Recent Advances in Defluoridation of Water using Alumina based Adsorbents: A Review

Madhu Sudan Sharma[1]*, Jai Shanker Acharya[2]

Department of Chemistry, Govt. Dungar College, Bikaner 334001,Rajasthan,India
Corresponding Email ID- mssharma2186@gmail.com

ABSTRACT
Fluoride ion in trace amount is essential for the growth of human bones but, the excess intake of this ion creates a toxic effect in the body. The acceptable limit for fluoride ion in the drinking water should be less than 1.5 mg/L. With the growing concern in the development of novel and eco-friendly adsorbent materials, it is also important to improvise and re-examine the strengths and shortcomings of the various techniques. Fluoride, being a hard base, the alumina based materials with hard cations such as Al(III) fosters effective coordination as Al–F bonding on the surface. Towards this direction, we present an overview on different alumina based adsobents to alleviate the fluoride contamination. The data base selected for this review was Science Direct. The search includes only Alumina based adsorption.The search results were restricted to English language only and includes research and review articles.In addition a constraint was applied for years of publication,which only includes articles in period from jan 2015 to Dec 2021. 65 results were found in which 19 were discarded by main title of article,12 results were exclude by abstract evaluation and 6 results were discarded by full paper reading. 28 results were selected and thoroughly invastigaed twice. Along with adsorption capacity a number of pertinent parameter that could affect the defluoridation eg. Solution P^H,competing anions, BET surface area,temperature,initial adsorption dose,experiment,initial fluoride concentration were carefully and comperehensively reviewed.Isotherm,Kinetics,Thermodynamics,regeneration capabilities were also reviewed. Alumina have good potential in fluoride removal from groundwater still, there is a need for further research on the utilization of these adsorbents in our day to day life on a commercial scale to combat with a real-life problem like water pollution.
Key words – Defluoridation, Alumina, Adsorption, Isotherm, Kinetics
----

Date of Submission: 01-01-2023   Date of acceptance: 08-01-2023


I.   Introduction

Safe and uncontaminated drinking water for every individual by 2030 is a sustainable development goal of United Nations Development Programme (UNDP n.d.).Over the years water pollution has emerged as a serious problem in India as well as world wide. Aquatic environment and ecosystem is affected by a variety of organic, inorganic and biological contaminants.

Fluoride is one of the major contaminants widely dispersed either naturally in ground water caused by solvent action of water on the rock and soil or by industrial effluent released from aluminium and steel production,glass and semiconductor manufacturing ,fertilizers and electroplating industries (M. Barathi a 2019).

The presence of fluoride(F-) in drinking water has some health benefits for consumers such as reducing dental cavaties but an excessive intake of this anion or its presence of high concentration(>1.5 mg/l) can lead to dental and skeletal fluorisis (Krishna Kumar Yadavb 2019).

Fluoride is an essential oligo-element which facilitates the proper growth and development of bone and teeth.Fluoride displaces the hydroxide ions from hydroxyapatites$[Ca_5(PO_4)_3OH]$ of bones and teeth as a result produce more harder and tougher fluorapatite $[Ca_5(PO_4)F]$,consequently strengthening enamel of teeth,when interaction at low concentration.

$$Ca_5(PO_4)_3OH + F- \longrightarrow Ca_5(PO_4)F + OH^- \text{-----------(1) (Manas Ranjan Naik a 2021)}$$
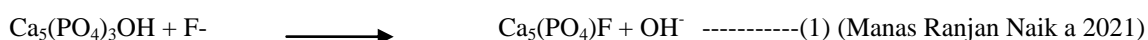
However at elevated concentration of fluoride (>1.5 ppm) displace calcium from bone and teeth thus causes dental and skeletal fluorosis. (Manas Ranjan Naik a 2021).

$$Ca_5(PO_4)_3F + 9F- \longrightarrow Ca_5F_{10} + 3PO_4^{3-} \text{---------(2)}$$

A large body of animal and human studies have demonstrated that high level of fluoride have adverse impact on neurodevelopment,manifesting as cognitive defect as well as behavioral abnormalities,which are due to reduction in triiodothyronine(T_3) and thyroxine (T_4) level and increase in thyroid stimulating hormone (TSH) (Mengwei Wanga 2020) .

Therefore considering harmful effect of fluoride on human an effective and robust technique is need of moment to curb the problem.A significant work has done on defluoridation of water,in which Precipitation, reverse osmosis ,ion exchange, technique, electrodialysis (Krishna Kumar Yadavb 2019), Nalgonda (Dr. Sreekanth Bose 2018) etc.are some of process reported for defluoridation.Each process has its own set of advantages and drawbacks. Developing countries like India needs a process which is effective,economical,easy handling and can be used as mass level.

