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# Application of Nanoclay in the Removal of Fluoride from Water: A Review

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**Abstract**

Water contamination with fluoride poses a significant threat to public health, leading to various adverse effects such as dental and skeletal fluorosis. Traditional methods for fluoride removal often involve the use of expensive and complex technologies. Nanotechnology offers a promising avenue for the development of efficient and cost-effective solutions. This research paper provides a comprehensive review of the current state of knowledge regarding the removal of fluoride from water using nanoclay adsorbents. It explores the synthesis, characteristic properties, performance mechanism and application of nanoclay adsorbents, along with their performance efficiency and potential challenges.

**Keywords:** Dental and skeletal fluorosis, Nanotechnology, Fluoride, Nanoclay adsorbents

## 1. Introduction

Fluoride contamination in water sources is a widespread issue affecting both developed and developing regions. Fluoride is beneficial for dental health in appropriate amounts, but disproportionate intake can lead to serious health issues. Excessive fluoride intake has been linked to dental and skeletal fluorosis, among other health problems (Kawamura, 2000; Qasim et al., 2002; Devi et al. , 2008; Dobaradaran et al., 2009). Fluoride is often added to drinking water and dental products, such as toothpaste, to prevent tooth decay (Naghizadeh and Gholami, 2017). But when it is being consumed in excessive amounts over a long period, it can lead to dental fluorosis. Dental fluorosis occurs when excessive fluoride is ingested during the development of teeth in childhood. This excess fluoride can disrupt the normal enamel formation process, leading to dental fluorosis. The most common sign of dental fluorosis is the appearance of white streaks or spots on the teeth. In more severe cases, teeth may have brown discoloration, pitting, and surface irregularities (Teimouri et al., 2015). Dental fluorosis doesn't typically cause pain or health problems, but it can affect the cosmetic appearance of teeth. In skeletal fluorosis, fluoride accumulates in bones and joints, causing changes in bone structure and mineralization, which causes joint pain, stiffness, limited joint movement, and bone deformities. In severe cases, it can lead to skeletal problems resembling arthritis or other bone diseases (Teimouri et al., 2015; Fernando et al., 2019). Fluoride can enter in body through water and food. Water is the major source of fluoride intake in human beings (Naghizadeh and Gholami, 2017). Preventing fluorosis involves monitoring and controlling the levels of fluoride in drinking water sources. In areas where natural fluoride levels are high, water treatment methods may be employed to reduce fluoride concentrations.

The common water treatment methods used for removal of excess concentration of fluoride from water are activated alumina adsorption, calcium precipitation, ion exchange, reverse osmosis, coagulation and precipitation, electrocoagulation (Fan et al., 2003; Çengeloglu et al. 2002; Tripathy et al., 2006 ; Wu et al., 2007 ; Kumar et al., 2009). But these methods have their own precincts such as disposal of the spent adsorbent & sludge, dependency on physical parameters such as pH & temperature, high operational and maintenance costs and requirement of skilled operators (Mahvi et al., 2006; Derakhshani & Naghizadeh, 2014; Naghizadeh, 2015). Therefore conventional water treatment methods may fall short in effectively removing fluoride from water sources, necessitating the exploration of alternative and innovative approaches, such as nanotechnology. Nano adsorbents such as metal oxide nanoparticles and carbon based nanomaterials, nano composites such as mixed metal oxide nanoparticles and polymeric nanocomposits, nano structured membranes, nano catalyst, nano electrodes all has potential for removal of fluoride from water (Teimouri et al., 2015; Fernando et al., 2019). Nanoclay is a type of nanomaterial that has gained attention for its potential applications in water treatment, including the removal of contaminants like fluoride. The use of nanoclay for fluoride removal from water is based on its high surface area, porous structure, and adsorption capabilities (Litchfield and Baird 2008; Jlassi et al., 2017). Furthermore nanoclay surfaces can be modified to enhance their adsorption capabilities. One advantage of using nanoclay is the potential for regeneration. After reaching saturation with fluoride, nanoclay can often be regenerated by desorption methods, allowing for multiple use cycles (Kamble et al., 2009). Nanoclay can be applied in both batch and continuous flow systems for fluoride removal (Kamble et al., 2009; Mudzielwana and Gitari, 2021). Thus nanoclay can be considered as a promising material for removal of fluoride from water.

