by a generalized diffuse layer model (DLM).

## 2. Experimental methodology

# 2.1. Materials

The laterite material obtained from southwestern part of Sri Lanka, was washed several times using distilled water to remove earthy impurities, air dried and ground using a ball mill. Then the powder was sieved to obtain the desired sieve size (63–105  $\mu$ m) for the experiments. X-ray fluorescence (XRF) and X-ray diffraction (XRD) analysis for the same fraction was performed by ARL 9800 OASIS X-ray spectrometer and Shimadzu XD-D1 diffractometer using Cu K $\alpha$  radiation ( $\lambda$  = 1.54 Å) radiation, respectively. Fourier transform infrared (FT-IR) spectral and X-ray photoelectron spectroscopy (XPS) analyses were carried out for raw laterite and fluoride sorbed laterite. FT-IR and XPS measurements were conducted using Nicolet 6700 spectrometer and Omicron ESCA Probe spectrometer with unmonochromatized Mg K $\alpha$  (energy = 1253.6 eV) X-rays, respectively. XPS spectra were calibrated by taking C 1s peak at 285.0 eV as an internal standard.

#### 2.2. Surface charge and area

Surface titration was carried out using 2 g/L laterite powder with three different ionic strengths (0.001, 0.01 and 0.1 M NaNO<sub>3</sub>). The suspension was equilibrated for 2 h prior to the potentiometric titration with desired NaNO<sub>3</sub> concentration as the ionic strength. Throughout the titration, N<sub>2</sub> was purged into the system to minimize CO<sub>2</sub> contamination. Orion EA960 auto-titrator was used to carry out the titration. Zero point charge (pH<sub>ZPC</sub>) of laterite was calculated based on the equilibrium concentration of protonated and deprotonated surface species. The surface area was then calculated based on the methylene blue method [26].

## 2.3. Batch experiments

Batch experiments were performed to determine the effect of pH, fluoride loading, adsorption kinetics and co-existing ions for fluoride adsorption on laterite. A stock solution of 1000 mg/L was prepared from NaF (Sigma–Aldrich) for the experiments. Laterite suspension of 2 g/L was equilibrated for 2 h and spiked with fluoride to obtain a final concentration of 25 mg/L. Then the system pH was decremented to ~4.0 and incremented at ~0.5 pH intervals up to 9.5. At each point, a 10 mL sample portion was transferred into polypropylene tubes and equilibrated for 24 h at 100 rpm (EYELA B603 Shaker). Final pH of the suspension was recorded, membrane filtered (0.45  $\mu$ m pore size) and directed to fluoride measurements with specific fluoride ion selective electrode (Orion 9409BN) by using an Orion EA960 auto-titrator.

A fluoride loading ranging from 1 to 1000 mg/L was used for adsorption isotherm experiments. The ionic strength was adjusted to 0.01 M of the 2 g/L laterite suspension, and equilibrated for 2 h. Adsorption isotherms were conducted at pH 5.0 since the maximum adsorption was recorded during adsorption edges. The laterite suspension of 10 mL was transferred to polypropylene tubes, fluoride spiked to desired concentrations and equilibrated



Fig. 1. XRD spectra of bare and fluoride loaded laterite.

for 24 h in the water bath shaker at 25 °C. After centrifugation, the supernatant was membrane filtered and measured for fluoride.

