Preparation of colloidal hydrated alumina modified NaA zeolite derived from rice husk ash for effective removal of fluoride ions from water medium

Milan Kanti Naskar
Central Glass & Ceramic Research Institute (CSIR), Kolkata, India

ABSTRACT
Alumina is found to be a good adsorbent for the removal of fluoride. In the present study, rice husk ash-derived NaA zeolite has been modified with colloidal hydrated alumina in a cost-effective process for efficient removal of fluoride ions. The prepared NaA zeolite powder was added into colloidal hydrated alumina under stirring at 70°C/2 h followed by drying at 100°C/6 h to obtain modified zeolite. The product reveals enhanced adsorption efficiency (95–99%) for the removal of fluoride ions at wide ranges of adsorbate concentration (~5–200 mg/L), adsorbent concentration (0.5–10 g/L), pH (3–10), and temperature (30–70°C). Regeneration study shows that adsorption remained >90% up to third cycle followed by gradual decrease of adsorption for consecutive cycles. Kinetics study of fluoride adsorptions shows best fit for pseudo-second-order model demonstrating chemisorption process through a monolayer formation. The adsorption isotherm reveals that Langmuir isotherm is the best fit model indicating maximum adsorption capacities of 104.16, 68.12 and 36.13 mg/g for the adsorbent doses of 0.5, 1 and 2 g/L, respectively. Colloidal hydrated alumina modified NaA zeolite derived from rice husk ash could be utilized as low cost adsorbent for effective removal of fluoride ions from water.

1. Introduction
Fluoride ions (F⁻) contamination in aqueous medium is a great environment concern worldwide. Due to the increased level of fluoride concentration, the rural people of fluoride-affected areas suffer from serious health problems like dental fluorosis, osteoporosis, arthritis, infertility, neurological damage, infertility, etc. According to the World Health Organization (WHO), the permissible limit of fluoride concentration is 1.5 mg/L [1]. Fluoride in groundwater is originated by slow dissolution of fluorine-containing rocks such as granite, shale, syenite, basalt, etc. [2,3], in addition to the effluents discharged from different industries like glass and ceramic industries, aluminum smelters, coal-fired power stations brick and iron works, etc. [4]. In tropical countries like India, an increase level of fluoride concentration is observed, particularly in arid region of the country. Defluoridation technique is important topic of research in both the basic and applied fields. It is a great challenge for the removal of F⁻ ions from water by a simple and cost-effective process. For the removal of F⁻ from groundwater, sustainable, inexpensive and locally available raw materials can be used to develop effective adsorbent. It will be beneficial to the rural emerging communities toward increasing access to safe drinking water.

For removal of fluoride, the common technologies available are chemical treatment, membrane process and adsorption. However, the presence of competing ions such as phosphate, nitrate, chloride, carbonate, silicate and sulfate affects the removal efficiency. Reverse osmosis (RO) and nanofiltration (NF) method could be suitable for the removal of fluoride in the presence of the above competing ions. However, high operating cost, limited electricity supply for water pumping and washing of fouled membrane and scraping in the above processes are the major setback for rural population. Adsorption technique has proved an effective method due to its simple operation, high efficiency, little toxic sludge generation and low cost. Many adsorptive materials have been developed for the removal of F⁻ ions, such as activated alumina [5,6], activated carbon [7], bone charcoal [8], hydrotalcite-like compounds [9,10] and mixed metal oxides [11,12]. We investigated the effects of mesoporous alumina modified with different organic acids for the removal of fluoride ions [13]. However, searching a new type of adsorbent with its interesting properties toward the removal of fluoride is of utmost important in terms of low cost and high efficiency. Zeolites have been used for the removal of radioactive cations like Cs⁺ and Sr²⁺ [14].

Rice husk (RH) is an agriculture-based waste material. During production of rice from paddy (Oryza sativa) in rice mill, the husk content of paddy is burnt into ash forming rice husk ash (RHA). It causes...
environmental pollution, disposal problem and even reducing land fertility in the long term. Therefore, for the removal of $F^-$ ions from water, utilization of RHA containing 80–95% silica for the synthesis of zeolites via a simple and direct process, and their modification with metal ions could be more significant in terms of sustainability, cost-effectiveness and improved adsorption efficiency. Modified zeolite can be a potential adsorbent for the removal of $F^-$ ions due to large internal surface area, high aqueous and thermal stability.