The primary objective of this research paper is to critically review the current research on the use of nanoclay adsorbents for the removal of fluoride from water. The paper aims to provide insights into the synthesis, characteristic properties, performance mechanism and potential challenges associated with the application of nanoclay adsorbents in water treatment.

## 2 Types of nanoclay

Nanoclays are a type of nanomaterial that consists of clay minerals with particle sizes in the nanometer range. They have gained attention in various applications, including water treatment, due to their unique properties. When it comes to removing fluoride from water, nanoclays can be employed in different forms. Different types of nanoclays that have been studied for fluoride removal are listed below in Table 1:

**Table 1: Different types of nanoclay for removal of fluoride from water**

| Type of nanoclay | Characteristics | Reference |
|---|---|---|
| Montmorillonite Nanoclay | • Montmorillonite is a common clay mineral belonging to the smectite group.<br>• Its high surface area and cation exchange capacity make it suitable for adsorption of fluoride ions.<br>• Modification of montmorillonite with organic or inorganic compounds can enhance its fluoride removal efficiency. | Fernando et al., 2019; Naghizadeh and Gholami, 2017 |
| Kaolinite Nanoclay | • Kaolinite is another clay mineral that has been | Nabbou et al., 2018 |

| | | |
|---|---|---|
| | investigated for fluoride removal.<br>• Its layered structure provides sites for the adsorption of fluoride ions.<br>• Surface modifications or functionalization of kaolinite can improve its adsorption capacity. | |
| Bentonite Nanoclay | • Bentonite is a clay composed mainly of montmorillonite.<br>• It is known for its high surface area and swelling properties.<br>• Bentonite nanoclays have been explored for their potential in fluoride adsorption. | Kamble et al., 2009 |
| Layered Double Hydroxide (LDH) Nanoclay | • LDHs are synthetic layered materials that consist of positively charged layers.<br>• They can be intercalated with anions, including fluoride, through ion exchange.<br>• LDH nanoclays can be designed for selective fluoride removal. | Tajuddin et al., 2023 |
| Mixed Metal Oxide Nanoclay | • Nanoclays with mixed metal oxides, such as iron and aluminum oxides, have shown promise in fluoride removal.<br>• These materials often have high surface reactivity and can effectively adsorb fluoride ions. | Teimouri et al., 2015; Mudzielwana and Gitari, 2021 |
| Functionalized Nanoclays | • Nanoclays can be functionalized with various organic or inorganic compounds to tailor their surface properties for enhanced fluoride removal.<br>• Amino-functionalized nanoclays, for example, may exhibit improved adsorption of fluoride ions. | Gammoudi et al., 2013 |

**3 Methods of preparation of nanoclay**

Nanoclays are nano-sized particles derived from natural clay minerals such as montmorillonite, kaolinite, and halloysite. They have attracted significant attention due to their unique properties and wide-ranging applications in various fields including materials science, nanotechnology, environmental science, and biomedicine. Some common methods for the preparation of nanoclays are shown in Figure 1and described below:

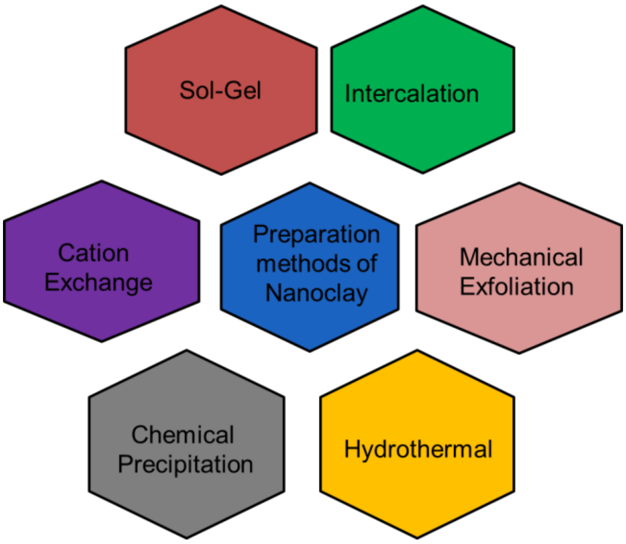


Figure1: Methods of preparation of nanoclay

1. **Sol-Gel Method**: This method involves the synthesis of nanoclays through the sol-gel process, where precursor solutions containing the clay mineral are hydrolyzed and condensed to form a gel, followed by drying and calcination to obtain the desired nanoclay structure (Qian et al., 2008). This method allows for precise control over the size and morphology of the nanoclays.