### 2.4. Surface complexation modeling

The surface-charging properties of the solid-solution interface have not been examined for laterite-fluoride interaction in terms of surface complexation assuming both 1-pK (surface =SOH, species  $\equiv$ SOH<sup>+1/2</sup>,  $\equiv$ SO<sup>-1/2</sup>) and 2-pK (species  $\equiv$ SOH,  $\equiv$ SOH<sup>+2</sup>, =SO<sup>-</sup>) approaches for the laterite-fluoride interface. When compared to the 1-pK model, the 2-pK approach is widely used, particularly on metal (hydro) oxides. In this case, the surface is hydroxylated in two consequent steps,  $\equiv$ SOH+H<sup>+</sup>  $\rightarrow \equiv$ SOH<sup>+2</sup> and  $\equiv$ SOH  $\rightarrow \equiv$ SO<sup>-</sup> + H<sup>+</sup>. The following factors further merit the selection of DLM for H<sup>+</sup> and fluoride adsorption data on laterite. Since the generalized DLM is capable of handling several surface sites simultaneously [27]. The DLM is both simpler and more versatile in that it corrects adsorption for ionic strength using Gouy-Chapman theory [28], it does not demand an input capacitance, and it demands the smallest number of input parameters [29]. Hence, this provides an excellent platform for the calculation of interfacial properties of laterite and its adsorption behavior.

# 3. Results and discussion

## 3.1. Characteristics of laterite solid material

The chemical composition of major elements was obtained using XRF. They were as follows;  $SiO_2$ : 21.13,  $AI_2O_3$ : 29.21,  $Fe_2O_3$ : 40.90, CaO: 2.22, MgO: 0.21, SO<sub>3</sub> 0.12, K<sub>2</sub>O: 0.02 and Na<sub>2</sub>O: 0.01%. The specific surface area determined by the methylene blue method was  $24 \text{ m}^2 \text{ g}^{-1}$ . These results are analogous to the findings by Partey et al. [31,34]. XRD results indicate that laterite is mainly composed of illite, gibbsite, goethite, hematite and kaolinite as dominant minerals. The XRD patterns of bare and fluoride loaded laterite are shown in Fig. 1. It is observed that there are significant changes in peak positions after fluoride adsorption, with some of the '*d*' spacing values in XRD spectra after fluoride adsorption indicates the formation of  $AIF_3$  (JCPDS No. 03 0355) and FeF<sub>3</sub> (JCPDS No. 02-0327). Similarly, Sujana and Anand [21] have observed corresponding peaks in their XRD study for the mixture of iron and aluminum oxides. SEM image of laterite is given in



Fig. 2. SEM (a), SEM-EDAX spectra of bare (b) and fluoride loaded laterite (c).

Fig. 2. The particles are very fine in size  $(1-40 \ \mu m)$  and irregular in shape. The energy dispersive X-ray (EDX) spectroscopy elemental analysis of fluoride adsorbed laterite provides direct evidence that the fluoride ions are adsorbed on the laterite surface (Fig. 2).

# 3.2. Zero point charge

Potentiometric titrations show the variation of surface charge of laterite,  $\sigma$ H suspensions as a function of pH in 0.1, 0.01, and 0.001 M NaNO<sub>3</sub> (Fig. 3). The titration data obtained in the pH range 4-9 were, therefore, taken for calculations. It is evident that the surface charge density is mainly controlled by the H<sup>+</sup> and OH<sup>-</sup> ions, which indicates that both surface hydroxyl functional groups of laterite, i.e., =AIOH and =FeOH, behave amphoterically. Experimentally obtained surface charge curves at different electrolyte concentrations cross at the zero point charge (pH<sub>ZPC</sub> value 8.72). Contrarily, Sarkar et al. [16] reported laterite with a low pH<sub>ZPC</sub> at 3.98. This difference may due to the disparity between the chemical composition of laterites as well as the sieve fraction. The laterite used in Sarkar's study [16] was dominated by  $SiO_2$  (=70%) and a very small quantity of Fe<sub>2</sub>O<sub>3</sub> (<4%) whereas in our laterite, SiO<sub>2</sub> is low and Fe<sub>2</sub>O<sub>3</sub> is dominant. However, several other studies on laterite have reported pH<sub>ZPC</sub> closer to our results, around pH 8.5 [30,31].