In the present work, colloidal hydrated alumina modified zeolite derived from direct use of RHA (without pre-treatment) has been prepared for efficient removal of fluoride from water. Instead of using aluminum salts, colloidal hydrated alumina in the pH range 4–5 is used for modification of rice husk-based zeolite.

2. Experimental

2.1. Materials

Sodium aluminate purchased from Sigma-Aldrich, aluminum nitrate, ammonium hydroxide, sodium hydroxide, sodium fluoride each purchased from Merck and RHA (95.5% SiO$_2$) collected from J.M. Biotech Pvt. Ltd., India were used. Ultrapure water was used during the experiment.

2.2. Preparation of NaA zeolite

9.6 g RHA was added into 100 mL 3 M NaOH solution under stirring for 15 min followed by adding 6.8 g of sodium aluminate in 20 mL deionized water, and stirring was continued for 1 h. The molar composition was maintained as 5.5 Na$_2$O:1 Al$_2$O$_3$:4 SiO$_2$:190 H$_2$O. The mixed dispersion was hydrothermally treated at 90°C for 6 h. The resulting product was washed with water followed by drying at 90°C for 4 h to obtain NaA zeolite.

2.3. Preparation of colloidal hydrated alumina

For the preparation of colloidal hydrated alumina, NH$_4$OH was slowly added into 1 M Al(NO$_3$)$_3$ solution under stirring (500 rpm) at 50–60°C. Stirring was continued for 8 h with dropwise addition of NH$_4$OH to reach pH up to 4–5. A colloidal hydrated alumina was formed.

2.4. Preparation of colloidal hydrated alumina modified NaA zeolite

For the preparation of colloidal hydrated alumina modified zeolite, 5 g of as-prepared NaA zeolite was added into 100 mL of as-prepared colloidal hydrated alumina (5% solid loading) under stirring at 70°C for 2 h. It was cooled down to room temperature followed by adding NH$_3$OH slowly to maintain pH ~6–7. Colloidal hydrated alumina modified zeolite thus prepared was dried at 100°C for 6 h. The dried product was used for adsorption of fluoride.

2.5. Characterization

The synthesized colloidal hydrated alumina modified NaA zeolite was characterized by XRD (Philips X’Pert Pro XRD, PW 3050/60), XPS (ULVAC-PHI), nitrogen adsorption–desorption isotherms (Quantachrome (ASIQ MP), FESEM (Zeiss, Supra™ 35VP) and TEM (Tecnai G2 30ST (FEI)).

2.6. Experiment for fluoride adsorption

The effects of different experimental parameters like contact time, adsorbate (initial fluoride concentration) and adsorbent concentrations, pH, temperature and competing ions were studied for fluoride ion adsorption. Temperature and pH of the experiments were maintained as 30 ± 2°C and 6.7, respectively. To study the effects of contact time, pH and temperatures, different concentrations (0.5, 1 and 2 g/L) of adsorbents were taken. However, 2 g/L of adsorbent was used for competing ions effect and recyclability test. To investigate the effect of adsorbent dose on fluoride adsorption, the adsorbent dose was varied from 0.5 g/L to 10 g/L. Adsorption kinetic studies were performed by using different adsorbent doses (0.5, 1 and 2 g/L) with varying fluoride concentrations each. The adsorption study was performed electrochemically with a fluoride ion selective electrode (Model: Orion Versa Star 90) using total ionic strength adjustment buffer (TISAB). The amount of adsorbed fluoride ion, $q_e$ (mg g$^{-1}$) was determined from the following equation:

$$q_e = \left( C_0 - C_e \right) \left( V/m \right)$$

where $C_0$ and $C_e$ represent the initial and equilibrium concentration of fluoride ion (mg L$^{-1}$), respectively, while V and m are the volume of solution (liters) and adsorbent mass (g), respectively. The point of zero charge ($pH_{pzc}$) was determined by Noh and Schwarz method [15]. Samples of varying weight (0.005–2 g) were stirred with 0.001 N NaCl solution (10 mL) each for 24 h followed by measuring their pH. The change in pH was plotted vs. mass of the samples. With increasing mass of the samples, the pH approached an asymptotic value which determined the $pH_{pzc}$ of the sample.

