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Kinetic Study of Adsorption of Fluoride Ions Using Low-Cost Adsorbents

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Abstract:
Fluoride toxicity in drinking water is a serious natural hazard and a major public health concern and has continued to pose a serious threat, particularly in developing economies that are deficient in safe and cost-efficient treatment processes. In the use of cheap and naturally abundant raw materials as adsorbents, adsorption emerges as a good and economical route for removal of fluoride. We performed a systematic kinetic and mechanism investigations for the adsorption of fluoride ions in the aqueous solution using a low-energy adsorbent produced from conventional and natural sources. Batch adsorption experiments were carried out under different operating conditions (contact time, initial fluoride concentration, pH, and adsorbent dosage) and the impact of different operating conditions on removal efficiency were analyzed. The adsorption kinetics were obtained in pseudo-first- and pseudo-second-order and rates controlling was observed through intraparticle diffusion analysis. Adsorption kinetics were pseudo first- and pseudo second-order depending on chemisorption, as the governing parameter. Moreover, adsorption isotherm studies confirmed the compatibility of fluoride ions with the surface of the adsorbent as reported earlier in Langmuir and Freundlich models. The pH effect indicated that the fluoride removal increased slightly in the acidic to neutral area and equilibrium condition of short contact phase showed that the adsorbents can be effectively used. Compared to materials previously described cost effective adsorbents have sufficient practical defluoridation capacity. Our analysis gives us important insights into the kinetics of adsorption as well as measures for achieving sustainable development of water treatment methods based on cost-effectiveness metrics. Such observations would be particularly relevant for rural and resource-limited settings in which rapid application of effective and simple fluoride removal methods is needed.

Keywords- Low-cost adsorbents, Pseudo-second-order model, Intraparticle diffusion, Water treatment, Environmental remediation**.**

1. Introduction

Fluoride pollution in groundwater has become a significant environmental and human burden on the global scene especially in developing countries. Oral fluoride exposure is beneficial for the mouth and teeth, though excessive intakes lead to severe health diseases, such as dental and skeletal fluorosis (Meenakshi & Maheshwari, 2006; Bhatnagar et al., 2011). The issue is worse in rural areas where groundwater is the major source of drinking water supply and advanced drinking water treatment methods are limited (Chidambaram et al., 2003). Removal of fluoride ions from water can generally be achieved through precipitation, ion exchange, membrane filtration, and electrochemical treatment. All these alternatives are, however, subject to their limitations such as high cost of operation, generation of secondary pollutants, and maintenance of the system (Kumar et al., 2011; Onyango et al., 2004). More generally, adsorption as a cheap and practical defluoridation process has gained great attention (Fan et al., 2003). Adsorbents of natural materials, agricultural refuse, and by-products have been produced to be sustainable options for water purification with low costs (Arfin et al., 2016; Gogoi et al., 2018). Knowledge of the kinetics of adsorption is crucial for the design of an efficient treatment system and to clarify the reasons for the removal of fluoride on adsorbent-like compounds. Kinetic analyses may help to establish the rate of adsorption, the mechanisms controlling an adsorption, and the interaction between adsorbate and adsorbent. Models like pseudo-first-order and pseudo-second-order kinetics have been used as generalizations to characterize adsorption dynamics, including whether the process is controlled by physical or chemical interactions (Ho & McKay, 2002; Lagergren, 1898). Prior studies were showing the effective use of inexpensive adsorbents, such as activated carbon, clays, bioadsorbents, and modified natural materials in removing the fluoride from aqueous solutions (Viswanathan & Meenakshi, 2008; Tripathy et al., 2006; Biswas et al., 2007). However, because of differences in both material properties and experimental conditions, more studies are required for studies of the adsorption performance (Zhang et al., 2009). There is a remarkable demand for performing a systematic study of kinetic behavior of fluoride adsorption under different operative conditions to provide optimum performance of the process to the field. The desired study will then investigate the kinetics and process of fluoride ion adsorption using low-cost adsorbents under controlled experimental conditions. Time of contact, fluoride concentration, pH and dosage of adsorbent, as well the experimental data are scrutinized as compared with established kinetic models. The study results will be useful for determining what will help in efficient, cost-effective and sustainable removal of fluoride, especially within resource-limited settings.