2. **Intercalation Method**: In this method, the interlayer spaces of the clay mineral are expanded by introducing organic or inorganic intercalating agents, followed by exfoliation to obtain nanoclays with increased surface area and improved properties (Naveen and Manoj, 2016).

3. **Mechanical Exfoliation**: Mechanical exfoliation involves the physical exfoliation of bulk clay minerals into nanosheets using techniques such as ball milling, shear mixing, or sonication (Chen et al., 2012; Agubra et al., 2013). This method is relatively simple and scalable for large-scale production of nanoclays.

4. **Hydrothermal Synthesis**: Hydrothermal synthesis involves the reaction of clay minerals with water or aqueous solutions at elevated temperatures and pressures, to the formation of nanoclays with controlled crystallinity and properties (Golubeva et al., 2013).

5. **Chemical Precipitation**: Chemical precipitation methods involve the precipitation of nanoclays from aqueous solutions of clay minerals by adding suitable precipitating agents or adjusting the pH and temperature conditions (Sirait et al. 2017).

6. **Cation Exchange:** Montmorillonite, a type of smectite clay, can be modified through cation exchange reactions. This involves replacing the exchangeable cations on the clay's interlayer with other metal cations, which can enhance the clay's adsorption capacity for fluoride ions (Ghorbanpour et al., 2018).

**4 Characteristics properties of nanoclay for removal of fluoride from water**

Nanoclay, specifically montmorillonite-based clays, has been studied for its potential in removing fluoride from water due to its unique characteristics. Here are some of the properties and characteristics of nanoclay that make it suitable for fluoride removal (Figure 2):

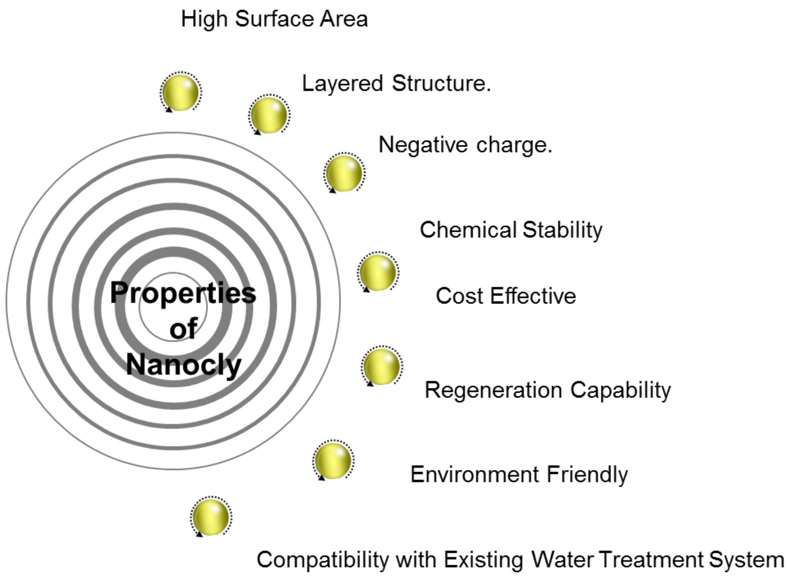


Figure 2: Characteristics properties of nanoclay for removal of fluoride from water

