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Fluoride adsorption onto an acid treated lateritic mineral from Kenya: Equilibrium studies

Enos W. Wambu[1,2*], Charles O. Onindo[2], Willis J. Ambusso[3] and Gerald K. Muthakia[4]

[1]Department of Chemistry, Bondo University College, P. O. Box 210 -60401, Bondo, Kenya.
[2]Department of Chemistry, Kenyatta University, P. O. Box 43844 -00100, Nairobi, Kenya.
[3]Department of Physics, Kenyatta University, P. O. Box 43844 -00100, Nairobi, Kenya.
[4]Department of Chemistry, Kimathi University College of Technology, P. O. Box 657 -10100 Nyeri, Kenya.

Adsorption of fluoride (F) ions from water using acid treated lateritic mineral (LM-1) from Kenya was studied by batch experiments. The effect of acid-treatment of adsorbent and change in temperature, mass of LM-1, pH and selected competing ions was evaluated. The adsorption process was strongly influenced by temperature, pH and adsorbent dosage. The percentage F removal increased the presence of the nitrate and the chlorate ions but decreased the presence of sulphates, chloride and phosphate ions. Adsorption isotherms were classified according to Giles' classification and the adsorption data validated using Langmuir and Freundlich isotherms. The data correlated to both the Langmuir and Freundlich isotherms although the data fit to the Freundlich model was somehow better. This showed that F adsorption onto LM-1 followed a mixed adsorption mechanism in which physisorption reactions involving intra-particle diffusion of F into mesoporous sites in LM-1 became increasingly important at higher concentrations and temperatures whereas ion-exchange mechanism involving surface OH⁻ appear to dominate at low surface coverage in more alkaline conditions. With maximum adsorption capacity of 10.5 mg/g, LM-1 could be used to remove F water.

Key words: Equilibrium analysis, fluoride adsorption, Langmuir and Freundlich isotherms, Lateritic mineral adsorbent, low-cost adsorbents.

INTRODUCTION

Although the subject of excess fluoride in water sources and its associated socio-economic and public health problems has been extensively discussed in relation to a number of areas in Kenya (Wambu and Muthakia, 2011; Kahama et al., 1997), the corresponding remediation measures have not received similar interest in the country. Nevertheless, recent rapid population growth (Imbernon, 1999) and adverse changes in rainfall patterns in the region have exacerbated levels of water scarcity and aggravated hazardous effects of excess fluoride in water sources (Showers, 2002). This has

made the need for interventional defluoridation measures even more pressing.

Technologies for F removal from water include: adsorption on commercial activated carbons and alumina (Chaturvedi et al., 1990), ion-exchange (Singh et al., 1999), electrodialysis (Amor et al., 2001), reverse osmosis and solar distillation (Ali et al., 2010). Most of these techniques are however unusable in rural areas of developing countries because of inadequate infrastructure, lack of energy and economic constraints. Adsorption techniques using low-cost natural and waste material adsorbents including clays and several biomass adsorbents have emerged as important alternative protocol. Coetzee et al. (2003) had shown that iron and aluminium oxide-based materials are most important in

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*Corresponding author. E-mail: wambuenos@yahoo.com.

Table 1. Main chemical compositions of LM-1.

Component	Percentage (%)
SiO_2	28.2
Al_2O_3	18.8
MgO	0.24
K_2O	0.36
TiO_2	0.77
MnO	3.00
Fe_2O_3	37.2
LOI (Lose on ignition)	13.9

the removal of F from aqueous solutions. Chen et al. (2010) has indicated that F adsorption onto FeOH-based adsorbents proceeds by surface exchange replacement of OH groups by F ions or by inner sphere complexation with FeOH surfaces but a more extensive examination of mechanistic behaviour of FeOH adsorbents has been provided by Waychunas et al. (2005).

However, while fluoride adsorption onto low cost soils and clay adsorbents including: fly ash (Chaturvedi et al., 1990) siderite (Liu et al., 2010), attapulgite (Zhang et al., 2009), coal (Borah and Dey, 2009), Boehmite (Ramos et al., 2008), goethite (Jinadasa et al., 1993) kaolinite (Gogoi an Baruah, 2008), bentonite (Karthikeyan et al., 2005), zeolites (Onyango et al., 2004), calcite (Min et al., 1999), and ceramic materials (Chen et al., 2010) have been extensively studied, many Kenyan clays and soils have not yet been assessed for their potential use as F sorbents. This study, based around Gilgil in Nakuru County of Kenya, therefore, evaluated the capacity of an Fe-rich lateritic clay minerals from Kenya for F removal from aqueous solution. The effect of solution parameters including the pH, temperature, concentration and competing anions was evaluated and adsorption isotherms used to characterize and validate the adsorption equilibriums.