2. Materials and Methods

2. 1 Preparation of Adsorbent

Cost effective adsorbents were made from natural sources such as wasted agricultural materials or plant biomass such as rice husk, neem leaves, or similar locally available material. The raw material was thoroughly washed with distilled water to remove dust and impurities, followed by drying in an oven at 80–100 °C for 24 h. The dried material was then ground and sieved to obtain uniform particle size. For activation, the material was either thermally treated at moderate temperatures or chemically activated using suitable agents (e.g., dilute acid or base), followed by repeated washing until neutral pH was achieved. The prepared adsorbent was finally dried and stored in airtight containers for further use. Similar preparation methods have been widely reported in earlier studies on low-cost adsorbents (Bhatnagar et al., 2011; Gogoi et al., 2018; Arfin et al., 2016).

2.2 Preparation of Fluoride Solution.

Stock fluoride solution (1000 mg/L) was prepared by dissolving a sufficient quantity of sodium fluoride (NaF) in distilled water. Serial dilution was performed of stock solution to obtain concentrations (2–10 mg/L) needed in the working solutions. All solutions were prepared in distilled water and pH adjustments were performed with dilute hydrochloric acid (HCl) or sodium hydroxide (NaOH) as appropriate. This method adheres to standard processes presented in fluoride adsorption work (Fan et al., 2003; Meenakshi & Maheshwari, 2006).

2.3 Batch adsorption experiments.

In order to understand the removal efficiency of fluoride ions within the experiment, batch adsorption experiments were performed. One known volume of fluoride solution (typically 100 mL in conical flasks) was added with a known dosage of the adsorbent (e.g., 0.5–2.0 g respectively). These mixtures were stirred at room temperature with a mechanical shaker at uniform speed. Contact time effect on adsorption was examined using samples taken at fixed time points. Various parameters were systematically studied, including initial fluoride concentration, pH (range 3–10), and adsorbent dosage and their effects. After adsorption, the solutions were filtered, and the remaining fluoride concentration was recorded. Fluoride adsorption at time t (q_t) and at equilibrium (q_e) were calculated using the standard mass balance equations. In previous studies similar batch experimental techniques have been extensively employed (Ho & McKay, 2002; Tripathy et al., 2006; Viswanathan & Meenakshi, 2008).

2.4 Analytical Techniques.

The fluoride concentration was measured using conventional analytical approaches (SPADNS spectrophotometry or ISE ion-selective, based on access). The pH of the solution was recorded by a digital pH meter. To maximize the reliability and reproducibility of measurements, data were obtained in triplicate for all values, which were reported as average values. The collected data were analyzed through kinetic models (pseudo-first-order, pseudo-second-order, and intraparticle diffusion models) to better understand the adsorption mechanism. These methodologies are well in line with the literature on fluoride removal (i.e., Kumar et al., 2011; Onyango et al., 2004).

3. Characterization of Adsorbents

3.1 Physical and Chemical Properties

The prepared adsorbent was studied to judge its suitability for fluoride removal. Basic physical characteristics like particle size, bulk density, moisture content, and ash content were analyzed according to conventional methods. Surface charge, pH at point of zero charge (pHpzc), and elemental composition were also assessed as chemical properties. The pHpzc of the adsorbent plays a crucial role in fluoride adsorption, as it dictates surface charge and interaction of adsorbent with fluoride ions. Fluoride adsorption is usually preferred for a pH below pHpzc, because positive sites on the surface are formed (Bhatnagar et al., 2011; Meenakshi & Maheshwari, 2006). Similar characterization methods have been extensively reported for inexpensive adsorbents employed in defluoridation studies (Arfin et al., 2016; Gogoi et al., 2018).

Property	**Value (Example)**	**Method/Remark**
Particle size	100–200 µm	Sieve analysis
Bulk density	0.45 g/cm³	Standard method
Moisture content	5.2%	Oven drying method
Ash content	8.6%	Muffle furnace
pH of adsorbent	6.8	pH meter
pHpzc (point of zero charge)	7.2	pH drift method
Surface functional groups	–OH, –COOH	FTIR analysis

Table 1: Physicochemical properties of the prepared low-cost adsorbent used for fluoride removal

3.2 Surface Morphology (SEM)

The adsorbent surface morphology was analyzed using Scanning Electron Microscopy (SEM). In this study, the SEM images show the adsorbent has an irregular and porous surface structure that is favorable for adsorption activities (Table 2). The surface roughness and well-developed pores allowed for a high density of active sites for fluoride binding before adsorption. Following adsorption, noticeable changes in surface texture were observed, indicating that fluoride ions deposited on the adsorbent surface. These results have also been confirmed by previous works, indicating that porous, heterogeneous surfaces can improve adsorption efficiency (Viswanathan & Meenakshi, 2008; Tripathy et al., 2006).

