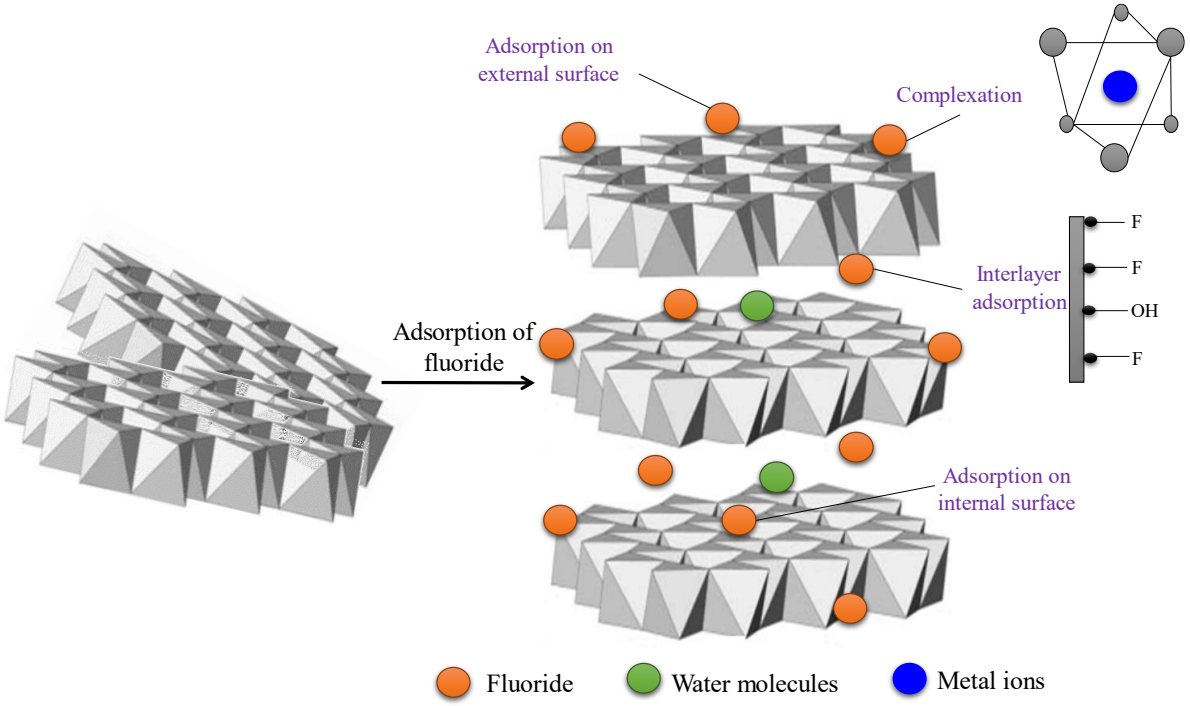
Chapter 4

a) Adsorption of fluoride using Al-Zn-Zr Hydrotalcite



4a.1 Introduction

Layered Double Hydroxides (LDHs), also known as hydrotalcite like compounds or anionic clays, have gain considerable attraction in recent years due to the presence of large interlayer spaces, positively charged layers and exchangeable anions in the interlayers (Behrens et al., 2010). The chemical composition of LDHs can be expressed by the general formula $[M^{2+}_{(1-x)} M^{3+}_{x}(OH)_2]_x+[A_x/n^-]_x \cdot mH_2O.]$ (Li et al., 2010). The divalent cations M^{2+} (Ca^{2+}, Mg^{2+}, Zn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, etc.) are partially substituted by trivalent ones M^{3+} (La^{3+}, Al^{3+}, Fe^{3+}, Co^{3+}, Mn^{3+}, Ni^{3+}, Cr^{3+}, etc.), or tetravalent M^{4+} (Zr^{+4}) for generation of a positively charged layer [2,3]. As a consequence, anions can be intercalated into the interlayer space of the LDHs to maintain charge neutrality (Li et al., 2010). The surface property of the hydrotalcite can be modified by introducing different anions in the interlayer regions (Ramkumar & Abathodharanan, 1997). The crystallinity and textural characteristics of both fresh and calcined samples are significantly influenced by the nature of interlayer anions. The nature of the anions also affects the order of the cation distribution like CO_3^{2-}> Cl^->NO_3^->SO_4^{2-} (Ramkumar & Abathodharanan, 1997).

The interest in hydrotalcites is due to their huge potential in a variety of applications as ion exchangers, absorbents, CO_2 capture, carrier of bioactive molecules, catalyst and catalyst support due to their high surface area, structural stability and phase purity. The lamellar structure of hydrotalcite like compounds is longitudinally stable which aids the metal ions and fluoride binding/contact during the adsorption. Thus, the charge transfer at the interface increases (Y. Wei et al., 2022). Moreover, the main layer of its surface contains hydroxyl groups which tend to bind with cations is many ways like hydrogen bonding and electrostatic gravitational forces. Thus, it can accommodate a large fluoride anion exchange capacity. Lu hungtao observed that the doping of hydrotalcite with high valent metal cations enhances the adsorption capacity (Hongtao et al., 2018). Since the main lamellae is positively charged, the interlayer anions being negatively charged, balances the overall charge.

It was reported in the literature that the replacement of Al^{3+} by Zr^{4+} is more effective in ZnAl hydrotalcites for transesterification of castor oils (Cabrera-Munguia et al., 2017). Zn/Al hydrotalcite-like compound, Mg/Al hydrotalcite-like compounds and their calcined products as well as Mg–Al–Fe hydrotalcite-like compound and its calcination product have been used for defluoridation purposes (H. Wang et al., 2007). Liangfu Wei et al. did defluoridation using Ca-Al-CO_3 layer double hydroxide (L. Wei et al., 2021). Wu P. et al. have reported that

the affinity of fluoride is further enhanced by introducing the rare earth metals to hydrotalcite. They synthesized Mg/Fe/La with layered porous structure which significantly enhanced the capacity of fluoride adsorption than that of Mg/Fe LDH (Wu et al., 2017). Magnesium zirconium hydrotalcite-like material doped with Fe_2O_3 and ZrO_2 was reported by Ruisong wang et al.(R. Wang et al., 2022).

In this study, we have directed our efforts in making a hydrotalcite having divalent, trivalent and tetravalent metal ion, a study which has not been reported hitherto to the best of our knowledge. Preliminary experiments were conducted using Ca^{+2}, Mg^{+2} and Zn^{+2} as divalent metal ions and Al^{+3} and Zr^{+4} as divalent and tetravalent metal ions respectively in different mole ratios. Al-Zn-Zr hydrotalcite-like compound (HLCs) (molar ratio Zn^{+2}/Zr^{+4} = 0.5 was found to be the most effective.