3. Results and discussion

3.1. X-ray pattern

X-ray pattern of colloidal hydrated alumina modified NaA zeolite shows the crystallization of NaA zeolite
(Figure 1) with the appearance of peaks at 2θ values of 7.3, 10.2, 12.5, 16.2, 21.7, 24.2, 26.2, 27.2, 30.8 and 34.3 having (hkl) values of (200), (220), (222), (420), (600), (622), (640), (642), (644) and (664), respectively (JCPDF File #39–222). However, alumina is not crystallized during preparation of colloidal hydrated alumina modified NaA zeolite. It demonstrates that during modification of NaA zeolite using colloidal hydrated alumina, alumina remained as amorphous stage.

3.2. Microstructures

Figure 2(a) shows the FESEM image of colloidal hydrated alumina modified NaA zeolite. It resembles that cube-shaped NaA zeolite is surrounded by nanometer-sized (100–150 nm) hydrated alumina particles. The hydrated alumina particles are highly agglomerated due to electrostatic interaction between negatively charged surface of NaA zeolite and

Figure 2. (a) FESEM, (b) EDX, (c) TEM (low magnification) and (d) TEM (high magnification) of colloidal hydrated alumina modified NaA zeolite.
positively charged surface of Al(OH)$_2^+$ in hydrated alumina. Alumina particles are also self-aggregated due to hydrogen bonding and weak van der Walls force. The atomic percentage (At%) of the compositions, Al, Si, Na and O was found to be 15.34, 10.14, 0.86 and 73.66%, respectively as evidenced from EDX analysis (Figure 2(b)). TEM microstructure of the sample (Figure 2(c)) reveals about 1 µm sized NaA particle in which some smaller particles of hydrated alumina were adhered (red mark). The particle size of hydrated alumina ranged from 100 to 150 nm (Figure 2(d)).

3.3. $N_2$ adsorption–desorption isotherm and pore size distribution

Figure 3(a) shows $N_2$ adsorption–desorption isotherm of colloidal hydrated alumina modified NaA zeolite. At lower relative pressure ($p/p_o$) up to 0.4, a nearly horizontal plateau of the isotherm is observed followed by the formation of small loop in the $p/p_o$ range of 0.4–0.99. It indicates that both zeolitic micropores and interparticle mesopores are present in the sample. BET surface area of the product was found to be 54 m$^2$ g$^{-1}$ comprising of micropore surface area of 23 m$^2$ g$^{-1}$ and mesopore surface area of 31 m$^2$ g$^{-1}$ with pore volume of 0.0092 cm$^3$ g$^{-1}$. From the pore size distribution curve obtained from BJH desorption model (Figure 3(b)), it is clear that pore size of the sample is centered at 3.9 nm. For the adsorption of fluoride ions, surface area, pore volume and pore size have important role. High surface area, pore volume and abundance of mesopores favor efficient adsorption of fluoride ions from aqueous solution.

3.4. X-ray photoelectron spectra

Figure 4(a) shows X-ray photoelectron spectra with full scan survey of colloidal hydrated alumina modified NaA zeolite.

![Figure 3](image-url) **Figure 3.** (a) $N_2$ adsorption–desorption isotherm and (b) BJH pore size distribution of colloidal hydrated alumina modified NaA zeolite.

![Figure 4](image-url) **Figure 4.** XPS spectra of colloidal hydrated alumina modified NaA zeolite (a) full spectrum (b) Al2p, (c) Si2p, (d) Na1s and (e) O1s spectra.
NaA zeolite sample confirming the presence of Si, Al, Na and O in the sample. The binding energy at 73.98 eV is due to Al 2p (Figure 4(b)). The peaks with binding energies of 102.11 and 1071.56 eV are attributed to Si 2p (Figure 4(c)) and Na 1s (Figure 4(d)), respectively. The signal at 531.56 eV corresponds to O1s (Figure 4(e)) in Al-O-Si [16]. The elemental analysis (atomic %) of Al, Si, Na and O was found to be 17.99, 5.77, 0.65 and 75.59%, respectively as evidenced from XPS analysis. Supplementary Figure S1 (Supplementary Information) shows the XPS spectra of NaA zeolite derived from RHA before modification with colloidal hydrated alumina. Supplementary Table S1 (Supplementary Information) shows that peak positions of Al2p, Si2p, Na1s and O1s shift a little extent for NaA zeolite as compared with those in colloidal hydrated alumina. It could be due to change in chemical environment of the neighboring atoms in the presence and absence of colloidal hydrated alumina in NaA zeolite. For unmodified NaA zeolite, the atomic % of Al, Si, Na and O was determined as 6.3, 14.32, 11.03 and 68.35%, respectively. Comparing with colloidal hydrated alumina modified NaA zeolite, atomic % of Na and Si is higher and that of Al is lower in unmodified zeolite. The drastic fall of Na content and increase of Al content in modified NaA zeolite helps facilitate adsorption of fluoride ions in aqueous solution.