Among the afore-mentioned methods, adsorption appears as a preferble choice owing to its lower operational cost,lesser sludge generation,regeneration of spent sorbent and easy availability.

This review paper aims towards discussing some selected alumina based adsorbents on their adsorption mechanism,various equilibrium studies,kinetic model,thermodynamics,tools and techniques.A summary of adsorbents used for defluoridation as per literature has also been discussed.

II. METHOD

The data base selected for this review was Science Direct. The search includes only Alumina based adsorption.The search results were restricted to English language only and includes research and review articles.In addition a constraint was applied for years of publication,which only includes articles in period from jan 2015 to Dec 2021. 65 results were found in which 19 were discarded by main title of article,12 results were exclude by abstract evaluation and 6 results were discarded by full paper reading. 28 results were selected and thoroughly invastigaed twice.

III. Adsorption by various Alumina based adsorbents

The adsorption of fluoride is known to be better captured by the metal oxides.The cause of this better adsorption is the electronegative nature of fluoride ions and electropositive nature of metal oxides. Among the reported metal oxides ,the alumina is found to be highly selective and high affinity to capture fluoride ions.Due to low adsorption capacity of alumina to F- ions ,which is major drawback, therefore various attempts had been carried out to enhance the fluoride adsorption capacity of alumina (Usha Kumari a 2020). Activated Alumina(AA) is one such adsorbent that is widely studied and used for the defluoridation process.The surface of AA becomes charged in aquous environment of particular interest in this context is the role played by Hydrogen ion.Hydration of AA surface which depends on the pH solution, changes the surface morphology.

3.1. Calcium and Zirconium modified acid activated alumina(CAZ)

The CAZ adsorbent exhibited satisfactory defluoridation performance of industrial water.The maximum defluoriadtion efficiency (97%) of CAZ was achieved at pH 6 and adsorbent dose 6g/l.The pHzpc of CAZ was found at 6.9.Maximum adsorption capacity was 216 mg/g found higher than parent alumina.The adsorption was found endothermic and spontaneous.

The fluoride adsorption on CAZ followed Langmuir isotherm and Pseudo second order kinetic model.BET analysis of CAZ adsorbent showed that it has lower surface area than fresh alumina and acid treated alumina (ATA).The possible reason of reduction in specific surface area may be due to blockage of pores of ATA by oxides of Zr and Ca or their loss during adsorbent preparation.

The initial pH of wastewater has major effect on adsorption phenomenon. Removal in fluoride increases with increase in pH from 3 to 6,further increase in pH deceases the adsorption of fluoride. Presence of coexisting ions like Cl^-,NO_3^-,SO_4^{2-},HCO_3^-,CO_3^{2-} have imparted reduction in fluoride removal efficiency.cl has least(15.2%) and CO_3^{2-} has highest(69%) effect on fluoride removal. (Usha Kumari a 2020).

3.2. ϒ- Al_2O_3

ϒ- Al_2O_3 valorised from secondary aluminium dross was used as adsorbent for fluoride removal.Purity of Al_2O_3 was revealed by XRF analysis.BET analysis revealed that specific surface area was 170m^2/g.Maximum adsorption capacity shown by Al_2O_3 was 16.5mg/g when adsorpyion dosage,initial fluoride concentration and pH was 1g/l,20ppm and 4 respectively. Adsorption follow Freundlich isotherm with nonlinear χ^2 test with value 1.833.It means that adsorption sites are distributed heterogeneously and fluoride adsorption is mainly carried out by chemisorption process.

The best fit kinetic model for this adsorption was found pseudo second order.Adsorption capacity is well influenced by initial fluoride concentration,contact time,pH and adsorbent dosages.The adsorption amount was improved by boosting the initial concentration of F^- solution due to concentration gradient.

One of the most significant parameters affecting the adsorption process is initial pH of solution .Amount of F^- adsorbed increased from 47% to 75% when pH rose from 2 to 4 and decreases with further increase in pH.

The F^- removal percentage increased from 38% to 98% when adsorbent dosage increased from 0.5 to 4 g/l .This is because its contact surface with adsorptive anions (F^-) increases and more active binding sites are ready to accept the adsorptive ions.

Various interfering ions like NO_3^-, Cl^-,$OH-$, CO_3^{2-},PO_4^{3-} compete with fluoride. Phosphate ion shows more interference with fluoride adsorption due to its lower hydrated radius. Al_2O_3 showed better regeneration abilities (Mostafa Mahinroosta ∗ 2021).

3.3. Nitric Acid Activated Alumina(HNAA)

Another alumina based adsorbent is HNAA.The physiochemical characterisation like SEM,XRF,BET($78.691 m^2/g$),pHzpc(5.825) results exhibited that HNAA is a good defluoridating agent.The maximum adsorption capacity showed in batch experiment was 45.75 mg/g.The adsorption of fluoride ions by HNAA followed Freundlich isotherm and pseudo second order kinetics model.