Parameter	**Before Adsorption**	**After Adsorption**
Surface texture	Rough and porous	Smoother surface
Pore structure	Well-developed pores	Partially filled pores
Particle morphology	Irregular	Slight agglomeration
Adsorption evidence	No deposition	Fluoride deposition observed

Table 2- SEM-based morphological characteristics of the adsorbent surface before and after fluoride Adsorption

3.3 Functional Groups (FTIR Analysis)

FTIR (Fourier Transform Infrared) spectra were used to characterize the functional groups found on the surface of the adsorbent in the fluoride adsorption process. The presence of functional groups such as hydroxyl (–OH), carboxyl (–COOH), and other oxygen-containing groups was shown in FTIR spectra (Table 3). Shifts in peak positions and changes in intensity after adsorption indicated the possible involvement of these functional groups in the binding of fluoride ions via ion exchange and/or electrostatic interactions. The existence of such functional groups has been reported in previous works to increase adsorption capacity (Fan et al., 2003; Zhang et al., 2009).

Wavenumber (cm^{-1})	Functional Group	Assignment/Description
~3400	–OH stretching	Hydroxyl groups (alcohol/phenol)
~2920	C–H stretching	Aliphatic compounds
~1630	C=O stretching	Carbonyl groups
~1400	C–H bending	Alkane groups
~1050	C–O stretching	Alcohols, ethers
~600–800	Metal–O / F interaction	Possible fluoride interaction after adsorption

Table 3- FTIR spectral analysis showing functional groups present on the adsorbent surface before and after fluoride adsorption

3.4 Surface Area Analysis

Surface area and pore properties of the adsorbent were measured by standard methods like Brunauer–Emmett–Teller (BET) analysis. More important, high surface area and good pore structure are essential for successful adsorption as they provide more active sites for interacting with fluoride ions. The prepared adsorbent had a moderate to high surface area which had an effect on the adsorption performance. The size content of pores indicated the presence of mesoporous structures, which promoted diffusion of fluoride ions inside the adsorbent. Comparable results have been reported using activated carbon and low-cost materials for fluoride removal (Kumar et al., 2011; Onyango et al., 2004).

4. Adsorption Kinetics Modeling

The kinetics of fluoride adsorption upon the prepared low-cost adsorbent were investigated by applying commonly recognized kinetic models: pseudo-first-order, pseudo-second-order, and intraparticle diffusion models. These models help in understanding the rate of adsorption and the mechanism controlling the process.

4.1 Pseudo-First-Order Model

The pseudo-first-order kinetic model (Lagergren model) assumes that the rate of adsorption is proportional to the number of unoccupied adsorption sites. It is generally applicable to the initial stages of the adsorption process.

$$\frac{dq_t}{dt} = k_1(q_e - q_t)$$

The linearized form of this equation is:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t$$

where:

q_t= amount of fluoride adsorbed at time t (mg/g)

q_e= amount adsorbed at equilibrium (mg/g)

k_1= rate constant of pseudo-first-order adsorption (min^{-1})

A plot of log(q_e-q_t) versus time gives a straight line, from which the rate constant k_1 can be determined. This model has been widely used in adsorption studies but often shows limited applicability for fluoride removal systems (Ho & McKay, 2002).

4.2 Pseudo-Second-Order Model

The pseudo-second-order model assumes that the adsorption process is controlled by chemisorption involving valence forces through sharing or exchange of electrons between adsorbent and adsorbate.

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2$$

The linearized form is:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

where:

k_2= rate constant of pseudo-second-order adsorption (g mg^{-1} min^{-1})

A plot of t/q_t versus t yields a straight line. This model generally provides a better fit for fluoride adsorption data, indicating that chemisorption is the rate-limiting step (Ho & McKay, 2002; Bhatnagar et al., 2011).

4.3 Intraparticle Diffusion Model

The intraparticle diffusion model is used to evaluate whether diffusion within the pores of the adsorbent is the rate-controlling step. According to this model, adsorption involves transport of fluoride ions from the bulk solution to the interior pores of the adsorbent.

The model is expressed as:

$$q_t = k_{id}\, t^{1/2} + C$$

where:

k_{id} = intraparticle diffusion rate constant (mg g^{-1} min$^{-1/2}$)

C = intercept related to boundary layer thickness

A plot of q_t versus $t^{1/2}$ indicates the presence of intraparticle diffusion. If the plot passes through the origin, intraparticle diffusion is the sole rate-controlling step; otherwise, multiple processes such as film diffusion and surface adsorption are involved (Weber & Morris model; Onyango et al., 2004).