Only  $\equiv$ AlOH and  $\equiv$ FeOH sites, which are believed to abut from the surfaces of Fe or Al bearing minerals, are treated as active. The  $\equiv$ SiOH sites, were not considered in the calculations, since we envisaged that these sites were not readily available for surface



**Fig. 3.** Surface charge density ( $\sigma$ ) of laterite as a function of pH in different ionic strengths. Titrations were carried out under N<sub>2</sub> environment.

complexing. Laterite offers several sites for surface complexation. However, in order to have the best fit for the observed data one surface species alone did not work and hence the system was treated with two sites,  $\equiv$ AlOH and  $\equiv$ FeOH. The proton affinity constants and the site densities of  $\equiv$ AlOH and  $\equiv$ FeOH were obtained by numerical optimization using FITEQL [32]. Hence both  $\equiv$ FeOH and  $\equiv$ AlOH were considered for surface complexation modeling (reactions (1) and (2)). It is seen that the surface hydroxyl groups behave amphoterically.

Amphoteric reactions at the laterite surface can be suggested as follows;

$$\equiv XOH + H^+ \Rightarrow \equiv XOH_2^+ \tag{1}$$

$$\equiv XOH - H^+ \Rightarrow \equiv XO^- \tag{2}$$

where  $\equiv$ XOH<sub>2</sub><sup>+</sup>,  $\equiv$ XO<sup>-</sup> and  $\equiv$ XOH represent positively charged, negatively charged and neutral surface hydroxyl groups for laterite surface and  $\equiv$ X could either be  $\equiv$ Al or  $\equiv$ Fe.

The titration data were used to estimate the intrinsic acidity constants and site density of laterite using DDLM. The calculated data are shown in Table 1. As shown in the data (Table 1), the intrinsic acidity constants of  $\equiv$ AlOH sites were almost comparable to that of illite [33], and those of  $\equiv$ FeOH sites were similar to that of laterite [34]. However, Partey et al. [34] have not considered  $\equiv$ AlOH sites since their aluminum concentrations are very low. Moreover, the intrinsic acidity constants of different sites of laterite were averaged according to the procedure shown by Dzombak and Morel [27].

## 3.3. XPS and FT-IR analysis

The peaks at 74 (Al 2p), 710 (Fe 2p) and 103 (Si 2p)  $(\pm 0.3)$  eV correspond to oxides of Al, Fe and Si, respectively in the survey spectrum (Fig. 4a). Raw laterite did not show any peak in the survey spectrum around 680 eV (F 1s) while fluoride loaded laterite showed a peak in the region of 684.5 eV (Fig. 4b) which confirms the presence of fluorine as F<sup>-</sup>. XPS data provides an important indication of the dominant interaction of aluminum sites in fluoride

Tab	le 1			
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Physico-chemical properties of laterite used in FITEQL calculations.

Parameter	Value	Reference
Surface area Equilibrium constants	$24m^2g^{-1}$	This study
$HF = H^+ + F^-$	3.18	[46]
$HF_2 = H^+ + 2F^-$	3.76	[46]
$FeOH + H^+ \Leftrightarrow FeOH_2^+$	7.30	[34]
$FeOH \Leftrightarrow FeO^- + H^+$	-9.10	[34]
$AIOH + H^+ \Leftrightarrow AIOH_2^+$	5.5	[47]
$AIOH \Leftrightarrow AIO^- + H^+$	-6.2	[47]



**Fig. 4.** XPS survey spectra (a) and expanded F 1s regions (b) of bare and 10 mg/L fluoride sorbed laterite for 15 and 1 h under 0.01 M ionic strength with 2 g/L laterite.

adsorption (Fig. 4a). This has been shown by the relative shift of the aluminum peak of the XPS spectrum. Also, the fluoride loaded laterite, washed a few times with distilled water also showed a similar spectrum indicating that the laterite–fluoride interaction is strong and possibly arises from chemisorption.