Adsorption is quite influenced by adsorption dosage, initial F^-concentration and pH respectively. The removal of fluoride ions rises sharply with increase of adsorbent dosage from 0 to 8 g/l. Further increment in adsorbent dosage from 10 to 26g/l gradually leads to the attainment of saturation in fluoride removal.

Fluoride removal efficiency of adsorbent is increased with the increase in pH from 2 to 3.5.But with increase of pH from 3.5 to 9, the decrease in fluoride removal efficiency is observed. PHzpc is 5.8 for HNAA, hence at pH> pHzpc surface of adsorbent is electronegative causing the electrostatic repulsion between adsorbent surface and electronegative fluoride ions.

The hindrance in fluoride removal by coexisting ions is in the order of $Cl^-< NO_3^-< SO_4^{2-}< HCO_3^-< CO_3^{2-}$.The defluoridation of waste water(40g/l)without coexisting ions was 97.44%.

Thermodynamic parameter shows that adsorption is endothermic and spontaneous. HNAA shows excellent regeneration capabilities. 3M NaOH is capable of desorbing almost all the adsorbed fluoride ions from the spent adsorbent (Usha Kumaria 2020).

3.4. Nano Alumina

Pure and modified nano alumina were tested for defluoridation of water under different experimental conditions such as agitation time, solute concentration and pH. Characterisation of nano alumina was done by IR,TEM,SEM and EDX analysis. The defluoridation using pure and modified nano alumina was achieved in 120 min and 30 minutes using an adsorbent dose of 10mg/l and 8 mg/l at near neutral solution pH respectively. Maximum adsorption capacity was found to be 2.55mg/g and 5.66 mg/g for pure and modified nano alumina respectively by batch study. The best fit adsorption isotherm was Langmuir isotherm. The kinetics of process was explained by pseudo second order and intra particle diffusion model.

Effect of various components such as initial fluoride concentration, contact time, adsorbent dosage, pH and coexisting ions. Fluoride adsorption capacity increased with F^- concentration in solution in case of pure and modified nano alumina. Due to sodium ions, which are complexed with aluminium oxide , adsorption capacity of modified nano alumina is enhanced.

Removal of fluoride increased with contact time in both cases.In the case of modified nano alumina ,the F^- uptake was rapid with in first 10 minutes and equilibrium sets up in 30 minutes.The sudden increase in the adsorption of F^- can be also due to the modified nano alumina being of lesser agglomeration and particles with well defined surfaces.

In the case of modified nano alumina ,pH did not have any significant effect on defluoridation capacity and percentage removal was much greater than pure nano alumina.for pure nano alumina adsorption capacity is decreased above pH 7.

Effect of co-ions normally present in ground water was also studied. For pure nano alumina it was found that the adsorption capacity was decreased by a great extent in presence of phosphate and sulphate ions. For modified nano alumina ,the impeding effect of ions was lesser than pure adsorbent. Thus above study indicates that modified nano alumina is better adsorption agent for defluoridation than pure nano alumina (Parimala Shivaprasad 2018).

3.5. La modified Alumina and Ce modified Alumina (La/MA & Ce/MA)

La/MA and Ce/MA are also effective adsorbents for removing fluoride. The adsorption was investigated in both batch and column adsorption systems. Characterisation of material was done by BET,XRD,XRF,FTIR,TEM and HRTEM analysis. Batch experimental results showed the adsorption capacities of adsorbents were recorded in following order - La/MA > Ce/MA > meso porous alumina(MA).Maximum adsorption capacity of La/MA was 26.45mg/g in SIPS model at the dosage of 2.0 g/l near pH

6.0.Thermodynamics parameter showed that adsorption was endothermic and spontaneous in nature. According to BET analysis specific surface area was found $318.19 m^2/g, 257.37 m^2/g, 236.86 m^2/g$ for MA ,Ce/MA and La/MA respectively. Adsorption efficiency of three adsorbents increased with increase in adsorbent dose from 0.5 to 2 mg/g. La/MA has higher removal efficiency of fluoride ions, which might be attributed to the enhancement of positive charge at the surface and La had a greater affinity for fluoride than Ce.

Appropriate pH range of adsorption is 5.5 to 6.5 and pH value decreased or increased lead to reduce the adsorption capacity. At acidic pH ,part of fluoride can be combined with H^+ to form hydrogen fluoride and with the pH raised to alkaline F^- were completely exposed to the solution, the OH^- will compete with F^- on the material surface.

The best fit kinetic model is Elovich model with correlation coefficient (R^2) 0.989 for La/MA.

Coexisting ions reduced F- removal in following order. $CO_3^{2-} > SO_4^{2-} > NO_3^- > Cl^-$. Carbonate and sulphate ions had more anionic charge and interference of anions on fluoride adsorption probably related to coulombic force.