1. **High Surface Area:** Nanoclay particles typically have a high surface area, which provides more active sites for the adsorption of fluoride ions. This increased surface area enhances the efficiency of fluoride removal (Litchfield and Baird 2008; Jlassi et al., 2017).
2. **Layered Structure:** Montmorillonite, a common type of nanoclay, has a layered structure with exchangeable cations between layers. This structure allows for ion exchange reactions, where fluoride ions can replace other ions between the clay layers (Jlassi et al., 2017).
3. **Negative Charge:** The surfaces of nanoclay particles are often negatively charged, facilitating the attraction and adsorption of positively charged fluoride ions. The electrostatic interaction between the negatively charged clay and fluoride ions is a key mechanism in the removal process but sometime it also restricts its application (Jlassi et al., 2017). This limitation can be resolved by improving mechanical properties of the clay through different modification (Sarkar et al., 2019).
4. **Chemical Stability:** Nanoclays are generally stable in various environmental conditions, ensuring the effectiveness of fluoride removal over time. The stability of the nanoclay prevents degradation and maintains its adsorption capacity (Jlassi et al., 2017).
5. **Cost-Effective:** Nanoclay is relatively cost-effective compared to some other materials used for fluoride removal. Its availability and affordability make it a viable option for water treatment in certain contexts (Litchfield and Baird 2008; Jlassi et al., 2017).

6. **Regeneration Capability:** Some nanoclays can be regenerated and reused for multiple cycles of fluoride removal. This is advantageous in terms of cost and environmental impact, as it reduces the need for frequent replacement of adsorbents (Kamble et al., 2009).

7. **Environmentally Friendly:** Nanoclays are considered environmentally friendly, as they are natural materials and do not introduce harmful chemicals into the water during the fluoride removal process. This characteristic is essential for sustainable water treatment practices (Litchfield and Baird 2008; Jlassi et al., 2017).

8. **Compatibility with Existing Water Treatment Systems:** Nanoclay-based materials can be integrated into existing water treatment processes, making it easier to implement them in water treatment plants and other facilities (Han et al., 2019; Mao and Gao,2021).

**5 Application of nanoclay adsorbents for removal of fluoride**

Different researchers used nanoclay based adsorbent for removal of fluoride from water (Table 1).

Naghizadeh and Gholami, 2017 used montmorillonite and bentonite nanoparticles in removal of fluoride from water. The experimental investigation was carried out under batch conditions to examine the influence of various parameters including contact time, pH, initial fluoride concentration, and adsorbent mass. Subsequently, the thermodynamics, isotherms, and kinetics of both adsorbents were analyzed. The maximum adsorption capacity for both adsorbents was observed at a fluoride concentration of 20 mg/L, contact time of 60 minutes, pH of 3, and adsorbent mass of 0.25 g/L. The adsorption process exhibited exothermic behavior. Results from Langmuir and Freundlich isotherm studies indicated that bentonite nanoparticles closely adhered to the Langmuir model, whereas montmorillonite nanoparticles adhered to both models. Additionally, the adsorption of fluoride by bentonite across all fluoride concentrations and montmorillonite at higher fluoride concentrations followed pseudo second-order kinetics.

Chitosan/montmorillonite/zirconium oxide (CTS/MMT/ZrO2) nanocomposites were synthesized by Teimouri et al., 2015 through varying the molar ratios of chitosan (CTS) to montmorillonite/zirconium oxide (MMT/ZrO2). These nanocomposites underwent characterization using FTIR, XRD, and SEM analyses. Utilizing the BET technique, surface area, pore volume, and pore size distribution of the CTS/MMT/ZrO2 were determined.

The study further explored the impacts of different molar ratios of CTS to MMT/ZrO2, initial pH of the fluoride solution, contact time, temperature, adsorbent dose, and initial fluoride concentration on adsorption capacities. Optimal conditions for fluoride removal were identified as follows: a molar ratio of CTS/MMT/ZrO2 at 1:1, pH at 4, temperature at 30°C, 60 minutes of contact time in 25.00 mL of 20 mg/L fluoride solution, utilizing 0.1 grams of adsorbent. Experimental data revealed a fluoride adsorption capacity of 23 mg/g for CTS/MMT/ZrO2.

Comparison of fluoride removal capacities among CTS, MMT, ZrO2, CTS/ZrO2, CTS/MMT, and CTS/MMT/ZrO2 nanocomposites indicated that the CTS/MMT/ZrO2 nanocomposite exhibited higher adsorption capacity than the average values of the individual components. Adsorption kinetics and isotherms were examined, revealing that pseudo-second-order kinetics and the Langmuir equation provided optimal descriptions for the sorption processes.