In the –OH stretching vibration region (3700–3300 cm<sup>-1</sup>), the FT-IR spectra show six absorption bands at 3695, 3620, 3526, 3454, 3394 and 3375 cm<sup>-1</sup> (Fig. 5a). The stretching modes of –OH bands related to free water (around 3600 cm<sup>-1</sup>) and the bending mode of H–O–H band was also observable (around 1633 cm<sup>-1</sup>). The band at 3695 cm<sup>-1</sup> can be attributed to stretching vibrations of outer hydroxyl groups coordinated to iron, aluminum or silica [35] and the band at 3620 cm<sup>-1</sup> can be associated with inner hydroxyl groups [36]. The absorption band near 3400 cm<sup>-1</sup> is reported by the hydroxyl bonded to trivalent cations such as Al<sup>3+</sup> or Fe<sup>3+</sup> [36]. Therefore, the bands at 3526, 3453, 3394 and 3375 cm<sup>-1</sup> indicate some portion of Al<sup>3+</sup> or Fe<sup>3+</sup> in the octahedral layer of laterite. In the region of 1200–900 cm<sup>-1</sup>, the FT-IR spectra display bands

In the region of 1200–900 cm<sup>-1</sup>, the FT-IR spectra display bands at 1098, 1012 and 968 cm<sup>-1</sup> originated by stretching vibrations of the Si–O–Si bonds [37]. Two bands at 1012 and 968 cm<sup>-1</sup> can be representative of Si–O in-plane stretching vibrations [38] while the band at 1032 cm<sup>-1</sup> may represent Al–O bond. Bands located at 799 and 939 cm<sup>-1</sup> may be attributed to Si–O bonds linked with trivalent cations (e.g., Al<sup>3+</sup>, Fe<sup>3+</sup>), thus, the presence of absorption bands at 799 and 939 cm<sup>-1</sup> indicates the occurrence of tetrahedrally coordinated trivalent cations in laterite.



Fig. 5. FT-IR spectra of bare and fluoride treated laterites in the regions of 400-4000 and 400-900 cm<sup>-1</sup> (a and b, respectively).

FT-IR spectrum of the fluoride adsorbed laterite shows (Fig. 5b) an evidence for increased hydrogen bonding, indicated by the broadening of the OH stretch features around 3300 cm<sup>-1</sup>. Most of the IR bands correspond to metal oxygen bonds (M–O) and metal hydroxide bonds (M–OH) show small wave number shifting to high wave number, after fluoride adsorption. The disappearance of bands at 558, 667, 778 and 799 cm<sup>-1</sup> indicates that the stretching and bending modes of M–O are affected by fluoride interaction on laterite surface.

# 3.4. Adsorption edges

Fluoride adsorption on laterite in the pH range from 4 to 10 as presented in Fig. 6 is based on 3 different ionic strengths. Although the adsorption is found to be influenced by solution pH, no such influence is found from the ionic strength. In all electrolyte concentrations, the percentage removal demonstrates a similar decrease in adsorption. No marked variation of adsorption based on the ionic strength indicates an inner-sphere complexation mechanism indirectly [39]. This has also been observed in FITEQL simulations (solid lines in Fig. 6). Desorption experiments well supported this data.



**Fig. 6.** Adsorption of fluoride with laterite in different pH at three different ionic strengths.

### Table 2

Optimized FITEQL results obtained for laterite-fluoride interaction.

Parameter	Value					
	0.1 M NaNO <sub>3</sub>	0.01 M NaNO3	0.001 M NaNO3	Weighted mean <sup>a</sup>		
Site density						
FeOH	$7.000  imes 10^{-4}$	$6.510  imes 10^{-4}$	$6.000  imes 10^{-4}$	$6.456 imes10^{-4}$		
AIOH	$8.003\times10^{-5}$	$8.000  imes 10^{-5}$	$8.000 \times 10^{-5}$	$8.000  imes 10^{-5}$		
Log K						
Protonation reactions						
$FeOH + H^+ \Leftrightarrow FeOH_2^+$	8.883	7.200	5.042	7.939		
$FeOH \Leftrightarrow FeO^- + H^+$	-4.540	-4.027	-3.622	-4.242		
$AIOH + H^+ \Leftrightarrow AIOH_2^+$	6.999	6.908	4.851	6.675		
$AIOH \Leftrightarrow AIO^- + H^+$	-6.719	-6.729	-5.544	-6.729		
Surface reactions						
$FeOH + F^- + H^+ \Leftrightarrow FeF + H_2O$	13.200	12.630	13.930	13.200		
$AIOH + F^- + H^+ \Leftrightarrow AIF + H_2O$	17.600	18.570	20.000	18.059		