La/MA showed better regeneration capabilities. Removal efficiency after 5 cycles was found 70.7%.the above result shows that La/MA is good defluoridating agent (Yuxuan He a 2019).

3.6. Other Al based adsorbents-

Tangsir et.al reported that,Al_2O_3 nanoparticle (synthesized by Flame Spray Method(FSP)) showed maximum adsorption capacity 9.73 mg/g.The material was tested under batch experiment,pH_{zpc} was 5.64 and optimum pH was 5.56. (S. Tangsir 2015).

Wang et. al reported that a nano composite of $(ZrO_2-Al_2O_3)/GO$ synthesized by a simple sonochemical method exhibited a large surface area($42.84 \ m^2/g$) and good adsorption capacity (62.2mg/g) and 13.80 mg/g when F^- equilibrium concentration was 1 mg/l.The above result shows that $(ZrO_2-Al_2O_3)/GO$ is among top adsorbents.The reusability of adsorbents is acceptable for a few reuse cycles (Qi Wanga 2020).

Muramasvina et. al reported that water hyacinth beads doped hydrous aluminium oxide(WH-HAO) is a satisfactory agent for fluoride removal showed 4.43 mg/g maximum adsorption capacity (Gabriel Murambasvina 2020).

Prabhu et.al synthesized aluminium and lanthanum binary oxy hydroxides on chitosan template (CS@ALMOH) showed excellent defluoridation ability.The material showed relatively fast adsorption kinetics to fluoride removal in 15 minutes and maximum adsorption capacity of 33.39 mg/g and can be used as broad pH range (Subbaiah Muthu Prabhu 2016).

Mahfoudhi et.al prepared a novel aluminium hydroxide modified porous aerogel,proved an effective adsorbents for removal of aquous solution.The $CNF(Al(OH)_3)$ modified aerogel showed adsorption capacity ranging from 20 to 35 mg/g and could be reused to 5 adsorption-desorption cycles without significant loss of its adsorption capacity (Norhene Mahfoudhi* 2020).

IV. Adsorption capacity of various adsorbents

S.No.	ADSORBENT	BET Surface Area(m²/g)	PH_{ZPC}	Experiment	PH	Adsorption Capacity(mg/g)	Initial conc. Of Fluoride (ppm)	Initial dose of Adsorbent(g/l)	Thermodynamics	Isotherm	kinetics	R²	Reference
1.	CAZ	45.4	6.9	-	6	216		6	Endothermic	Langmuir	PSO	0.99	(Usha Kumari a 2020)
2.	Υ-Al₂O₃	170.8	7.8	Batch	4	16.5	20	4	-	Freundlich	PSO	0.99	(Mostafa Mahinroosta * 2021)
3.	HNAA	78.691	5.825	Batch	3.5	45.75	-	20	Endothermic	Freundlich	PSO	0.99	(Usha Kumaria 2020)
4.	Nano Alumina(pure)	170	<7	Batch	7	2.55	10	10	-	Langmuir	PSO	0.99	(Parimala Shivaprasad 2018)
5.	Nano Alumina(modified)	170	<7	Batch	4-9	5.66	10	8	-	Langmuir	PSO & IPD	0.99	(Parimala Shivaprasad 2018)
6.	Modified Alumina	318.19	-	Batch	6.9	12.32	-	2	Endothermic	SIPS	Elovich	0.99	(Yuxuan He a 2019)
7.	La-Alumina	236.86	-	Batch	6	26.45	-	2	Endothermic	SIPS	Elovich	0.99	(Yuxuan He a 2019)
8.	Ce-Alumina	257.37	-	Batch	6	14.29	-	2	Endothermic	SIPS	Elovich	0.99	(Yuxuan He a 2019)
9	Al(OH)₃ loaded Zeolite synthesized from coal fly ash	53.5	5.52	Batch	6	18.12	50	12	Endo	Langmuir	PSO	0.99	(Jiabin Chen 2022)
10.	Al –coated natural Zeolite	-	7.45	Batch	6.5	11.52	10	40	Endo	Freundlich	PSO	0.99	(Yohannes Desalegn Wirtu

													a 2021)
11.	Mg-Al-Zr	200.7	NA	Batch	7	22.9	500		1	Endoth ermic	Langmuir &Freundl ich	PSO	0.93	(Mei Wang 2017)
12.	Zn-Mg-Al Oxide	94.64	NA	Batch	7	84.24	10		0.5	Endoth ermic	Langmuir	PSO	0.99	(Ming Gao 2020)
13.	Fe-Al-Mn oxyhydroxide@chit osan	41.6	NA	Batch	3.4 -8	40	20		0.5	Endoth ermic	Freundlic h	PSO	0.99	(Mohit Chaudharya 2019)
14.	AC-Al	561	NA	Batch	6.1 5	13.03	-		1.5	-	Langmuir	-	-	(Vibha Sinha * 2020)
15.	Al/Hap	142.15	NA	Static	5.7 0	19.68			0.1	Endoth ermic	Langmuir	PSO	0.99	(Zhenzhen Chen 2017)