A novel composite system of hydroxyapatite montmorillonite (HAP-MMT) was synthesized by Fernando et al., 2019 through a straightforward wet chemical in situ precipitation approach. Additionally, pristine nano hydroxyapatite (HAP) was synthesized for comparative analysis. Comprehensive characterization of these materials involved Fourier Transform Infrared Spectroscopy (FT-IR), Scanning Electron Microscopy (SEM), X-ray Diffraction (XRD), and Brunauer–Emmett–Teller (BET) isotherms to examine functional groups, morphology, crystallinity, and surface area, respectively.

Batch adsorption and kinetic studies were conducted to assess fluoride adsorption capabilities of both HAP-MMT and neat HAP. The investigation encompassed parameters such as contact time, pH, initial concentration, temperature, and thermodynamic factors, as well as the influence of coexisting ions on fluoride adsorption by HAP-MMT. Isotherm experiments were analyzed using four adsorption models: Langmuir, Freundlich, Temkin, and Dubinin Radushkevich.

The Freundlich adsorption isotherm model best described fluoride adsorption over HAP-MMT, demonstrating a more than twofold enhancement in adsorption capacity (16.7 mg g^-1) compared to neat HAP. The pseudo-second-order kinetic model was identified as the most fitting for both adsorbents. Thermodynamic analysis indicated that fluoride adsorption by HAP-MMT is more favorable across the temperature range of 27°C–60°C. The improved fluoride adsorption observed with HAP-MMT is attributed to its exfoliated structure.

Fernando et al., 2019 suggested that the improvement in fluoride adsorption is may be due to the expansion of layers of MMT and incorporation of HAP in to the layers.

Kamble et al., 2009 investigated the adsorption potential of bentonite clay incorporated with metal oxides (lanthanum, magnesium, and manganese) for removing fluoride from drinking water. Batch equilibrium experiments were conducted to understand the adsorption behaviour, kinetics, and mechanisms of fluoride ion adsorption. Various physicochemical parameters such as pH, adsorbent dose, initial fluoride concentration, and the presence of interfering co-ions were examined.

Results of this research indicated that the 10% La-bentonite exhibited superior fluoride uptake capacity compared to Mg-bentonite, Mn-bentonite, and bare bentonite clay for defluoridation of drinking water. Fluoride uptake was higher in acidic pH conditions compared to alkaline pH. Equilibrium adsorption data fitted well with both Langmuir and Freundlich isotherm models and kinetic data indicates towards first order kinetics with intraparticle diffusion mechanism.

Additionally Kamble et al., 2009 found that, certain co-existing ions were found to enhance fluoride removal, while carbonate and bicarbonate anions had a detrimental effect. The adsorption rate was relatively fast, with maximum fluoride uptake achieved within 30 minutes. Fluoride removal decreases by 55.20% and 75.11% after the first and second uses of the adsorbent, respectively. Nevertheless, it is feasible to regenerate the adsorbent through alkali–acid treatment. The modified adsorbent material demonstrated improved fluoride removal properties for real-world field water samples, possibly due to the positive influence of other co-ions present in the water.

In the research conducted by Obijole et al., 2019, clay soils enriched with aluminosilicates were prepared via mechanochemical activation for removal of fluoride from water. Analysis of their chemical and mineralogical characteristics was conducted using X-Ray Fluorescence (XRF) and X-ray diffraction (XRD). The investigation extended to the assessment of functional groups, morphology, and surface area through Fourier Transform Infra-Red (FTIR), Scanning Electron Microscopy (SEM), and Brunauer-Emmett-Teller (BET) analysis, respectively. Batch experiments were employed to gauge defluoridation efficacy.

Results of this study indicated a maximum adsorption capacity of 1.87 mg/g with a 32% fluoride removal rate. Interestingly, fluoride adsorption diminished in the presence of $Cl^-$, $PO_4^{3-}$, and $CO_3^{2-}$ ions, while it increased in the presence of $SO_4^{2-}$ and $NO^{3-}$ ions. Data fitting to Freundlich isotherms confirmed heterogeneous multilayer adsorption. Kinetic analysis revealed a good fit to the pseudo-second-order model, suggesting the sorption process follows this mechanism. The sorption of fluoride onto the clay surfaces followed intra-particle diffusion, as evidenced by the results of kinetic studies. Furthermore, a high correlation coefficient indicated that particle diffusion significantly influenced the sorption process, whereas pore diffusion had minimal impact. These findings underscored the potential of activated clays for defluoridation purposes.