Table 4a. 1 Different ratio of HLC

Zr^{4+}	Al^{3+}	Ca^{2+}	Mg^{2+}	Zn^{2+}	$\frac{M^{3+}+M^{4+}}{M^{2+}+M^{2+}+M^{3+}+M^{4+}}$
0.5 M	1 M	0.5 M	0.5 M	-	0.6
0.5 M	0.25 M	0.5 M	0.5 M	-	0.4287
0.5 M	0.25 M	0.25 M	0.25 M	-	0.6
3 M	1 M	-	-	1 M	0.66 (Zn^{+2}/Zr^{+4}= 0.33)
2 M	1 M	-	-	1 M	0.60 (Zn^{2+}/Zr^{4+}= 0.5) (Zr-Al-Zn HLC)

Al-Zn-Zr hydrotalcite-like compound (HTlc) (molar ratio Zn^{2+}/Zr^{4+} = 0.5, Al^{3+}/Zr^{4+} = 0.5) was prepared and its efficiency to absorb fluoride ions was investigated. Experiments were conducted to assess the adsorption kinetics, isotherms and effect of pH and adsorbent dosage on the performance of the system in removing fluoride ions.

4a.2 Material and methods

4a.2.1 Materials

All chemicals like $AlCl_3$, $ZnCl_2$, $ZrOCl_2.8H_2O$ used in this study were of analytical grade without further purification and were purchased from Spectrochem, India. A fluoride stock solution (1000 mg/L) was prepared by adding 0.2210 g of NaF to 100 mL deionized water. Working solutions were prepared by suitable dilution of standard stock solution.

4a.2.2 Synthesis of Zr-Al-Zn HLC

Hydrotalcite-like compounds were synthesized by co-precipitation technique. In a typical synthesis, 100 mL each of 2 M Zr^{4+} ($ZrOCl_2.8H_2O$), 1 M Al^{3+} ($AlCl_3$), 1 M Zn^{2+} ($ZnCl_2$) was mixed maintaining the Zr^{4+}:Al^{3+}:Zn^{2+} ratio 2:1:1. The mixture was stirred for 1 h and the hydrotalcite was precipitated using 1 N NaOH. After complete precipitation the mixture was stirred for 4 h at room temperature and the resultant product was filtered and washed until neutral and then dried at 90^{o}C for 24 hours. The resultant material was termed Zr-Al-Zn HLC (figure 4a.1).

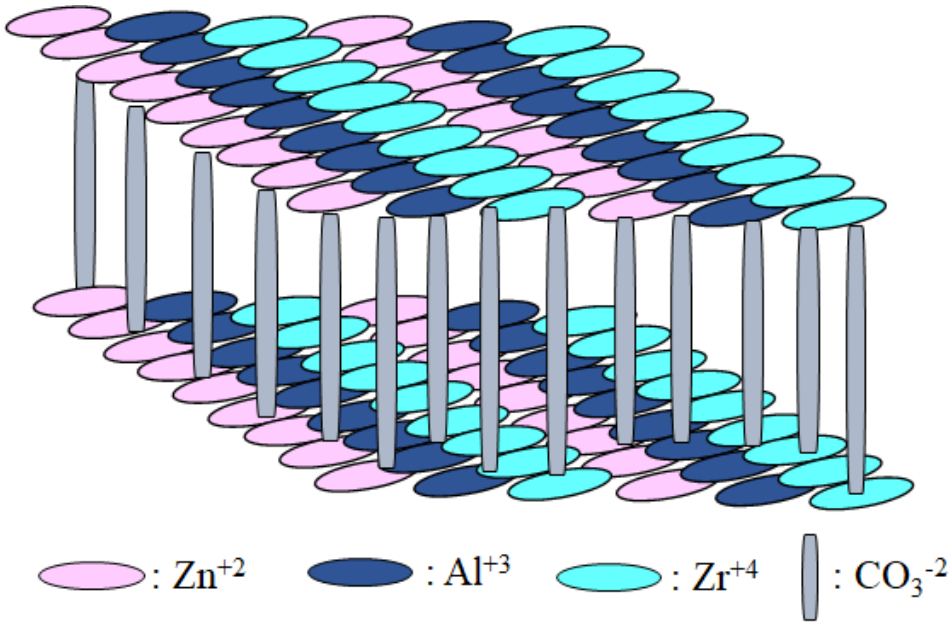


Figure 4a.1 Structure of Zr-Al-Zn HLC

4a.2.3 Adsorption experiments

The fluoride adsorption potential of Zr-Al-Zn HLC was investigated using batch adsorption studies. The pH of the solutions was adjusted using 0.1 N NaOH or HCl to the desired value. For the batch tests, 50 mg/L fluoride containing solution was agitated with 25 mg Zr-Al-Zn HLC in polypropylene flasks at 150 rpm for 3 hours at room temperature (25-32^{o}C). The initial fluoride concentration was with 25 mg dose for uptake studies. After fluoride uptake, the adsorbent was filtered and dried for further study. A fluoride ion selective electrode was used to measure the fluoride that remained un-adsorbed in the solution (Thermo scientific ORION STAR A214). The equipment was calibrated by analysing a known concentration of fluoride solution and calculating the unknown fluoride concentration. TISAB buffer (5 mL/50 mL) was used for the analysis.

4a.3 Result and discussion

4a.3.1 Characterisation of Zr-Al-Zn HLC

Thermogravimetric analysis and DSC spectra

The TGA of HLC exhibited the first weight loss of 17.4% at ~200 °C and may be attributed to the loss of physically adsorbed (surface) and interlayer water (figure 4a.2a). The 2nd weight loss at ~200-500°C was attributed to the decomposition (dehydroxylation) of the hydroxide layers and the removal of interlayer anions resulting in formation of mixed metal-oxides.