MATEREIALS AND METHODS

The adsorbent materials were collected from road side quarries along Kimaeti-Mianga Road in Bungoma County, Kenya. They were ground to pass through <1 mm mesh and activated by agitating 100 gram portions of the material in 1000 mL aqueous aliquots containing 0.1 *N* HCl for different time intervals of between 5 and 240 min. At the end of the agitation period, the mixtures were filtered and dried in an oven at 110°C overnight. The mineralogical analysis on the soil samples was carried out by X-ray powder diffraction (XRD) using P Analytical X' pert PRO PW-3040/60 with Cu Kα radiation at a scan speed of 1.2° min[-1] over a range of 5 to 70° and elemental analysis by spectrophotometric techniques on a Varian Spectra Model 10.

The adsorption experiments were performed as follows: A given mass of acid pre-treated adsorbent was placed in a known volume

of the adsorbate solution of known F concentration (20 to 1000 mg/L) and pH (1.59 to 7.68) and the mixture agitated on a water bath at preset temperature (293 to 333 K) for selected time length (5 to 120 min). At the end of shaking, a 10 mL portion of the soil slurry was withdrawn and centrifuged. The fluoride concentration of the supernatant solution was determined using a Tx EDT Model 3221 fluoride ion-selective electrodes according to a procedure used by Kahama et al. (1997) and the adsorbed amount, *qe* (mg/g), determined according to the appropriate literature (Wambu et al., 2011).

RESULTS AND DISCUSSION

Characterization of adsorbent materials

Spectrophotometric results (Table 1) and x-ray diffraction analysis (Figure 1) showed that the main minerals composition in LM-1 were of Haematite (Fe_2O_3), Gothite (FeO(OH)), quartz (SiO_2) and crystobalite (SiO_2). The chemical composition showed that the adsorbent had a stable (low-exchangeable-cations) mixed sorptive surface which was high in alumino-silicate, 47.0%, as well as high-affinity iron and Manganese oxide based surfaces, 40.2%. It was therefore anticipated that the material would exhibit high F adsorption capacity (and affinity) due to high proportion of iron (hydr)oxide levels (Chen et al., 2010). The high chemical and surface heterogeneity in the material showed that the adsorbent could exhibit mixed adsorption mechanism. The high surface stability also meant that the materials could be applied in a wide range of aqueous conditions without significant adsorbent loss and surface deterioration through dissolution. It was clear therefore that the material could form a plausible adsorbent for the removal of F from aqueous media.

Effect of acid activation

As can be seen from Figure 2, the percentage fluoride adsorption increased rapidly with increasing time of acid activation from just about 20% for untreated materials to about 80% after 30 min pre-treatment of the adsorbent with 0.1 *N* HCl. Then, there was no significant change in F uptake by the material even after increasing time of contact of the adsorbent with the acid to 240 min.

The rapid increase in F adsorption capacity of the material on pre-treatment with the acid showed that when the adsorbent is placed in the acid, the surface sites in the materials were quickly protonated increasing the overall surface positive charge and potential for F adsorption.

As expected, there was no significant change in F uptake of the material when acid pre-treatment time was increased above 30 min. This shows that there was little or no structural damage to the material by the acid during
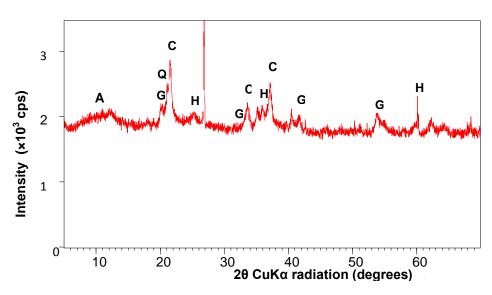
Figure 1. XRD pattern of Lateritic mineral adsorbent material (LM-1), Q=Quartz, C=Cristobalite, G= Goehtite, H = Haematite, A = Contribution from Amorphous matrix.
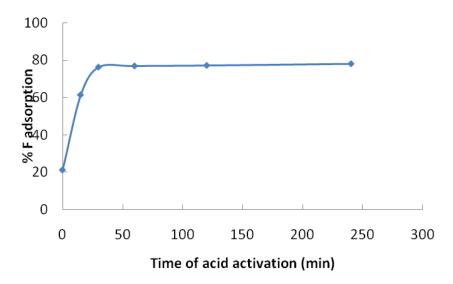