3.5. Adsorption study of fluoride ions from water
3.5.1. Effect of contact time
The fluoride adsorption on colloidal hydrated alumina modified zeolite sample was investigated as a function of contact time using initial fluoride concentration of 4.83 mgL$^{-1}$ with different adsorbent doses (0.5, 1 and 2 gL$^{-1}$) at pH 6.7 and temperature 30°C (Figure 5(a)). It shows that percentage adsorption of fluoride ions increased sharply up to 20 min for 0.5 gL$^{-1}$ adsorbent dose followed by slow increase up to 120 min, while with increase in adsorbent dose (1 and 2 gL$^{-1}$) there is slow increase in percentage adsorption with time. It reveals that at 120 min the adsorption equilibrium is reached for all the adsorbent doses. Initially after 20 min of adsorption, the percentage adsorptions were 90.8, 89.8 and 99.1% for adsorbent doses of 0.5, 1 and 2 gL$^{-1}$, respectively. However, after 120 min of adsorption the percentage adsorption became 97.4, 98.1 and 99.5% for adsorbent doses of 0.5, 1 and 2 gL$^{-1}$, respectively.

3.5.2. Effect of adsorbent dose
Figure 5(b) shows the change in percentage adsorption with variation of adsorbent dose on the uptake of fluoride ions using initial fluoride concentration of 4.83 mgL$^{-1}$ with contact time of 120 min at pH 6.7 and temperature 30°C. It is noticed that adsorption
capacity (%) sharply increased with increase in adsorbent dose up to 4 g L\(^{-1}\). However, with further increase in adsorbent dose, the fluoride uptake capacity is not enhanced significantly. With increase in adsorbent dose, higher accessibility of adsorbent surface causes large amount of fluoride uptake [17]. However, after a certain concentration of adsorbent dose, the adsorbent surface sites become saturated resulting a little change in fluoride uptake capacity. For adsorbent dose of 4 g L\(^{-1}\), the percentage fluoride removal was found to be 99.5 which reached up to 99.7 for adsorbent dose of 10 g L\(^{-1}\).

3.5.3. Effect of initial fluoride concentration
Figure 5(c) depicts variation of defluoridation efficiency in percentage with the concentration of initial fluoride ions (adsorbate) for the adsorbent concentrations of 0.5, 1 and 2 g/L at pH 6.7 with contact time of 120 min. It shows that there is a decrease trend of % of adsorption with increase in adsorbate concentration for all the adsorbent doses. However, for 0.5 g/L of adsorbent dose, a significant decrease of fluoridation efficiency is noticed compared to other adsorbent doses (1 and 2 g/L). It can be explained that with increase in fluoride ion concentration (adsorbate dose), more fluoride ions are accumulated in the adsorbent sites resulting saturation of co-ordination sites [18].