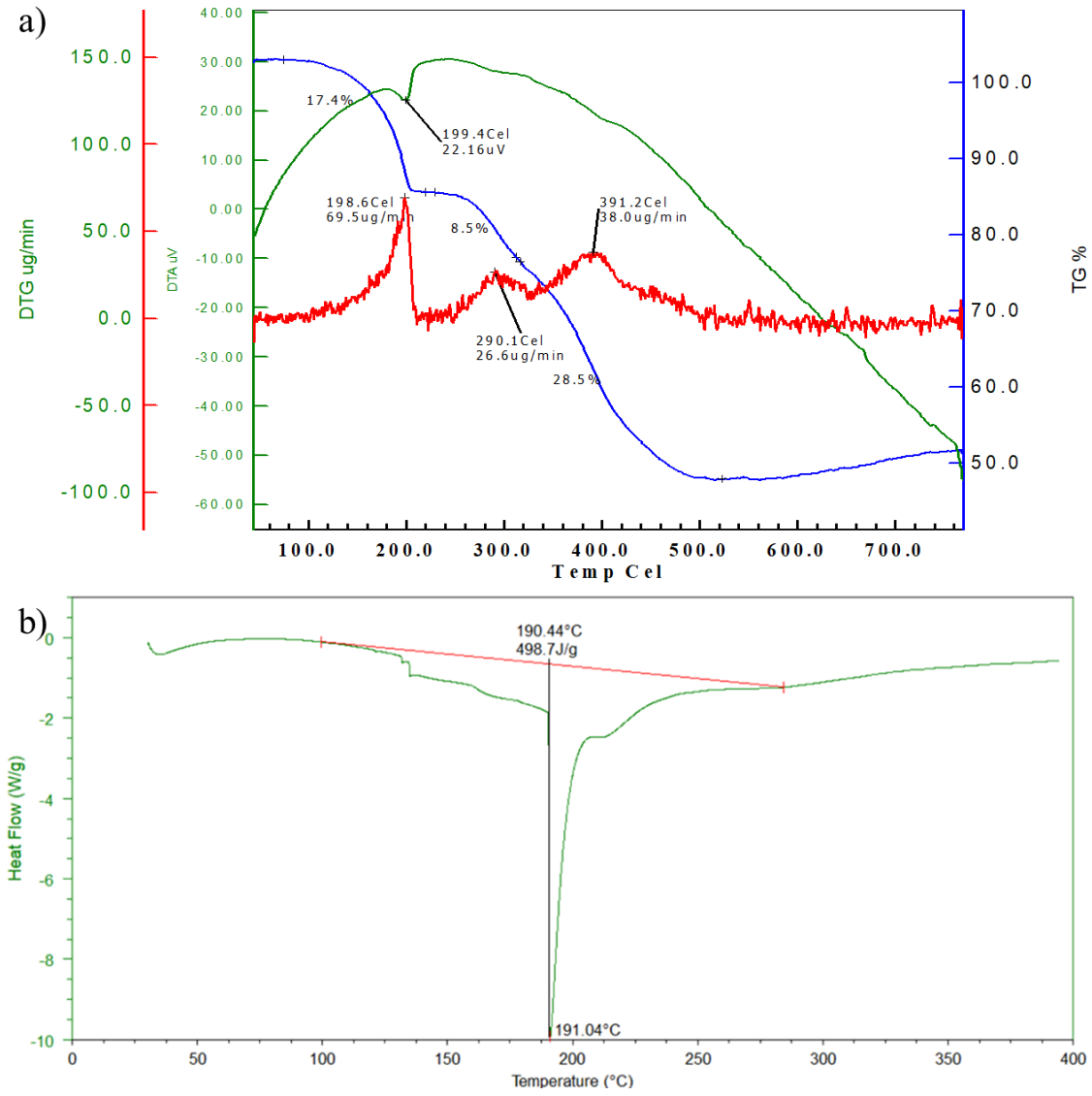


Figure 4a.2 a) TGA and b) DSC spectra of Zr-Al-Zn HLC

The DSC curve exhibited an endothermic peak at 190.44-191.04°C attributed to dehydroxylation of the hydrotalcite (figure 4a.2b).

SEM EDAX analysis

The SEM-EDAX spectra of Zr-Al-Zn HLC before and after fluoride is represented in the figure 4a.3. The EDAX spectra corelates with the experimental ratio of Zr^{4+}:Al^{3+}:Zn^{2+}=2:1:1. The SEM was taken to reveal surface morphology of the HLC. Figure shows clusters of type of morphology (figure 4a.3a).

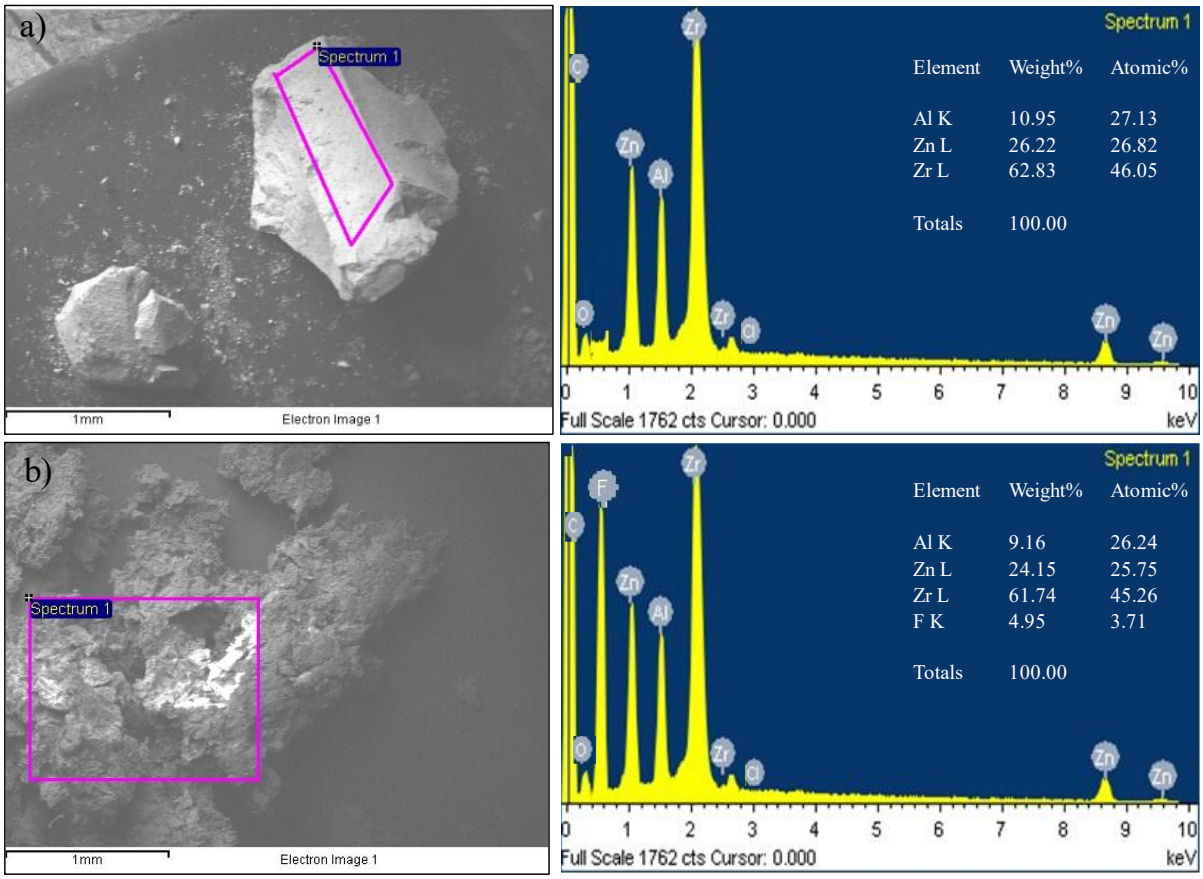


Figure 4a.3 EDAX spectra of Zr-Al-Zn HLC a) before and b) after fluoride adsorption

FTIR spectra

Figure 4a.4 shows the FTIR spectra of Zr-Al-Zn HLC before and after adsorption of fluoride.