Figure 2. Effect of acid activation on LM-1 adsorption of F from 1000 mg/L F solution using 2 g per 10 mL adsorbent dosage at 297 K.

pre-treatment as earlier postulated in section 3.1 and that observed activation of LM-1 was therefore only limited to surface modification of the adsorbent by protonation of the reactive sites. A 30-min contact time with the acid, which was then employed in all subsequent tests, was therefore adequate to activate LM-1 for F adsorption.

Effect of adsorbent dosage

The effect of LM-1 dosage on its removal of F from solution was studied by varying the mass of LM-1 from 0.5 to 8 g while maintaining the volume (20 mL) and concentration of adsorbate (1000 mg/L) of F solution constant. The results of these tests are shown in Figure 3.

Fluoride adsorption increased rapidly with increasing mass of LM-1 and remained constant at 80% above 4 g per 20 mL adsorbent dosage. This shows that at low adsorbent dosage the number of available sites increased with the mass of LM-1. However, it is clear that as the mass of LM-1 was increased, less and less F
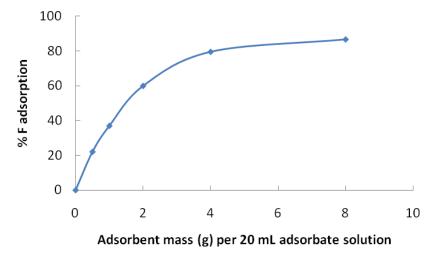
Figure 3. Effect of change in mass of LM-1 on its adsorption of F from 1000 mg/L F solution at 297 K.
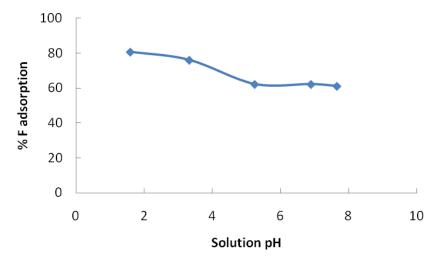

Figure 4. Effect of solution pH on F adsorption onto LM-1 from 1000 mg/L F solution using 2 g per 10 mL adsorbent dosage at 297 K.

particles in the solution could access sorptive sites in the adsorbent resulting in gradual decrease in F surface loading in LM-1. This indicates that at higher adsorbent dosage, the colloid particles of LM-1 aggregate reducing available sorptive sites in solution. It means that acid treatment of LM-1 greatly increased the positive charge density on LM-1 surface creating reactive sites required for anionic adsorption. New protonated sites then facilitated interlinking hydrogen bonds between individual LM-1 colloids leading to high aggregation at high LM-1 dosage in the adsorption mixture. High F removal percentages recorded in this work show that LM-1 could effectively be used to adsorb F from aqueous solutions.

Effect of solution pH

The effect of pH on F adsorption onto LM-1 was studied at initial solution pH values between 1.59 and 7.68 while maintaining other solution parameters including temperature, concentration and adsorbent doses constant and the results presented in Figure 4.

Figure 4 shows that percentage F adsorption decreased with increasing solution pH from about 80% at pH 1.59 to 60% at pH 5.24 and remained constant to pH 7.68. The F adsorption onto LM-1 was therefore more favourable in acidic pH because of high protonation of surface sites which are normally responsible for anion
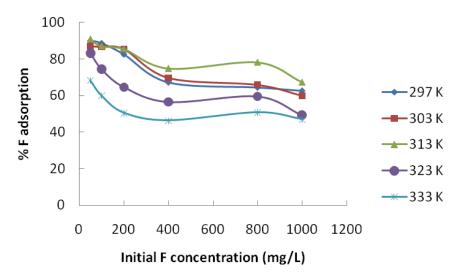
Figure 5. Effect of solution temperature on LM-1 uptake from 1000 mg/L F solution using 2 g per 10 mL solution.