3.5.4. Effect of pH
The pH of aqueous solution has an important role on the adsorption of fluoride ions because it monitors the surface charge with positively charged hydrogen ions and negatively charged hydroxyl ions. Accordingly, it influences the co-ordination of fluoride ions with the surface of the adsorbent. Figure 5(d) shows the change of fluoride adsorption (%) with the variation of pH for different adsorbent doses using initial fluoride concentration of 4.83 mg L\(^{-1}\) with contact time of 120 min at 30°C. It is noticed that at pH 4.5, the adsorption % is maximum followed by a decreasing trend of adsorption up to pH 10. Interestingly, at pH 3, a slight decrease of adsorption is observed compared to that of pH 4.5. At very low pH (pH 3), fluoride ions combine with H\(^+\) ions in aqueous solution forming soluble HF, as well as positively charged adsorbent surface generating electrostatic interaction between adsorbent and adsorbate species. However, with slight increase in pH (pH 4–5) below the point of zero charge (pH\(_{pzc}\)), the colloidal hydrated alumina modified zeolite surface having –Al-OH\(_3^+\) tends to adsorb more fluoride ions in aqueous solution. For the determination of point of zero charge (pH\(_{pzc}\)), the pH of the solution was plotted against the mass of the adsorbent (Supplementary Figure S2, Supplementary Information). After a certain mass, an equilibrium pH was reached which determined the pH\(_{pzc}\). The pH\(_{pzc}\) of the sample was found to be 5.6. Interestingly, at pH above the pH\(_{pzc}\) (pH > pH\(_{pzc}\)), the abundance of negatively charged (OH\(^-\) ions) surface of the adsorbent repels the negatively charged fluoride ions hindering its adsorption. At more alkaline pH (pH 10), hydrated aluminum hydroxide complex is formed which covers the surface of colloidal hydrated alumina modified zeolite (adsorbent) restricting the adsorption of fluoride ions significantly [19].

3.5.5. Effect of temperature
The effect of temperature on the adsorption of fluoride ions was studied varying temperatures from 30 to 70°C for different adsorbent doses using initial fluoride concentration of 4.83 mg L\(^{-1}\) with contact time of 120 min at pH 6.7. Figure 6(a) shows that with increase in temperature, percentage adsorption increased significantly endothermic process of adsorption [20]. It is worth mentioning that with increase in temperature, the diffusion rate of fluoride ions is increased through the decrease boundary layers and internal pores of adsorbent resulting higher rate of adsorption [21].

3.5.6. Effect of co-existing anions
Many co-existing anions present in natural groundwater may compete with fluoride ions during adsorption affecting the removal efficiency of adsorbent. The effect of different co-existing anions like chloride, nitrate, phosphate and sulfate on the uptake of fluoride ions was studied using initial fluoride concentration of 5.61 mg L\(^{-1}\), adsorbent dose of 2 g L\(^{-1}\), contact time of 120 min, pH 6.7 and temperature 30°C. Figure 6(b) reveals that co-existing ions decreased the uptake of fluoride ions to a certain extent. Among all these co-existing ions, PO\(_4^{3-}\) ions significantly for fluoride adsorption because of competition between PO\(_4^{3-}\) and fluoride ions for the same active sites of the adsorbent [4,22]. Due to larger hydrated ionic radius of phosphate ion, it forms outer sphere complexes which is held by long range electrostatic force compared to other anions having smaller hydrated radius [23].

3.5.7. Desorption and regeneration test
Desorption and regeneration studies were proceeded with 2 g/L of adsorbent dose after adsorption of 4.57 mg/L of fluoride solution in 120 min at pH 6.7 and temperature 30°C. The adsorbed adsorbent was treated with 0.1 M Na\(_2\)CO\(_3\) solution under stirring for 20 h. It was then washed with deionized water, filtered and dried to obtain regenerated sample. Thus, regeneration process was continued up to five consecutive cycles. Figure 6(c) shows that percentage adsorption remained >90% up to third cycle followed by gradual decrease of adsorption for fourth and fifth cycles.

3.5.8. Adsorption kinetics
The adsorption kinetics study was applied to pseudo-first-order and pseudo-second-order models. The mathematical expressions of the two models are
presented in Table 1. For the first-order reaction, a linear plot of \( \ln(q_e - q_t) \) vs. \( t \) produced a straight line, where \( q_e \) (amounts of fluoride adsorbed at equilibrium) and \( k_1 \) (first-order rate constant) can be determined by the intercept and slope of the curve, respectively. In case of second-order reaction, a straight line is obtained by plotting \( t/q_t \) vs. \( t \), where \( q_e \) and \( k_2 \) (second-order rate constant) can be determined by the intercept and slope of the curve, respectively. Figure 7 shows the linear fitting of kinetic data of the adsorbent for (a) pseudo-first-order and (b) pseudo-second-order kinetic models. Table 1 shows the kinetic parameters calculated from the above plots for the fluoride adsorption by different adsorbent doses. The correlation co-efficient \( (R^2) \) values indicate that pseudo-second-order model is better fitted for adsorption data. It demonstrates that adsorption of fluoride is governed by chemisorption process through a monolayer formation. It is noticed that the amounts of fluoride adsorbed at equilibrium increased with decreasing adsorbent dose.