The bands observed at 1358 and 1556 cm^{-1} are characteristic peaks of Zr-O bending vibration while the bands at 1102 and 3419 cm^{-1} were attributed to Al-O stretching vibration and the Zn-O stretching vibration was observed at 432 cm^{-1}. Asymmetric stretching vibrations of Zr-O observed at 614 and 553 cm^{-1} (Mazumder et al., 2020). The broad peak at 3419 cm^{-1} in Zr-Al-Zn HLC indicated the presence of intercalated hydroxyl ions which was not seen after the adsorption of fluoride as the host molecules (OH^- ions) were replaced by fluoride ions. There

was weakening of all the absorption bands indicating loss of structure and interaction of metals with fluoride.

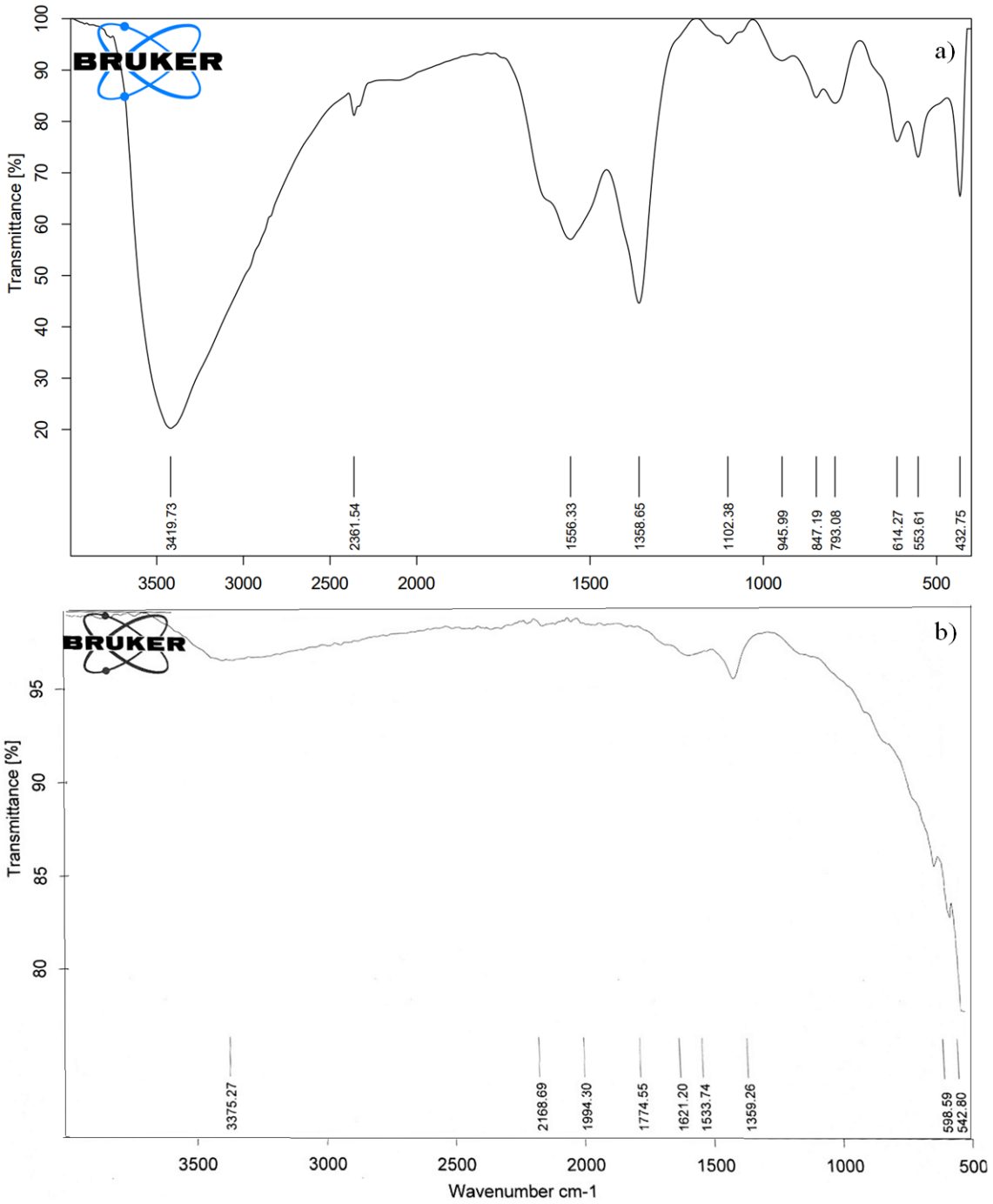


Figure 4a. 4 FTIR spectra of Zr-Al-Zn HLC a) before and b) after fluoride adsorption

XRD spectral analysis

The XRD patterns show the typical diffraction signals of hydrotalcite-like Zn-Al materials, at 2θ 11.7, 23.5, 34.6, 39.3, 46.9, 60.2, and 61.6° (figure 4a.5). It was reported in the literature

that the replacement of Al^{3+} by Zr^{4+} is more effective in ZnAl hydrotalcites with a Zn/Al molar ratio of 2 due to the higher content of Al (Cabrera Munguia et al., 2017).