<sup>a</sup> Weighted averages were calculated using  $\log K = \sum \omega_i (\log K)_i$  where  $\omega_i = (1/\sigma_{\log K})_i / \Sigma(1/\sigma_{\log K})_i$ , where  $\sigma_{\log K}$  is the standard deviation obtained from FITEQL calculations.

Fluoride interaction with laterite surface may happen electrostatically, through protonated iron and aluminum hydroxyl sites or via ligand exchange with the uncharged surface sites [25]. XPS investigations of distilled water washed fluoride loaded laterite (consecutive stirring, 20 min and washing, 3 times) indicated that the laterite–fluoride interaction was strong and fluoride is well sorbed to laterite surface by no change in XPS spectra. This has been denoted by XRD and FT-IR spectra as well showing the formation of =AIF and =FeF complexes (Figs. 1 and 5).

High adsorption of fluoride was observed at low pH levels (pH < 6.5). At pH < pH<sub>ZPC</sub>, most of the surface sites are positively charged and attract negatively charged fluoride by electrostatic interaction. Compared to the results of Sarkar et al. [16], our fluoride adsorption results showed high values probably due to the presence of a higher percentage of  $\equiv$ FeOH and  $\equiv$ AlOH sites. On further increase of pH, fluoride adsorption on laterite remains constant due to the change of the electrostatic charge of laterite surface.

Selection of fluoride surface species was done based on the XRD, FT-IR spectra and previous studies. As the spectral information showed the formation of  $\equiv$ AlF and  $\equiv$ FeF complexes and the rapid exchange with hydroxyl ions the multidentate complex formation was not considered in this modeling framework similarly in other cases [12,17,40-43]. This is possible due to the replacement of fluoride ion with the hydroxyl ion at the surface sites due to the ionic similarity. Although fluoride can form monodentate, multidentate, inner-sphere and outer-sphere complexes, multidentate and outer-sphere complexes were neglected due to the reactivity of fluoride and the system pH > 4 and also due to the fact that DDLM is not able to model outer-sphere complexes. One another reason behind this was the limitations of the model to incorporate both monodentate and multidentate species for 2 surface sites. It can also be suggested that fluoride adsorption is favored if the adsorbent is positively charged at low pH. Furthermore, relative to the surface complexation model taken into account, positively charged  $\equiv$ AlOH<sub>2</sub><sup>+</sup> and  $\equiv$ FeOH<sub>2</sub><sup>+</sup> laterite sites and negatively charged F<sup>-</sup> ions can form surface complexes. Similar results were observed by Sposito [48] for fluoride adsorption on soils. Furthermore, laterite surface hydroxyl groups  $(OH^{-})$  can be replaced by fluoride  $(F^{-})$  ions due to the similarity of ionic potential. Hence only the following reactions were considered in modeling laterite-fluoride interface interactions. Considering the above factors and based on previous literature on the adsorption experiments and surface complexation modeling of fluoride on laterite, we used reactions (3) and (4) for DDLM calculations.

Thus the possible reactions of fluoride into laterite are suggested via the ligand exchange mechanism of uncharged surface sites;

$$\equiv AIOH + H^+ + F^- \Rightarrow \equiv AI - F + H_2O \tag{3}$$

$$\equiv FeOH + H^+ + F^- \Rightarrow \equiv Fe - F + H_2O \tag{4}$$

The stability constants calculated from each electrolyte concentration set, average and weighted mean are compiled in Table 2. Inclusion of both stoichiometries exhibited a good fit with the experimental results. Although  $\log K$  values are slightly different for  $\equiv$ Fe sites, the affinity to  $\equiv$ Al sites was shown to be higher in the FITEQL results. Simulations were based on the monodentate binuclear mechanism. Although we incorporated monodentate binuclear mechanism to FITEQL convergence did not occur. Also, modeling results demonstrated that the fluoride ion shows more attraction towards aluminum sites than iron sites of the laterite surface which was later supported by XPS data.