V. BET ANALYSIS

The Brunaur-Emmett-Teller(BET) method is commonly applied to calculate the specific surface area on the basis of nitrogen adsorption isotherm measurement at 77 K. Usually data in the relative pressure range from 0.05 to 0.3 are used. The BET model assumes multilayer adsorption of gas on the adsorbents surface. Therefore, caution needs to be exercised in the data selection for the surface area analysis of mesoporous material surface(MMS),in which the capillary condensation rather than multilayer adsorption may take place in the above pressure region, especially for small pores(2-3 nm in diameter) or poorly ordered materials. (Naderi 2015).

$$S_{BET} = V_o N_a s / M_v$$

Where V_o is the volume of single monolayer of adsorbed gas
N_a is the Avogadro number
M_v is molar volume of gas adsorbate
s is surface area of a single gas molecule adsorbed on solid

The SSA for the known mass of dry sample can be calculated from BET surface area ,as follow

$$SSA = S_{BET}/M$$

VI. Point of zero charge (pH$_{PZC}$)

Point of zero charge (pzc) is the pH where the surface charge is equal to zero. This parameter has a very important role in adsorption experiments(in connection with the solution pH) and it is characteristic from the adsorbent material. If pH$_{PZC}$ is higher than the solution pH; then coulombic attraction takes place which promotes adsorption. This phenomenon is due to the creation of a net positive surface charge on the adsorbent surface (by adsorption of excessive H^+). However, if pH$_{PZC}$ is less than solution pH, then coulombic repulsion occurs between the adsorbed anions and surface of the adsorbent (net surface charge is negative due to the desorption of H^+). Therefore, the adsorbed anions on the negatively charged surface compete for the coulombic repulsion during the process and affect the fluoride adsorption capacity (Analia Iriela 2018).

VII. ADSORPTION ISOTHERMS

7.1 The Freundlich isotherm

In late 1909, Freundlich isotherm was introduced in the field of adsorption which applies to the non-ideal and reversible adsorption on the heterogeneous surface with no restriction of monolayer formation, i.e., multilayer adsorption. Whereas the distribution of heat release during adsorption and affinities over the heterogeneous surface is also non-uniform. This model gives the exponential equation that is

$Q_e = K_f C_e^{1/n}$ (1)

Where;
K_f = Freundlich isotherm constant (mg/g)
n = adsorption intensity;
C_e = the equilibrium concentration of adsorbate (mg/L)
Q_e = the amount of metal adsorbed per gram of the adsorbent at equilibrium (mg/g).
Linearizing Eq. (1), we have:

$log Q_e = log K_f + 1/n log C_e$ (2)

Limitation: Does not justify Henry's law at very low concentration (Amit Kumar Yadav* 2020).

7.2 The Langmuir isotherm

In 1916, Langmuir proposed the model named as Langmuir adsorption isotherm. It is generally for the gas-solid phase adsorption butalso applicable to liquid-solid phase adsorption process. This model refers to the homogeneous adsorption, which depends upon two major assumptions:

1. It must be monolayer adsorption; and 2. Forces of interaction between adsorbed molecules must be negligible . Based upon these two significant assumptions, Langmuir represents the
equation (Eq. 3) in the form of:

$$q_e = Q_oK_LC_e/1+K_LC_e \qquad (3)$$

To simplifying the eqn.(3),it converts in linear form

$$1/q_e = 1/Q_o + 1/Q_oK_LC_e \qquad (4)$$

Where:

C_e = the equilibrium concentration of adsorbate (mg/L)

q_e = the amount of adsorbate adsorbed per gram of the adsorbent at equilibrium (mg/g).

Q_o = maximum monolayer coverage capacity (mg/g)

K_L = Langmuir isotherm constant (L/mg).

This model was the most widely applied isotherm model. At shallow fluoride ions concentration, it effectively reduces to linear isotherm and hence satisfies Henry's law. On the other hand, at higher concentration of fluoride ions, it assumes monolayer adsorption (Amit Kumar Yadav* 2020).