### 3.5.9. Adsorption Isotherms

Study of adsorption isotherms is important to understand the adsorption process and adsorption capacity at equilibrium. To obtain equilibrium data, the initial fluoride concentration was varied for the adsorbent doses of 0.5, 1 and 2 g/L at pH 6.7 with contact time of 120 min (Section 3.5.3). The adsorption isotherms for different adsorbent doses are described by Langmuir isotherms [24] and Freundlich isotherms [25] models. The linear
expression of Langmuir and Freundlich isotherms are shown in Table 2. In Langmuir isotherms, by plotting $C_e/q_e$ vs. $C_e$, the maximum adsorption capacity, $q_m$ (mg/g) and Langmuir adsorption constant, $K_L$ can be determined from the slope and intercept of the linear plot, respectively. In Freundlich isotherms, the adsorption intensity, $n_F$ and adsorption capacity, $K_F$ (Freundlich constant) can be calculated from the slope and intercept of the linear curve, respectively by plotting log $q_e$ vs. log $C_e$. Figure 8 reveals the linear fitting curves of (a) Langmuir and (b) Freundlich adsorption isotherms. The adsorption isotherm parameters obtained from Langmuir and Freundlich isotherms curves are listed in Table 2. It is clear that adsorption of fluoride by colloidal hydrated alumina modified NaA zeolite fitted well with Langmuir isotherm model as evidenced from higher correlation co-efficient ($R^2$) than that obtained from Freundlich isotherm. The maximum fluoride adsorption capacities ($q_m$) were found to be 104.16, 68.12 and 36.13 mg/g for the adsorbent doses of 0.5, 1 and 2 g/L, respectively. It is obvious that adsorption capacity increased with decrease in adsorbent doses.

3.5.10. Thermodynamic parameters
Changes of energy in adsorption process are explained by thermodynamic analysis. The thermodynamic parameters, Gibbs-free energy ($\Delta G^\circ$), enthalpy ($\Delta H^\circ$) and

| Table 2. The parameters obtained from Langmuir and Freundlich models. |
|-----------------|--------|--------|
| Langmuir isotherm | $C_e/q_e = C_e/q_m + 1/K_L q_m$ | $K_L$ (L/mg$^{-1}$) | $q_m$ (mg/g) | $R^2$ |
|                 |                                  | 0.0216 | 104.1666 | 0.8970 | 0.0973 | 36.1271 | 0.9983 |
| Freundlich isotherm | log $q_e = \log K_F + 1/n_F \log C_e$ | $K_F$ | $n_F$ | $R^2$ |
|                 |                                  | 10.4580 | 2.6539 | 0.8781 | 11.6923 | 2.7642 | 0.9826 | 3.3624 | 0.8717 |

Note: $q_e$ is the amounts of fluoride adsorbed at equilibrium and $q_m$ is $q_e$ for a complete monolayer, i.e., maximum adsorption capacity (mg/g), $K_L$ is adsorption equilibrium constant (L/mg); $K_F$ and $n_F$ are empirical constants, indicating the adsorption capacity and adsorption intensity, respectively.

Figure 7. Linear fitting of kinetic data of the adsorbent for (a) pseudo-first-order and (b) pseudo-second-order kinetic models.

Figure 8. (a) Langmuir and (b) Freundlich isotherms of fluoride ions adsorption on the adsorbent.
entropy ($\Delta S^o$) can be determined using the following equations.

$$\Delta G^o = -RT \ln K_d,$$

where $K_d = \frac{q_e}{C_e}$

$$\ln K_d = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT}$$

where $K_d$ is the equilibrium constant, $R$ is the universal gas constant (8.314 J mol$^{-1}$ K$^{-1}$) and $T$ is the temperature in Kelvin scale. From Equation 3, by plotting $\ln K_d$ vs. $1/T$ (van’t Hoff plot), a straight line is obtained. The $\Delta H^o$ and $\Delta S^o$ can be calculated from the slope and intercept of the plot, respectively (Figure 9). The values of thermodynamic parameters are presented in Table 3. It reveals that $\Delta G^o$ values for all the adsorbent doses are negative signifying spontaneity of the adsorption process. It also indicates that with increase in temperature, spontaneity of the adsorption reaction increased. The negative values of $\Delta H^o$ demonstrate the exothermic process of adsorption, while positive $\Delta S^o$ values signify increasing number of adsorbate molecules/ions at the solid–liquid interface during adsorption process [26].