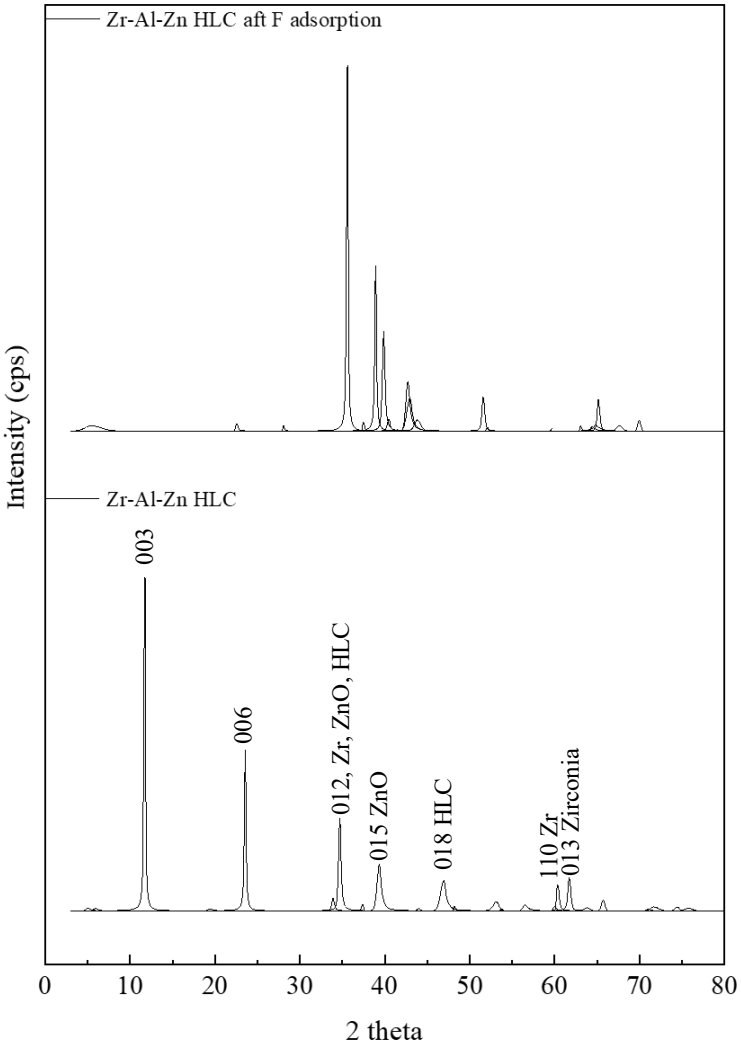


Figure 4a. 5 XRD spectra of Zr-Al-Zn HLC before and after adsorption

4a.3.2 Effect of solution pH

The surface charge of Zr-Al-Zn HLC is affected by the pH of the initial solution due to protonation-deprotonation of the cations present in the host layer (Zhang et al., 2012). The effect of initial pH on the adsorption of fluoride was studied in the pH range 1.0–11.0 at an initial fluoride concentration of 50 mg/L using 100 mg of HLC and agitation time of 3h at ambient temperature (27-32^{o}C).

It can be seen from figure 4a.6 that there is a significant effect of pH on fluoride adsorption. The maximum percentage uptake of fluoride was observed at acidic pH and the percentage uptake of fluoride decreased with increase in pH. This is due to the fact that, at low pH the surface of the adsorbent was positively charged which facilitated the electrostatic interactions

with fluoride. At higher pH, there is competition between F^- and OH^- ions for the adsorption sites thus decreasing the percentage uptake of fluoride. Further studies were carried out at neutral pH considering the practical application of water treatment.

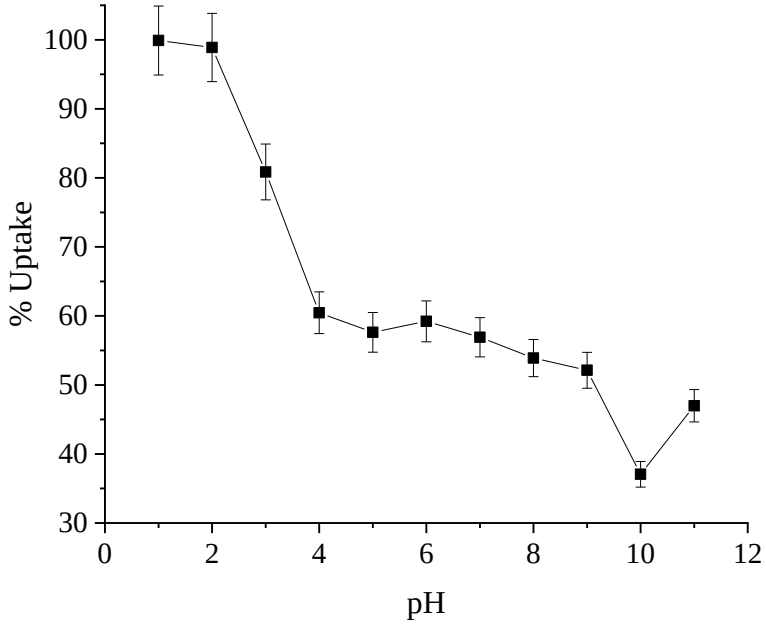


Figure 4a. 6 Effect of pH on % uptake of fluoride (dose: 100 mg, time: 3 h, conc.: 50 mg/L)

4a.3.3 Effect of dose

At a given fluoride concentration (50 F mg/L), pH 7 and temperature of 303 K, the proportion of fluoride removal increased as the adsorbent dose is increased from 1.0 to 30.0 g/L (figure 4a.7). This is due to the fact [18] that the surface sites of oxide systems are heterogeneous. The binding energies of the adsorption sites have a range according to this concept. All types of sites are fully exposed to the interaction with the adsorbate at low adsorbent fractions and surface saturation is quickly attained. Higher particle concentrations result in a decrease in the availability of high-energy sites and an increase in the occupancy of low-energy sites. In other words, with a constant adsorbate concentration, there are more active adsorption sites. At an adsorbent concentration of 25–30 g/L, the given curve depicts a maximum fluoride removal rate.