adsorption. As the solution pH increases simultaneous deprotonation and hydroxylation of LM-1 surface reduces fluoride binding sites while increasing surface coulombic repulsions for F. As a result, F adsorption onto LM-1 reduced significantly between pH 3.32 and 5.24. The apparent equilibrium attainment between pH 5.24 and 7.68 indicated that ion-exchange reactions involving surface hydroxyl groups and solution F ions could be the main sorption mechanism at this pH values. The solution pH therefore played an important role in controlling F adsorption on LM-1. We noted that more than 60% F (corresponding to 6.0 mg/g F surface concentration) could be adsorbed at pH values $\geq$ 5.24 indicating that the fluoride-hydroxyl-equilibrium at LM-1 surfaces favoured adsorption of F over OH^- at the LM-1 surfaces. This shows that LM-1 has higher affinity for F than OH^- ion and the adsorbent could therefore be used to adsorb F from aqueous media over a wide range of pH values. Nonetheless, highest F adsorption was recorded within acidic pH values and therefore subsequent tests were carried out at ambient surface pH of the acid treated-materials which was about 3.32.

Effect of temperature and initial F concentration

The effect of change in solution temperature on F adsorption onto LM-1 was then studied at temperatures ranging from 293 to 333 K and the results depicted in Figure 5.

Fluoride adsorption increased with increasing temperature from about 70% (for 400 mg/L initial F concentration) at 297 K to about 75% at 313 K and then steadily dropped to 50 % at 333 K. These variations were well pronounced for initial F concentrations between 200 and 800 mg/L. The initial increase in adsorbate uptake can be ascribed to increase in energy of the adsorbate particles with increase in temperature which meant that more F ions could attain required activation energy for adsorption thereby resulting in more adsorptions than at lower temperature. Eventual decline in adsorption when the temperature is further increased has been attributed to thermo-degradation of sorptive sites (Al-Asheh and Duvnjak, 1995). The highest percentage adsorptions of F onto LM-1 could be achieved at 313 K. This temperature was then adopted for the rest of the adsorption tests.

Effect of other anions

Consequently, the effect of other potential competing anions including the chlorate, chloride, nitrate, phosphate and sulphate on F adsorption by LM-1 was evaluated and the results presented in Figure 6.

We observed that fluoride removal slightly increased in the presence of NO_3^- and ClO_4^- but decreased in presence of the SO_4^{2-}, Cl^- and the PO_4^{3-}. Chen et al. (2010) observed that fluoride adsorption onto a ceramic adsorbent increased in presence of Cl^- and NO_3^- and decreased in presence of the SO_4^{3-}, CO_3^{2-} and PO_4^{3-} ions. They explained increased F uptake in presence of some anions on the rise in the ionic strength and a reduction in repulsive interactions of the adsorbed F ions on the adsorbent surface. It is apparent therefore that the influence of other anions on F adsorption on clay adsorbent may vary from adsorbent to adsorbent
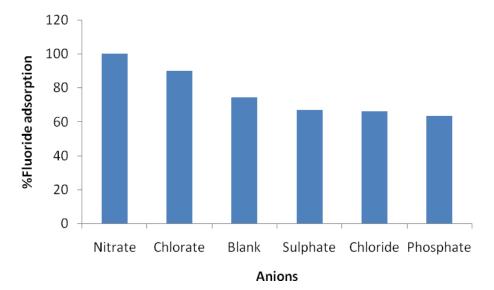
Figure 6. Effect of different anions on adsorption of F onto LM-1 from a 1000 mg/L F solution at 2 g per 10 mL adsorbent dosage and 297 K.

depending on the dominant mineralogical, chemical and surface characteristics of the material. Other than the adsorbent properties affecting the influence of anionic species on F adsorption, different solution matrixes may amplify or diminish certain properties of the anions including, ease of mobility in the aqueous media and through the electrochemical double layer close to the adsorbent surface, adsorption affinity and degree of surface coulombic repulsions relative to the adsorbate ion.

Equilibrium analysis

Bulk adsorbate concentration is often the main driving force of an adsorption process. The influence of F concentration on its adsorption onto LM-1 was studied using NaF solutions containing F ions between 50 and 1000 mg/L at pH 3.32, 0.2 g/mL adsorbent dosage and temperatures between 293 and 333 K. As could be seen from Figure 3, %F adsorption rapidly decreased with increasing adsorbate concentration before a very gradual approach to initial equilibrium at 400 mg/L. The percentage F removal then remained constant to 800 mg/L F before a further decline at 1000 mg/L F. This shows that at low concentrations, aqueous F is quickly sorbed to high affinity exposed sites in the adsorbent which are quickly exhausted as the F concentrations approach the 400 mg/L. However, at this point more sorptive sites become available which steadily remove F from solution maintaining a constant partition of the adsorbate between the solid and solution up to 800 mg/L

concentration.