A composite adsorbent for fluoride removal was created by Mudzielwana and Gitari, 2021 through blending locally sourced smectite-rich clay with MnO2-coated bentonite clay. The adsorbent material was characterised with X-ray diffraction, X-ray fluorescence and Fourier Transform Infrared Spectroscopy. To assess its effectiveness, fixed-bed column experiments were conducted. Results indicated that increasing parameters such as bed height and initial fluoride concentration enhanced adsorption capacity, while higher flow rates reduced it. The maximum adsorption capacity was achieved at a breakthrough point of 0.6 mg/g, with a flow rate of 0.65 mL/min, bed height of 2.5 cm, and fluoride concentration of 3.75 mg/L. The composite could be regenerated using 0.01 M $Na_2CO_3$ and reused for up to 2 cycles. Analysis using the Thomas breakthrough model suggested that fluoride adsorption involved chemical interaction and ion transfer into the internal layers of the adsorbent particles. These findings highlight the potential of the $MnO_2$-bentonite-smectite composite for groundwater defluoridation applications.

Lamayi et al., 2018 used montmorillonite clay, a natural nanomaterial, underwent collection, purification, and subsequent application in fluoride removal in their study. The process involved the preparation of activated montmorillonite clay by refluxing 150 g of ground clay in 500 mL of 1M HCl at 120°C for ninety minutes. Fluoride levels were measured using SPADNS reagent and a UV/visible spectrophotometer at a wavelength of 570 nm. The study investigated adsorption parameters such as adsorbent dose, contact time, and pH effects. Optimal conditions for fluoride removal were observed at a pH of 2, a contact time of 50 minutes, an adsorbent dose of 2.0 g, and a temperature of 25°C, achieving a maximum removal efficiency of 83.5%. Kinetic models including pseudo-first order and pseudo-second order were employed, with experimental data favoring the pseudo-second order kinetic model. This research underscores the potential of montmorillonite clay as a natural nanoadsorbent for fluoride removal, contributing to the prevention of dental fluorosis.

Nabbou et al., 2018 investigates the utilization of kaolinite clay for extracting fluoride ions from Saharan groundwater in the Tindouf region of Algeria, where elevated fluoride concentrations pose a threat to potable water safety. Adsorption experiments reveal that fluoride ion removal is notably effective within a pH range of 4.5 to 6, exhibiting adsorption capacities of 0.442 and 0.448 mg/g, respectively. The adsorption process is aptly described by applying kinetic and isotherm adsorption correlations. Notably, the pseudo-second-order kinetic model and Freundlich isotherm exhibit strong fits with the experimental data.

In this study thermodynamic assessments highlight that fluoride sorption into clay intensifies with rising temperatures from 30 to 55°C, indicating an endothermic sorption process. Examination of fluoride removal from simulated potable water reveals that the presence of nitrate and chloride ions has no discernible effect on fluoride uptake. However, sulphate and carbonate ions lead to a reduction in adsorption capacity. These findings suggest a competitive interaction among ions, potentially resulting in electrostatic repulsion forces between fluoride and the clay surface. This investigation underscores kaolinite as an effective and economically viable material for mitigating fluoride ion contamination in groundwater.