### 3.5.11. Fluoride adsorption mechanism

Figure 10 shows schematically a proposed mechanism for fluoride adsorption by colloidal hydrated alumina modified NaA zeolite. Zeolite A (NaA zeolite) particles possess surface hydroxyl (-OH) groups. These surface

![Figure 9](image)

**Figure 9.** Plot of $\ln K_d$ versus $1/T$ for fluoride ions adsorption.

![Figure 10](image)

**Figure 10.** A proposed mechanism for fluoride adsorption by colloidal hydrated alumina modified NaA zeolite.

| Adsorbent dose (g/L) | $\Delta H^o$ (kJ/mol) | $\Delta S^o$ (J/mol/K) | $\Delta G^o$ (kJ/mol) |
|---------------------|-----------------------|------------------------|-----------------------|
| 0.5                 | -6.18                 | 56.60                  | -10.98 at 303 K       |
|                     |                       |                        | -11.46 at 313 K       |
|                     |                       |                        | -12.14 at 323 K       |
|                     |                       |                        | -12.66 at 333 K       |
|                     |                       |                        | -13.25 at 343 K       |
| 1.0                 | -13.10                | 76.85                  | -10.23 at 303 K       |
|                     |                       |                        | -10.89 at 313 K       |
|                     |                       |                        | -12.08 at 323 K       |
|                     |                       |                        | -12.46 at 333 K       |
|                     |                       |                        | -13.38 at 343 K       |
| 2.0                 | -9.30                 | 69.33                  | -11.61 at 303 K       |
|                     |                       |                        | -12.40 at 313 K       |
|                     |                       |                        | -13.22 at 323 K       |
|                     |                       |                        | -13.84 at 333 K       |
|                     |                       |                        | -14.40 at 343 K       |
-OH groups interact with colloidal hydrated alumina through hydrogen bonding. Colloidal hydrated alumina having surface hydroxyl groups gets protonated at pH 4–5 below pH_{pzc} (pH < pH_{pzc}). Thus, zeolite adsorbed colloidal hydrated alumina having protonated surface hydroxyl group (–OH_{3}⁻) combines with negatively charged fluoride ions via electrostatic interaction. However, at higher pH above pH_{pzc} (pH < pH_{pzc}), there is a competition between negatively charged hydroxyl ions and fluoride ions to bind with colloidal hydrated alumina modified zeolite resulting its diminished adsorption efficiency.

4. Conclusions
Colloidal hydrated alumina modified NaA zeolite with solid loading of 5% was prepared at 70°C under stirring for 2 h maintaining pH 6–7. It shows specific surface area of 54 m² g⁻¹ comprising micropores and mesopores. The atomic % of aluminum, silicon, sodium and oxygen in the product was found to be 17.99, 5.77, 0.65 and 75.59%, respectively as evidenced from X-ray photoelectron spectroscopy. Comparing unmodified NaA zeolite, the drastic fall of sodium content and increase of aluminum content in modified NaA zeolite helps facilitate adsorption of fluoride ions in aqueous solution. The synthesized materials showed efficient adsorption capacity for the removal of fluoride. Within a very short time (20 min), the adsorption % reached >90%. The adsorption % sharply increased with decrease in pH and increase in adsorbent dose. Among the co-existing ions, phosphate ions affect significantly for fluoride adsorption because of larger hydrated ionic radius to compete with fluoride ions for the same active sites of the adsorbent. The maximum efficiency of fluoride adsorption remained practically unchanged up to three cycles of the regenerated samples. The adsorption studies showed pseudo-second-order kinetics and Langmuir isotherm model to be fitted well. The amounts of fluoride adsorbed at equilibrium increased with decreasing adsorbent dose. The thermodynamics study indicates spontaneous and exothermic process of adsorption.

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Disclosure statement
No potential conflict of interest was reported by the author.

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