VIII. KINETICS

8.1. Pseudo second-order equation model

This model helps to determine the chemisorptions nature of a particular adsorption process. In this model, the rate-controlling step is the chemical reaction and this pseudo second-order chemical reaction kinetics give the best correlation of the experimental data and the adsorption mechanism is chemically rate controlling. This is why it is known as chemisorption. The sorption kinetics must correspond to a reversible second order reaction at low sorbate/sorbent ratios which are initially very low, and two competitive reversible second order reactions at higher sorbate/sorbent ratios. Eq. (5) represents the
pseudo second-order kinetic model.

$$t/q = 1/b_2q_e{}^2 + 1/q_e.t \qquad (5)$$

Where, qe (mg/g) is the equilibrium adsorption capacity and k_2 (g/mg h) is the pseudo-second order constant. These can be experimentally determined from the slope and intercept of t/qt versus t plot (Shraboni Mukherjee 2018).

8.2. Elovich Model

Other than the pseudo-first order and pseudo-second order kineticmodels, Elovich model is also one among them which is usedto
describe a sorption process and is represented in Eq. (6).

$$dq/dt = \alpha e_t{}^{-\beta q} \qquad (6)$$

$$q_t = 1/\beta ln(\alpha\beta) + 1/\beta ln(t) \qquad (7)$$

Where α (mg/g/min) refers to the initial adsorption rate and β (g/mg)is the desorption constant related to the extent of the surface coverage. Eq. (7) represents the activation energy for chemisorptions, where qt is the amount of gas chemisorbed at time t. Eq.(7) is the simplified form of Eq. (6) when α β> >t by applying boundary conditions qt=0 at t=0 and qt=qt at t=t. If fluoride adsorption fits the Elovich model, a plot of qt vs. ln (t) will give a linear relationship with a slope of (1/β) and an intercept of (1/β) ln(αβ). Fluoride adsorption by groundnut shell and sweet lime was found to obey the Elovich kinetic model (Shraboni Mukherjee 2018).

8.3. Weber and Morris intra-particle diffusion model

The sorption rate is often used to determine the nature of the rate controlling step in regard of which, the intra-particle diffusion model has been greatly investigated which is shown in Eq. (8) and the linearized form is presented by Eq. (9) (Shraboni Mukherjee 2018). If the intra-particle diffusion model is the rate-limiting step, the amount of fluoride adsorbed at anytime t has to be directly proportional to the square root of contact time t and will pass through the origin.

$$q_t = k_{id}\, t^{0.5} \qquad (8)$$

$$\log q_t = \log k + 0.5 \log t \qquad (9)$$

Where, qt (mg/g) is the amount of fluoride adsorbed, t (min) refers to the contact time and kid is the intra-particle diffusion coefficient. Higher the value of kid, higher is the rate of adsorption. However, intra-particle

diffusion model is rarely used due to its complex nature of mathematical relationships which vary in form as a function of the sorbent's geometry .

8.4. Lagergren or pseudo first order equation model
This equation is considered to be the first one for defining sorption kinetics of liquid/solid system which is based on solid capacity
and is expressed in Eq. (10).

$$dq/dt = K_{ad}(q_e - q_t) \qquad (10)$$

Where, q_e (mg/L) and q_t (mg/g) refer to the solid phase concentration of fluoride at equilibrium and average solid phase concentration at contact time t respectively and k_{ad} (min^{-1}) is the rate constant of pseudo first-order adsorption. Eq. (10) is expressed in the linearised form by Eq.(11).

$$\ln(q_e - q_t) = \ln q_e - K_{ad}t \qquad (11)$$

This model also suggests a sorption process to be physisorption in nature. This indicates that the rate-limiting step in such kind of mechanismis diffusion and does not depend on the concentrations of both reactants, that is, physical exchange . The values obtained from $\ln(q_e - q_t)$ are correlated linearly with that of t and the plot between these two gives a linear relationship from which the value of kad is calculated from the slope. Eq. (11) is found to be different from a true first-order equation mainly in two ways: firstly, the number of available binding sites is not represented by the parameter $k_{ad}(q_e - q_t)$ and secondly, $\ln q_e$ is an adjustable parameter and it is usually not found equal to the intercept of the plot $\ln(q_e - q_t)$ vs. t whereas, in a first-order equation, the $\ln q_e$ must be equal to the intercept (Shraboni Mukherjee 2018).

IX. Thermodynamic studies
The thermodynamic factors are interrelated with the adsorption procedure;
$\Delta H°$- change in standard enthalpy
$\Delta S°$- change in standard entropy,
$\Delta G°$- change in standard free energy
The change in Gibbs
free energy can be calculated from the equation $\Delta G = -RT \ln k$. The adsorption distribution coefficient ($\ln K$) may be expressed in terms of ΔH^o and ΔS^o as a function of temperature,

$$\ln K = \Delta S^o/R - \Delta H^o/RT$$

where ΔH^o is the standard enthalpy change (kJ/mol) and ΔS^o is standard entropy change (J/mol/K). The values of ΔH^o and ΔS^o can be obtained from the slope and intercept of the plot of $\ln K$ against $1/T$. From the results, the $\Delta G°$ values are negative which confirms the fluoride removal is spontaneous and both the $\Delta S°$ and $\Delta H°$ values show positive value which confirms the endothermic and randomness increased at the solid solution interface during the fluoride removal (Nagaraj Ammavasi 2018).