| **Nanoclay adsorbent** | **Type of study** | **Optimum parameters** | **Adsorption capacity** | **Isotherm followed** | **Kinetic behaviour** | **Reference** |
|---|---|---|---|---|---|---|
| Montmorillonite nanoparticles | Batch study | Contact time = 60 minutes, pH = 3, Fluoride solution= 20 mg/L, Adsorbent mass = 0.25 g/L | | Langmuir and Freundlich | Pseudo second-order kinetics at higher fluoride concentration | Naghizadeh and Gholami, 2017 |
| Bentonite nanoparticles | Batch study | Contact time = 60 minutes, pH = 3, Fluoride solution= 20 mg/L, Adsorbent mass = 0.25 g/L | | Langmuir model | Pseudo second-order kinetics | Naghizadeh and Gholami, 2017 |
| Chitosan/montmorillonite/zirconium oxide | Batch study | pH = 4, temperature = 30°C, contact time = 60 min, Fluoride solution= 20 mg/L, Adsorbent dose=0.1 g | 23 mg/g | Langmuir model | Pseudo second-order kinetics | Teimouri et al., 2015 |
| Hydroxyapatite montmorillonite composite | Batch study | pH=5, contact time= 30 min, Fluoride solution = 30 mg/L | 16.7 mg/g | Freundlich model | Pseudo second-order kinetics | Fernando et al., 2019 |
| La-bentonite | Batch | Adsorbent dose = 4g/ L pH=5, Contact time= 30 min | 1.4 mg/ g | Langmuir and Freundlich | First order kinetics with intraparticle diffusion | Kamble et al., 2009 |

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|---|---|---|---|---|---|---|
| | | | | model | | |
| Clay soils enriched with aluminosilicates | Batch | Adsorbent dose = 2.0 g/100 mL, pH=5, Contact time= 60 , fluoride concentration of 3.2 mg/L min | 1.87 mg/g | Freundlich model | Pseudo second order kinetics with intraparticle diffusion | Obijole et al., 2019 |
| MnO2 bentonite-smectite rich clay soils composite | Fixed bed colum n | Flow rate of 0.65 mL/min, bed height of 2.5 cm, and fluoride concentration of 3.75 mg/L | 0.6 mg/g | - | Thomas breakthrough model | Mudzielwana and Gitari, 2021 |
| Montmorillonite clay | Batch study | pH of 2, a contact time of 50 minutes, an adsorbent dose of 2.0 g, and a temperature of 25°C | 83.5% | - | Pseudo second-order kinetics | Lamayi et al., 2018 |
| Kaolinite clay | Batch study | pH 5.8 and temperature 28 ± 02 C, Fluoride = mg/L, adsorbent dose of 1.0 g | 0.45 mg/g | Freundlich model | Pseudo second-order kinetics | Nabbou et al., 2018 |

## 6 Performance mechanism of removal of fluoride by nanoclay adsorbents

The removal of fluoride using nanoclay adsorbents involves several mechanisms that exploit the properties of nanoclay materials to effectively adsorb fluoride ions from water. Nanoclay adsorbents typically refer to clay minerals that have been processed into nanoscale particles, offering a high surface area and enhanced reactivity compared to their bulk counterparts. Here are some mechanisms involved in the removal process:

1. **Surface Adsorption**: Nanoclay materials have a high specific surface area due to their nanoporous structure, providing ample sites for the adsorption of fluoride ions. The fluoride ions are attracted to the charged surfaces of nanoclay particles through electrostatic interactions. The surface area-to-volume ratio of nanoclay enhances the accessibility of fluoride ions to adsorption sites, improving the efficiency of the process (Litchfield and Baird 2008; Jlassi et al., 2017).

2. **Ion Exchange**: Nanoclay materials often possess a net negative surface charge due to the presence of hydroxyl groups and isomorphic substitutions within their structure. Fluoride ions, being negatively charged, can undergo ion exchange with the exchangeable cations present on the surface of nanoclay particles, such as sodium, potassium, or calcium ions. This mechanism involves the replacement of the exchangeable cations with fluoride ions, leading to their removal from the aqueous solution (Ghorbanpour et al., 2018).

3. **Chemical Precipitation**: Some nanoclay materials contain active sites capable of promoting the precipitation of insoluble fluoride compounds, such as calcium fluoride (CaF2) or aluminum fluoride (AlF3). These compounds form as a result of chemical reactions between fluoride ions and components of the nanoclay structure. Precipitation helps in the removal of fluoride ions by reducing their concentration in the aqueous phase (Ayalew, 2023).

4. **Complexation**: Certain nanoclay materials may contain functional groups capable of forming complexes with fluoride ions through coordination chemistry. Functionalized nanoclays with organic ligands or metal oxides/hydroxides on their surface can effectively bind fluoride ions through coordination bonds, facilitating their removal from water (Guo et al., 2018).