Therefore, to clarify this observation, adsorption isotherms were constructed by plotting equilibrium F adsorption, q_e (mg/g) versus equilibrium concentration of F in the aqueous phase, C_e (mg/L) at various temperature conditions and the results presented in Figure 7.

Indeed the isotherms were typically L4 type with two adsorption plateaus indicating heterogeneity in LM-1 surface. It was clear that the adsorbent consisted of two types of sites at which F ions adsorbed in succession. This helped to clarify why upon saturation of surface sites in the material, the F uptake by the mineral increased rapidly with increasing initial concentration between 400 and 800 mg/L. It showed that new sorptive sites were made available as more and more F adsorbed. It can be assumed that that LM-1 has a highly porous structure and that at higher concentrations F ions were able to access more sorptive sites in the mineral which were inaccessible to other particles in the aqueous system. The second plateau was clearer at higher temperatures indicating that the second adsorption phase; favoured at high temperatures could be endothermic in nature and diffusion-controlled.

As expected, the action stops at 1000 mg/L initial F concentration when the mesoporous site in the material get used up (Giles et al., 1960). This analysis indicated that whereas ion-exchange reactions involving surface hydroxyl ions could be the underpinning process at lower surface coverage in acidic media, intra-particle diffusion of F into mesoporous sites of the material played a more significant role in F adsorption onto LM-1 at higher F concentrations, higher pH and higher temperatures.
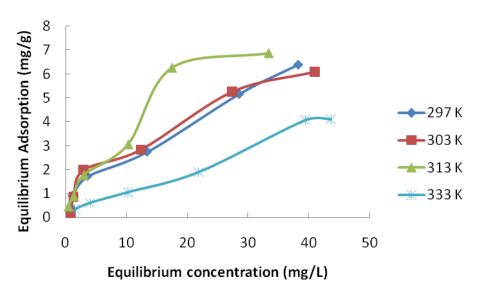
Figure 7. Adsorption isotherms for F uptake by LM-1 from 1000 mg/L F solution at pH 3.32 using 0.2 g/mL adsorbent dosage and 297 -333 K.
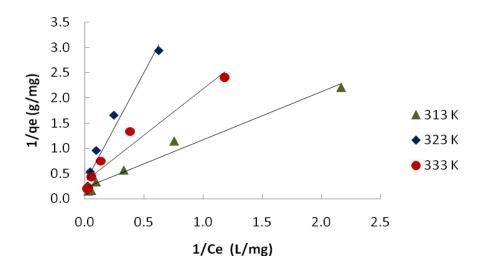

Figure 8. Langmuir adsorption isotherms for F adsorption onto LM-1 at 313 K,   323 K and 333 K.

To further validate the adsorption data, the Langmuir and Freundlich isotherm equations were applied to the adsorption results in the form:
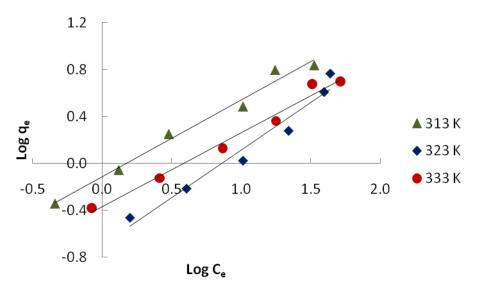
$$^1\!/q_{eq} = {}^1\!/bq_{max}C_{eq} + {}^1\!/q_{eq} \tag{1}$$

$$\log q_{eq} = \log K_f + n \log C_{eq} \tag{2}$$

respectively, where q_e is the amount of fluoride ion adsorbed per unit mass of the adsorbent and C_e is the amount of fluoride ion in liquid phase at equilibrium. K_f, n, q_{max} and b are well known Langmuir and Freundlich constants, respectively. Figure 8 and 9 show some of the resulting   isothermal   plots   and   the   corresponding isothermal constants are presented in Table 2.

The data correlated to both the Langmuir and Freundlich   isotherms   with   correlation   coefficients averaging 0.9514 for the Langmuir and 0.9658 for the Freundlich isotherm. This showed that the data fit to the Freundlich   model   was   somehow better. The   high

Figures 9. Freundlich adsorption isotherms for F adsorption onto LM-1 at 313 K, 323 K and 333 K.