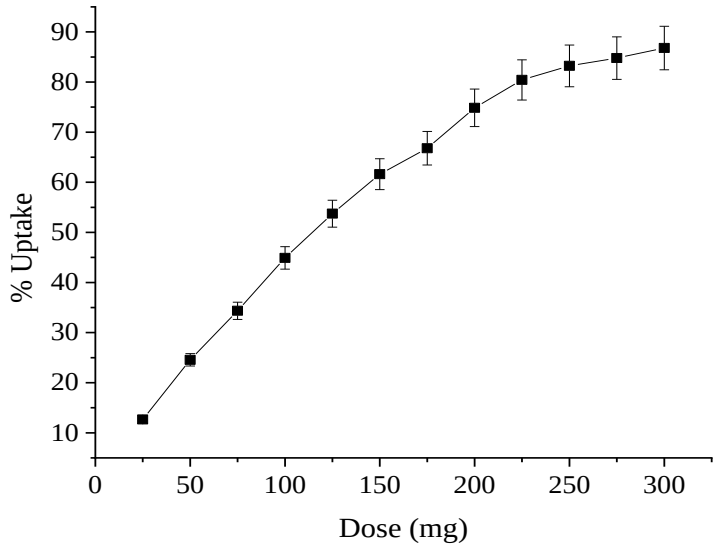


Figure 4a. 7 Effect of Zr-Al-Zn HLC dose on % uptake of fluoride (conc.: 50 mg/L, time: 3 h)

4a.3.4 Effect of time

The kinetics of fluoride adsorption by Zr-Al-Zn HLC were examined by equilibrating 25 mL of a 50 mg/L fluoride solution at pH 7 with 250 mg of Zr-Al-Zn HLC at various time periods (figure 4a.8). After 3 hours of equilibration, the maximum uptake was detected and remained stable. Because all adsorbent sites were initially unoccupied and the solute concentration gradient was significant, the rate of removal may have changed. Due to a decrease in the number of adsorption sites as well as fluoride concentration, the fluoride adsorption rate by adsorbent reduced dramatically later [31].

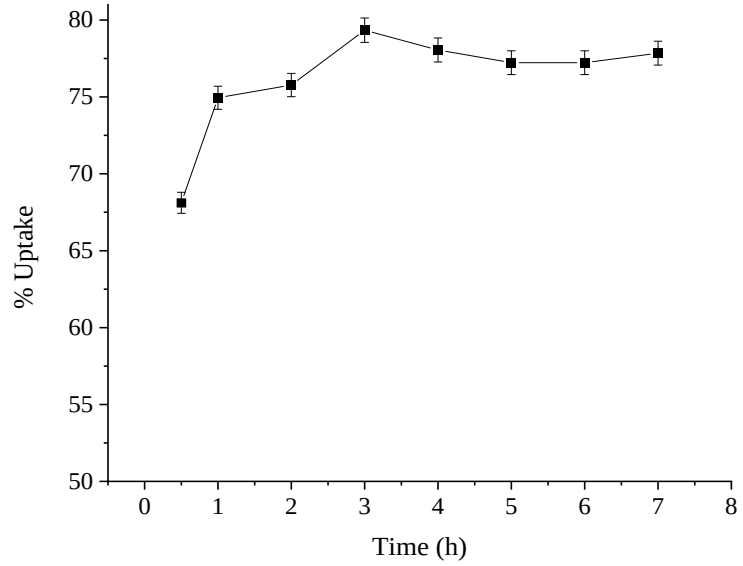


Figure 4a. 8 Effect of time on % uptake of fluoride

The pseudo-second order kinetics models' (details in chapter 2, table 2a.2), high coefficients of determination (R^2) and closeness of the calculated q_e values to the experimental values indicated that the model was the best fit to explain the kinetics of fluoride uptake onto Zr-Al-Zn HLC (table 4a.2). This demonstrated that the process was diffusion-controlled.

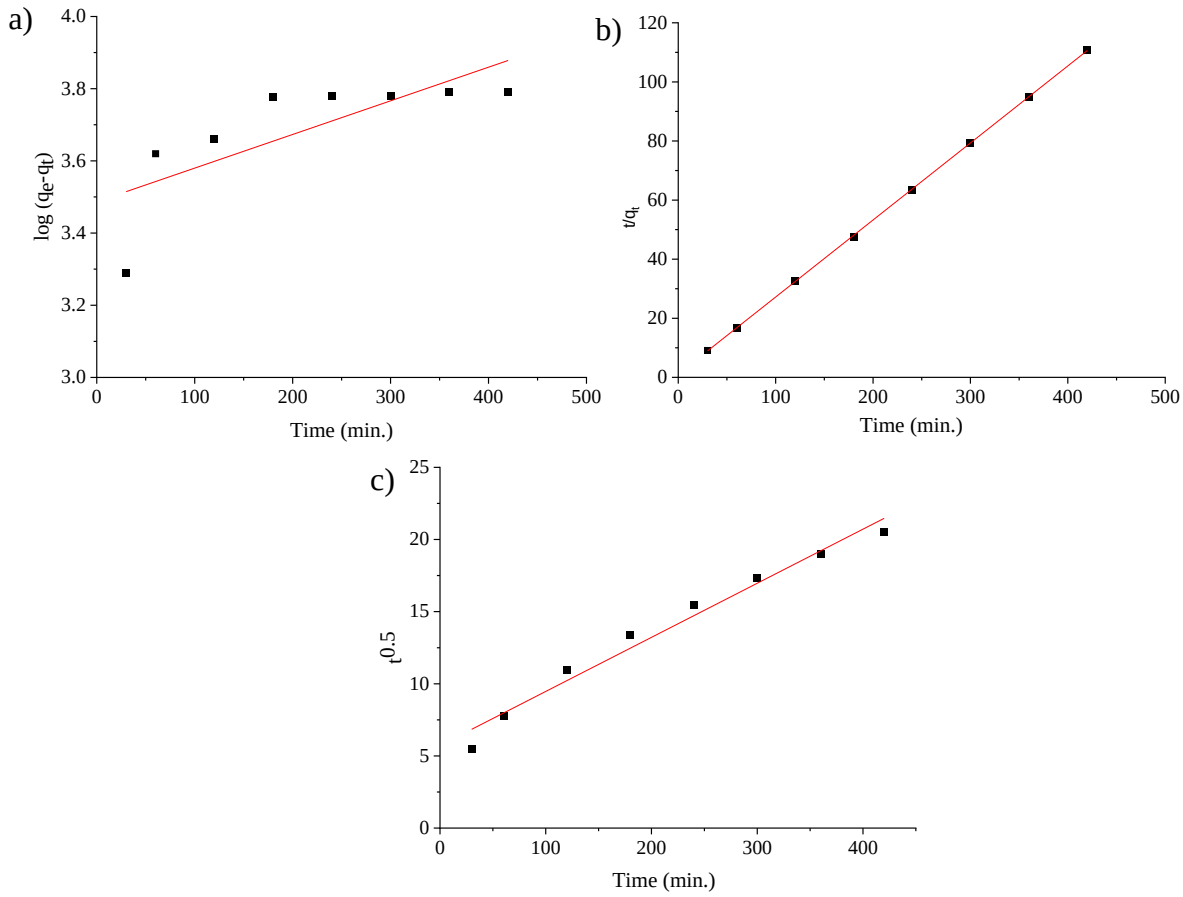


Figure 4a. 9 Kinetic models for fluoride adsorption onto Zr-Al-Zn HLC a) Pseudo first order, b) Pseudo second order, c) Intraparticle diffusion

Table 4a. 2 Kinetic parameters

q_e (exp): 3.78 mg/g	**q_e**	**K**	**r^2**
Pseudo First order	1.36	0.0186	0.92
Pseudo Second order	3.83	1.11	1
Intraparticle diffusion	-	0.037	0.97

4a.3.5 Effect of initial fluoride concentration

Figure 4a.10a shows the results of the effect of initial fluoride concentration (5 to 100 mg/L) on the adsorption process. Due to a lack of available active sites, it was shown that fluoride

uptake reduced as fluoride concentration increased. To further model the experimental data, Langmuir and Freundlich isotherms were applied (figure 4a.10b).