5. **pH Dependent Adsorption**: The pH of the solution can influence the adsorption capacity of nanoclay adsorbents for fluoride ions. At lower pH values, the surface of nanoclay materials may become protonated, leading to increased electrostatic attraction between the positively charged surface and fluoride ions. However, at higher pH values, competition between hydroxide ions and fluoride ions for adsorption sites may reduce the overall removal efficiency (Ayalew, 2023).

Therefore the performance mechanism of nanoclay adsorbents for fluoride removal involves a combination of physical and chemical interactions, including surface adsorption, ion exchange, chemical precipitation, complexation, and pH-dependent processes. Optimization of these mechanisms through material modification and process conditions can enhance the efficacy of nanoclay-based adsorption systems for water treatment applications.

## 7 Advantage and challenges in use of nanoclay adsorbents for removal of fluoride

Using nanoclay adsorbents for fluoride removal offers several advantages over traditional methods. Nanoclay materials typically have high surface areas due to their nanostructure, providing more active sites for fluoride adsorption compared to conventional adsorbents. The nanoscale structure of nanoclays allows for increased interaction with fluoride ions, leading to higher adsorption capacities per unit mass compared to bulk clay materials. Nanoclay adsorbents can be engineered to exhibit selective adsorption towards fluoride ions while minimizing interference from other ions present in the water, resulting in efficient removal of fluoride with minimal impact on water quality. Nanoclay adsorbents can often be regenerated and reused multiple times without significant loss of adsorption capacity, thereby reducing operating costs and environmental impact compared to disposable adsorbents. Although initial costs for nanoclay synthesis or modification may be higher, the long-term cost-effectiveness of nanoclay adsorbents can be advantageous due to their high adsorption capacities and regeneration potential (Litchfield and Baird 2008; Jlassi et al., 2017; Kamble et al., 2009).

The utilization of nanoclay adsorbents for fluoride removal presents several challenges despite its promising potential. Nanoclay materials might exhibit limited adsorption capacity for fluoride ions due to their inherent properties. Enhancing the adsorption capacity while maintaining other desirable properties is crucial. The adsorption kinetics of nanoclay adsorbents might be slower compared to other materials, leading to longer contact times or the need for additional treatment step. Presence of other ions in water, particularly those with higher affinity for the adsorbent, can hinder fluoride adsorption efficiency. Developing selective adsorbents or strategies to mitigate interference from co-existing ions is essential. Scaling up the production of nanoclay adsorbents for practical applications while maintaining cost-effectiveness is a significant challenge that needs to be addressed for large-scale fluoride removal.

Addressing these challenges requires interdisciplinary research efforts involving materials science, environmental engineering, and chemistry to develop efficient and sustainable nanoclay-based adsorbents for fluoride removal.

## 8 Future scope

Regeneration methods such as desorption with suitable eluents restore adsorption capacity. Reusability of nanoclay adsorbents reduces operational costs and environmental impact. Long-term stability and performance of nanoclay based adsorbent for defluoridation need to be evaluated for practical applications. It is essential to sScale up nanoclay production for commercial applications. Integration of nanoclay-based adsorbents into existing water treatment systems is one of the important aspects for water defluoridation.

## 9 Conclusion

Fluoride contamination in water sources poses significant health risks. Various methods have been employed for fluoride removal, including adsorption techniques. Nanotechnology offers promising solutions, with nanoclay emerging as a potential adsorbent as it possesses high surface area and porosity which is ideal for adsorption applications. Its layered structure provides numerous active sites for fluoride binding and it is biocompatible and environmentally friendly material.Various methods such as intercalation, functionalization, and grafting enhance its adsorption properties. Surface modification increases selectivity and efficiency for fluoride removal. Composite materials incorporating nanoclay with other adsorbents show improved performance.

Langmuir and Freundlich isotherms used to model adsorption equilibrium for fluoride removal from water by nanoclay adsorbent and pseudo-first-order and pseudo-second-order kinetics describe its adsorption rate. Knowledge of these parameters is crucial for designing efficient adsorption systems.

Nanoclay holds promise as an effective adsorbent for fluoride removal from water. Further research is needed to optimize its performance and overcome existing challenges. Application of nanoclay offers a sustainable solution to mitigate fluoride contamination and safeguard public health.

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