Conclusions, recommendations and future perspectives
The goal of this paper is to assess the fluoride contamination of groundwater issue and to assess various alumina-based adsorbents as potential solutions. The activity of various alumina-based adsorbents can be summed up as follows based on this literature review.
The likelihood of commercialization and the viability of using these alumina-based adsorbents in practise, however, have not been investigated.

- Aluminum oxide by itself cannot produce the desired adsorption behaviour for the defluoridation process. Other metal oxides, either in bimetallic or trimetallic form, are required to support it. The complexity of this kind of structure formation raises the price of production.
- Even the most effective adsorbent for aluminium oxide by itself cannot achieve the desired adsorption behaviour for the defluoridation process.
  Other metal oxides, either in bimetallic or trimetallic form, are required to support it. The complexity of this kind of structure formation raises the price of production.
- Activated alumina is the most effective adsorbent for the defluoridation procedure. Although there are many adsorbents with a high adsorption capacity, activated alumina is the most effective in terms of implementation. The only issue with activated alumina is the potential for health problems due to leaching at lower pH ranges.
- The modified activated alumina created by adding some oxide to the alumina to stop it from leaching was also found to increase the adsorbent's capacity for defluoridation within acceptable pH and temperature ranges. The surface modification reduces the adsorbent's surface area but also makes fluoride ions and hydroxyl ions more reactive, leading to chemisorption in the system. Because of this, it has been necessary to modify the surface using multivalent metal ions such as $Al^{3+,}$ $Ca^{2+,}$ $Fe^{3+},$ $La^{3+},$ and Zr^{4+} through oxide

coatings or impregnation methods in order to increase the fluoride adsorption capacity and prevent alumina from leaching. Since nano-alumina adsorbents have a larger surface area and more activation sites, their performance is anticipated to be better. Focus on nano-ceramic coatings or impregnation of nano-ceramics on granular adsorbents like activated alumina may be the future perspective for the researchers.

The regeneration study of the used adsorbents for future use was conducted to demonstrate the process's economic viability, but more research is required before it can be commercialised. The majority of studies used batch experiments with synthetic water to calculate the impact of fluoride removal on a lab scale. As a result, the suggestion for synthetic water fails to demonstrate its originality or novelty with regard to groundwater defluoridation. Therefore, a globally viable, inexpensive adsorbent with a high capacity for removing fluoride that also has high social acceptance and is environmentally friendly is still a distant goal.

Acknowledgement-
Declaration of Competing Interest
The authors declares that they have no known competing financial interests or personal relationships that could have appeared to influence the analysis reported in this paper.

References

[1]. Amit Kumar Yadav*, Sunipa Bhattacharyya. "A review of the emerging ceramic adsorbents for defluoridation of." Journal of Water Process Engineering 36, 2020: 101365.

[2]. Analia Iriela, □, Stijn P. Bruneelb, Nahuel Schenonea, Alicia Fernández Cirellia. "The removal of fluoride from aqueous solution by a lateritic soil adsorption:." Ecotoxicology and Environmental Safety 149, 2018: 166-172.

[3]. Dr. Sreekanth Bose, Dr. Yashoda R and Dr. Manjunath P Puranik. "A review on defluoridation in India." International Journal of Applied Dental Sciences, 2018: 167-171.

[4]. Gabriel Murambasvina, Courtie Mahamadi *. "Effective fluoride adsorption using water hyacinth beads doped with." Groundwater for Sustainable Development 10, 2020: 10032.

[5]. Jiabin Chen , Renjie Yang , Zhiyong Zhang , Deyi Wu *. "Removal of fluoride from water using aluminum hydroxide-loaded zeolite." Journal of Hazardous Materials 421 (2022) 126817, 2022: 126817.

[6]. Jiabin Chen, Renjie Yang , Zhiyong Zhang , Deyi Wu *. "Removal of fluoride from water using aluminum hydroxide-loaded zeolite." Journal of Hazardous Materials 421 (2022) 126817, 2022: 126817.

[7]. Krishna Kumar Yadavb, Sandeep Kumarc, Quoc Bao Phamh, Neha Guptab, Shahabaldin Rezaniad,. "Fluoride contamination, health problems and remediation methods in Asian." Ecotoxicology and Environmental Safety 182 (2019) 109362, 2019: 109362.

[8]. M. Barathi a, A. Santhana Krishna Kumar a,b, N. Rajesh a,⇑. "Impact of fluoride in potable water – An outlook on the existing." Coordination Chemistry Reviews 387, 2019: 121-128.