Table 2. Langmuir and Freundlich isotherm constants.

Temperature (K)	Langmuir constants			Freundlich constants		
	$q_{max\ (mg/g)}$	b (L/mg)	R^2	$K_{f\ (mg/g)}$	N	R^2
297	7.9619	0.0764	0.9175	0.6353	1.6145	0.9581
303	10.4792	0.0524	0.9515	0.6322	1.6526	0.9455
313	4.78215	0.2192	0.9781	0.7684	1.5241	0.9831
323	2.9998	0.1815	0.9495	0.4244	1.5827	0.9831
333	3.32705	0.0685	0.9606	0.1976	1.2274	0.9595

correlation coefficients in both cases were consistent with heterogeneity in LM-1 surface sites discussed in preceding paragraphs in this section and in section 3.1. The R^2 values confirmed that more Freundlich surfaces became available at higher F concentrations and at elevated temperatures. This showed that F adsorption onto LM-1 follows a mixed adsorption mechanism in which Freundlich physisorption reactions involving intra-particle diffusion of F into mesoporous sites in LM-1 become more important at higher concentrations and temperatures whereas ion-exchange with surface OH^- appear to dominate at low surface coverage in alkaline conditions.

The q_{max} values calculated using Langmuir isotherm compared well with F uptake values obtained experi-mentally indicating that the Langmuir constants could be used to represent F uptake by LM-1 at lower concentrations. Thus, Langmuir F adsorption capacity, q_{max}, of LM-1 was compared with those of other low-cost adsorbents in the literature and presented in Table 3.

Although the adsorption capacity of LM-1 was lower when compared to that of modified attapulgite, it was found to be higher than that of silica, activated alumina, synthetic siderite, ceramic adsorbent and montmorillonite. According to Weng et al. (2007), differences in adsorption capacities of adsorbents arise from variation in surface, chemical and structural properties of the adsorbents as well as from experimental conditions employed. Chen et al. (2010) have demonstrated that the F adsorption capacity of clay adsorbents is correlated to the iron and aluminium content of the adsorbent. It can be deduced that the high fluoride adsorption capacity of LM-1 obtained in this work is due in part to the high Fe content in the material and the acid pre-treatment protocol employed in preparation of the adsorbent. The results in this study have shown that acid activated lateritic material, obtainable from parts of Kenya can be used to treat F contaminated water safely and cheaply. The material which is found in abundant deposits in many other areas in the tropics can be obtained from the

Table 3. Comparison of LM-1 with that of various low-cost adsorbents.

Adsorbent	q_{max} (mg/g)	Source
Modified attapulgite	11.1-44.0	Zhang et al., 2009
Acid activated lateritic mineral	3.00-10.48	This work
Activated alumina	2.69-8.27	Ramos et al., 2008
Synthetic siderite	1.41-3.79	Liu et al., 2010
Ceramic adsorbent	2.16	Chen et al., 2010
Montmorillonite	1.49-1.91	Karthikeyan et al., 2005

natural deposits cheaply and requires minimal preparation to generate the chemically stable and highly sorptive surface suitable for anionic adsorption.

Conclusion

The sorptive surface in LM-1 was strongly enhanced by acid treatment in dilute HCl and it was not adversely affected by prolonged exposure to the acid showing that it was chemically stable and could be used to adsorb F in a wide range of aqueous conditions. Although the actual F adsorption onto LM-1 was highly dependent on the mass of the adsorbent, pH and temperature, it was observed that the material could sorb F equally well in a wide range of pH and temperature conditions because the mechanism of F uptake appeared to change with concentration, temperature and pH due to high heterogeneity in the adsorbent surface. The F adsorption isotherms conformed to L4 type according to Giles' classification of isotherms confirming this heterogeneity. The adsorption data was therefore correlated to both the Langmuir and the Freundlich isotherms with the later model posting a better fit. It was obvious therefore that physisorption played a more dominant role in F adsorption onto LM-1 at high concentrations and temperatures but ion-exchange mechanisms involving surface OH groups were more dominant at low concentrations, lower temperatures and higher pH values. A high adsorption capacity of 10.5 mg/g was recorded at 303 K showing that LM-1 could be used as an efficient low-cost adsorbent for the removal of F from water.

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