## 3.5. Effect of fluoride loading on adsorption

The decrease in fluoride sorption affinity with increasing fluoride concentration is clearly seen in the constant pH isotherm plot (Figure S1). The agreeable fits of experimental data to an isotherm model do not essentially provide conclusive evidence for the actual adsorption mechanism but they do provide (indirect) evidence for site heterogeneity and/or surface heterogeneity. The slopes of logarithmic plots of anions were always less than or equal to 1 [27]. In this study, the data were plotted in the log-log scale to identify the adsorption mechanism based on Langmuir and Freundlich equations. When a single type binding site is present, as in the case of gibbsite or goethite, the Langmuir isotherm is linear at low concentrations and levels off at higher concentrations. The Freundlich isotherm applies to solid surfaces with different affinities. The linear form of Freundlich adsorption isotherm takes the following form:

$$\log \Gamma_{ads} = \log k_f + \frac{1}{n} \log M \tag{5}$$

where  $\Gamma_{ads}$  is the adsorption density (mol m<sup>-2</sup>); *M* is equilibrium concentration (mol m<sup>-3</sup>); *n* is affinity of the adsorbent for the adsorbate and  $k_f$  is Freundlich coefficients related to the absorbent capacity (mol m<sup>-2</sup>/(mol m<sup>-3</sup>)<sup>1/n</sup>).

Therefore, the models fitting with the Freundlich isotherm can be considered to have multilayer adsorption as well as surface heterogeneity [44]. With multiple sites, sorption affinity varies as higher-affinity sites are filled and more abundant lower affinity sites become dominant. In this perception, the amount adsorbed is the summation of adsorption on all sites, with the stronger binding sites being occupied first, until the adsorption energy is exponentially decreased upon the completion of the adsorption process. This system is represented by the Freundlich isotherms corresponding to straight lines with slopes <1.0 on log–log scale (Figure S1). This implies that the multisite adsorption on laterite surface supports rather high retention of fluoride from water. The slope ranges between 0 and 1 is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero. In our study the slope or 1/n of an adsorption isotherm study, is 0.65. Whereas, a value below unity implies chemisorption process [45]. This evidence is supported by the spectroscopic data. The constants  $k_f$  and n were calculated from Eq. (5) and Freundlich plots (Figure S1). The values for Freundlich constants and correlation coefficients ( $r^2$ ) for the adsorption process are  $1.83 \times 10^{-5}$  and 0.988 respectively. The values of n between 1 and 10 (i.e. 1/n less than 1) represent a favorable adsorption [45]. The 1/n values obtained for the adsorption process represented a beneficial adsorption.

## 4. Conclusion

Laterite used in this study was rich in iron and it showed high zero point charge around pH 8.72 which was modeled as being close enough by the diffused double layer (pH 8.9). Results also indicate that the fluoride adsorption reaches a maximum when the pH is close to 5, and then decreases with further increase of pH. Despite the concentration of the background electrolyte used, laterite fluoride interaction was always interpreted in terms of chemisorption. In both single and dual site systems, fluoride sorption was modeled successfully using DDLM as monodentate mononuclear interaction. The involvement of two sites for adsorption was also indicated by the isotherm modeling. Adsorption of fluoride has resulted in changes as disappearance of bands, shifts and decreases in the percentage of transmittance in the IR and XPS spectra of the solid surface demonstrating high affinity to aluminum sites of all sorbents. Combining surface complexation modeling, FT-IR and XPS data with batch experiments it can be concluded that the laterite-fluoride interaction is strong chemisorptive surface complexation.

## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.colsurfa.2012.02.011.

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