Using the batch equilibrium method, the adsorption isotherms were obtained by agitating a fixed quantity of adsorbent (100 mg) with fluoride solutions of various concentrations (0-80 mg/L) for 4h.

Table 4a.3 lists the calculated values for the Langmuir and Freundlich isotherm constants.

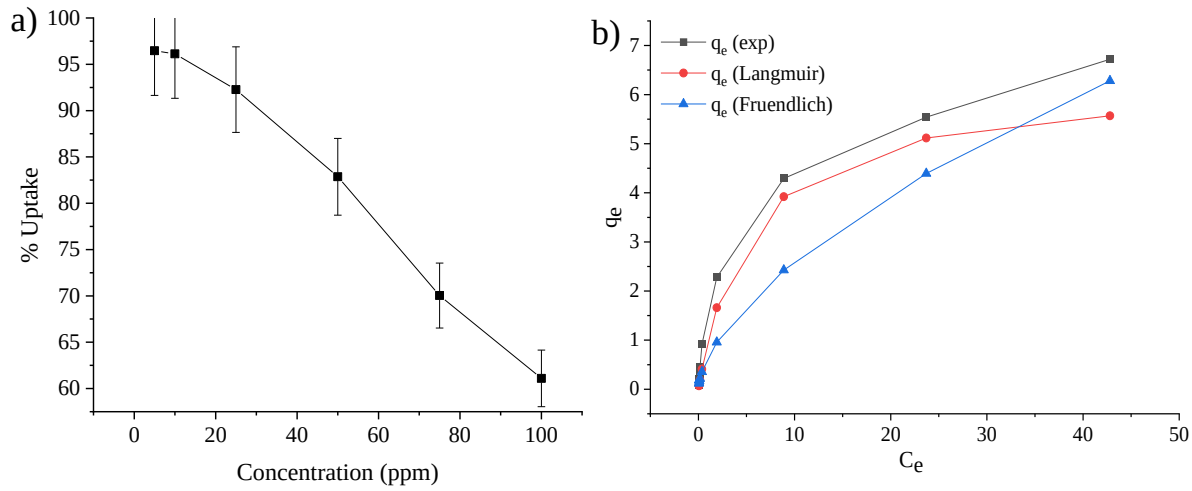


Figure 4a. 10 a) Effect of initial concentration of fluoride, b) isotherm models for fluoride adsorption

Table 4a.3 Isotherm parameters

	Isotherm Parameters		
Langmuir	Q_m	K_L (L.mmol^{-1})	r^2
	6.96 (at pH 7), 44.84 (at pH 2)	0.288	0.98
Freundlich	N	k_F(L.g^{-1})	r^2
	1.979	1.229	0.97
Temkin	A_T (Lg^{-1})	b_T	r^2
	0.564	0.0045	0.94
Halsey	k_H (L.g^{-1})	n_H	r^2
	6.7*10^6	5.33	0.92

Based on the correction coefficient R^2, the adsorption data were found to fit Langmuir models. The Langmuir parameters with the best fit are q_m = 6.96 mg/g and K_L = 0.288 L.mmol^{-1}. The Freundlich parameters are K_F = 0.994 and n = 1.6534. As n value is >1, this indicates the physical adsorption.

4a.3.6 Effect of temperature

The effect of temperature on the % uptake of fluoride was studied by taking 50 mg/L 25 mL fluoride solution using 250 mg dose and agitation time of 3 h, at 30, 40, 50, 60^{o}C temperature (figure 4a.11). The plot indicates a mild exothermic nature of the adsorption process. This can also be affirmed by the reasonably good correlation value of 0.94 and positive heat of sorption.

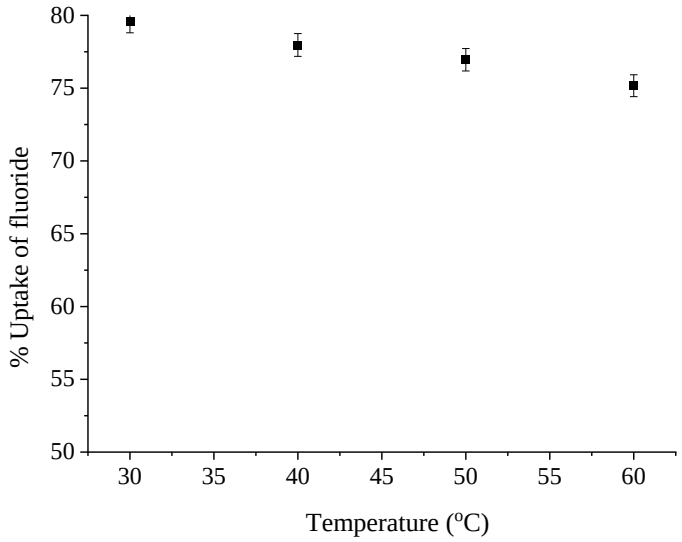


Figure 4a. 11 Effect of temperature on % uptake of fluoride

The table 4a.4 below lists the thermodynamic characteristics that were determined for the adsorption of methylene blue, including change in free energy (G°), enthalpy (H°) and entropy (S°).

Table 4a.4 Thermodynamic studies

Thermodynamic parameter	Value
ΔG	-12.19 kJ/mole
ΔS	40.36
ΔH	-10375.8

The exothermic nature of adsorption accounts for the negative value of enthalpy, whereas the negative value of free energy demonstrates the process's viability and spontaneity (Gerçel et al., 2007).

4a.3.7 Effect of competing anions

There are several anions in natural water frequently. The effect of co-existing anions (Cl^-, NO_3^-, SO_4^{2-}, HCO_3^-, and CO_3^{2-}) on the Zr-Al-Zn HLC capacity to adsorb fluoride is shown in figure 4a.12. Fluoride adsorption over Zr-Al-Zn HLC was investigated by agitating 50 mg/L of fluoride solution in the presence of 50 mg/L /100 mg/L of various anions with 10g/L of Zr-Al-Zn HLC at pH 7 for 3 hours.