[9]. Manas Ranjan Naik a, Manas Barik a, Vivekanand Jha b, Sunil Kumar Sahoo b,. "Spatial distribution and probabilistic health risk assessment of fluoride in." Groundwater for Sustainable Development 14, 2021: 100604.

[10]. Mei Wang, Xiaolin Yu, Chongling Yang, Xueqin Yang, Mengya Lin, Litao. "Removal of fluoride from aqueous solution by Mg-Al-Zr triple-metal composite." Chemical Engineering Journal, 2017.

[11]. Mengwei Wanga, Ling Liua, Huijun Lib, Yonggang Lic, Hongliang Liud, Changchun Houd,. "Thyroid function, intelligence, and low-moderate fluoride exposure among." Environment International 134, 2020: 105229.

[12]. Ming Gao, Wei Wang, Hongbing Yang□, Bang-Ce Ye. "Efficient removal of fluoride from aqueous solutions using 3D flower-like." Chemical Engineering Journal 380, 2020: 122459.

[13]. Mohit Chaudharya, Shweta Rawata, Nishant Jaina, Amit Bhatnagarb, Abhijit Maitia,□. "Chitosan-Fe-Al-Mn metal oxyhydroxides composite as highly efficient." Carbohydrate Polymers 216, 2019: 140-148.

[14]. Mostafa Mahinroosta ∗, Ali Allahverdi. "Pilot-scale valorization of hazardous aluminum dross into." Environmental Technology & Innovation 23, 2021: 101549.

[15]. Naderi, Majid. "Surface Area: Brunauer–Emmett–Teller (BET)." Progress in Filtration and Separation, 2015: 585-608.

[16]. Nagaraj Ammavasi, Rajan Mariappan. "Enhanced removal of hazardous fluoride from drinking." Journal of Environmental Chemical, 2018.

[17]. Norhene Mahfoudhi*, Sami Boufi*. "Porous material from cellulose nanofibrils coated with aluminum hydroxyde." Journal of Environmental Chemical Engineering 8, 2020: 103779.

[18]. Parimala Shivaprasad, Prakash Kumar Singh, Virendra Kumar Saharan, Suja George *. "Synthesis of nano alumina for defluoridation of drinking water." Nano-Structures & Nano-Objects 13, 2018: 109-120.

[19]. Qi Wanga, b, Pinghua Chena,b,□, Xiong Zengc, Hualin Jianga,b,□, Feifan Mengd, Xueqin Lia,b,. "Synthesis of (ZrO2-Al2O3)/GO nanocomposite by sonochemical method and." Journal of Hazardous Materials 381, 2020: 120954.

[20]. S. Tangsir, L.D. Hafshejani, A. Lähde, M. Maljanen, A. Hooshmand, A.A. Naseri, H. "Water defluoridation using Al2O3 nanoparticles synthesized by flame spray." Chemical Engineering Journal , 2015.

[21]. Shraboni Mukherjee, Gopinath Halder□. "A review on the sorptive elimination of fluoride from contaminated." Journal of Environmental Chemical Engineering 6, 2018: 1257-1270.

[22]. Subbaiah Muthu Prabhu, Murugan Subaramanian, Sankaran Meenakshi ⇑. "A simple one-pot in-situ method for the synthesis of aluminum." Chemical Engineering Journal 283, 2016: 1081-1089.

[23]. UNDP. https://www.undp.org/sustainable-development-goals.

[24]. Usha Kumari a, ⇑, Hammad Siddiqi a, Manisha Bal a, B.C. Meikap a,b,c. "Calcium and zirconium modified acid activated alumina for adsorptive." Advanced Powder Technology 31 (2020) 2045–2060, 2020: 2045-2060.

[25]. Usha Kumaria, □, Sushanta K. Beheraa, Hammad Siddiqia, B.C. Meikapa,b. "Facile method to synthesize efficient adsorbent from alumina by nitric acid." Journal of Hazardous Materials 381, 2020: 120917.

[26].   Vibha Sinha ∗, Sumedha Chakma. "Synthesis and evaluation of CMC-g-AMPS/Fe/Al/AC composite." Environmental Technology & Innovation 17, 2020: 100620.

[27].   Yohannes Desalegn Wirtu a, d, Fekadu Melak a,b,*, Menberu Yitbarek b,c, Higemengist Astatkie a. "Aluminum coated natural zeolite for water defluoridation: A." Groundwater for Sustainable Development 12, 2021: 100525.

[28].   Yuxuan He a, Liming Zhang a, Xiao An a, GengpingWanb,Wenjie Zhu a, Yongming Luoa,□. "Enhanced fluoride removal from water by rare earth (La and Ce)." Science of the Total Environment 688, 2019: 184-198.

[29].   Zhenzhen Chen, Yiling Liu, Lianzhen Mao,. "Effect of cation doping on the structure of." Ceramics International, 2017.