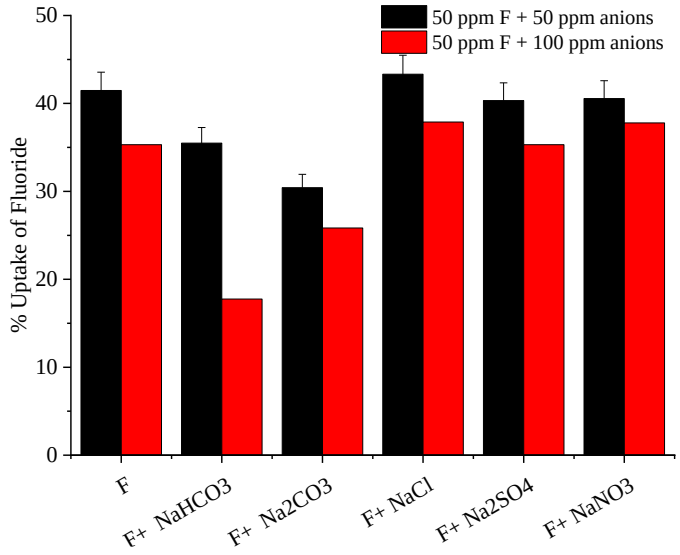


Figure 4a. 12 Effect of other anions

Table 4a. 5 Comparison of the fluoride maximum adsorption capacity by Zr-Al-Zn HLC with other reported adsorbents

Adsorbents	pH	q_e (mg/g)	Equilibrium time	References
Mg–Al layered double hydroxides	10	3.3	120 min	(Kameda et al., 2015)
Calcined La Mg/Al LDHs	6.0	62.33	24 h	(Elhalil et al., 2016)
Nanocrystallised Li-Al LDHs	4.0	32.6	150 min	(Cai et al., 2016)
La-doped Li-Al LDHs	5.0-9.0	16.7-17.2	60 min	(Cai et al., 2018)
Mg/Fe/La CHLc	6.8	59.34	100 min	(Wu et al., 2017)
Calcined Ca-Al(NO_3)	8.0	8.48	-	(Ghosal & Gupta, 2015)
Mg-Fe LDHs	7.0	50.91	10 h	(Kang et al., 2013)
Zr–La complexed polyvinyl alcohol films	7.0	11.57	45 min	(M et al., 2021)
Zr-Al-Zn HLC	7.0	6.96	180 min	This study

4a.3.8 Plausible mechanism

Figure 4a.13 describes the mechanism of the fluoride adsorption by Zr-Al-Zn HLC. The adsorption of fluoride on such hydrotalcite like material is attributed due to complexation of fluoride ion with metal ions comprising HLC, adsorption of fluoride ion on external surface, adsorption in interlayer and internal surface and external surface of HLC as well as exchange with hydroxyl ions.

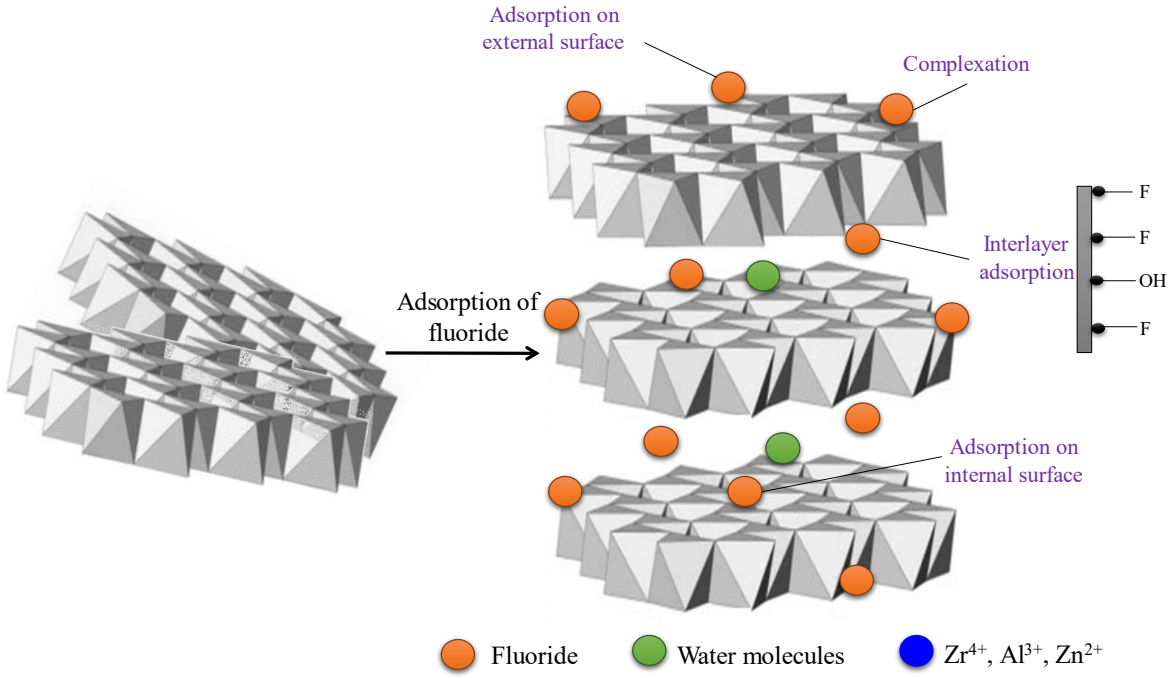


Figure 4a. 13 Plausible mechanism for fluoride adsorption by Zr-Al-Zn HLC

4a.4 Conclusions

In conclusion, Zr-Al-Zn HLC was synthesized and its surface nature and properties were studied using XRD, XPS, TGA, EDAX, SEM and FTIR spectroscopic techniques. Fluoride adsorption by Zr-Al-Zn HLC was efficient even at acidic and neutral pH and as well as in the presence of competing anions such as sulphate, carbonate, chloride, nitrate, and bicarbonate. The Zr-Al-Zn HLC adsorption data was satisfactorily fitted to the Freundlich model and the maximum adsorption capacity at neutral pH conditions was 6.96 mg/g.

Furthermore, adsorption equilibrium was reached in about 3 hours with maximum adsorption occurring in 120 minutes and could be described by a pseudo-second-order kinetic model. Fluoride removal by Zr-Al-Zn HLC could be attributed to ion exchange with hydroxyl ions, complexation with metal ions as well as complex formation with the metal ions constituting

the HLC. The use of Zr-Al-Zn HLC for fluoride removal from ground water samples was demonstrated.

4a.5 References

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