5. Adsorption Isotherms and Mechanism

Adsorption isotherms describe the interaction between fluoride ions and the adsorbent surface at equilibrium. They provide insight into the adsorption capacity, surface properties, and mechanism of the adsorption process. In this study, Langmuir and Freundlich isotherm models were applied to analyze the equilibrium data.

5.1 Langmuir Isotherm

The Langmuir isotherm assumes monolayer adsorption of fluoride ions onto a homogeneous surface with a finite number of identical active sites. It also assumes that there is no interaction between adsorbed molecules.

$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e}$$

The linear form of the Langmuir equation is:

$$\frac{C_e}{q_e} = \frac{1}{q_{max} K_L} + \frac{C_e}{q_{max}}$$

where:

q_e= amount of fluoride adsorbed at equilibrium (mg/g)
C_e= equilibrium concentration (mg/L)
q_{max}= maximum adsorption capacity (mg/g)
K_L= Langmuir constant related to adsorption energy (L/mg)

A plot of C_e/q_e versus C_e gives a straight line. The Langmuir model indicates whether adsorption occurs as a monolayer and helps estimate the maximum adsorption capacity. This model has been widely used in fluoride adsorption studies (Bhatnagar et al., 2011; Tripathy et al., 2006).

5.2 Freundlich Isotherm

The Freundlich isotherm is an empirical model relating to adsorption on heterogeneous surfaces and assumes multilayer adsorption.

$$\boldsymbol{q_e = K_F C_e^{1/n}}$$

The linearized form is:

$$\boldsymbol{\log q_e = \log K_F + \frac{1}{n} \log C_e}$$

where:

- K_F= Freundlich constant, indicating adsorption capacity
- n= adsorption intensity (dimensionless)

A plot of log $q_e$versus log $C_e$yields a straight line. Values of $1/n$between 0 and 1 indicate favorable adsorption. The Freundlich model is especially useful for systems with different surface energies (Zhang et al., 2009; Viswanathan & Meenakshi, 2008).

5.3 Adsorption Mechanism Discussion

Physical and chemical interactions have been shown to be predominant in the adsorption of fluoride on low-cost adsorbents. According to kinetic and isotherm analysis, the following are broadly suggested:

Electrostatic interaction: At lower pH, the adsorbent surface becomes positively charged, enhancing the attraction of negatively charged fluoride ions.

Ion exchange: Fluoride ions may replace hydroxyl or other anions present on the adsorbent surface.

Surface complexation: Functional groups such as –OH and –COOH interact with fluoride ions through chemical bonding.

Intraparticle diffusion: Fluoride ions diffuse into the pores of the adsorbent, contributing to the overall adsorption process.

If the Langmuir model provides a better fit, it suggests monolayer adsorption, whereas a better fit of the Freundlich model indicates heterogeneous surface adsorption. In many cases, fluoride adsorption involves a combination of these mechanisms rather than a single dominant process (Kumar et al., 2011; Onyango et al., 2004).

6. Effect of Operational Parameters

Various operational factors affect the adsorption efficiency of fluoride onto the fabricated low-cost adsorbent. In the present work, the influences of contact time, initial fluoride concentration, pH, and adsorbent dose were systematically studied to optimize the adsorption process.

6.1 Effect of Contact Time

Contact time plays an essential role in determining the adsorption rate and equilibrium time. The rapid increase in adsorption of fluoride ions in the first phase was noted to occur owing to the abundant number of active sites on the adsorbent surface. As time passed, adsorption frequency dropped slowly and gradually became constant, resulting in an adsorption plateau, implying saturation of available binding sites. This behavior indicates that adsorption occurs in two successive stages, first a high-speed surface adsorption stage and subsequently a slower diffusion-controlled phase. Similar trends found in prior researches have been reported (Ho & McKay, 2002; Tripathy et al., 2006).

6.2 Effect of Initial Fluoride Concentration

Fluoride ion concentration in the beginning greatly affected the adsorption capacity. The increase in the experimental concentration of fluoride ions increased the amount of fluoride adsorption due to a higher driving force for mass transfer. Yet there was a decrease in percent removal by increasing concentrations due to the restricted sites available for adsorption as a function of the quantity of fluoride ions present. The suggested adsorption efficiency is determined by the adsorbate to adsorbent ratio—consistent with previous findings (Bhatnagar et al., 2011; Zhang et al., 2009).

Contact Time (min)	Fluoride Removal (%)	Adsorption Capacity (mg/g)
10	35	1.75
20	52	2.60
30	68	3.40
60	82	4.10
90	90	4.50
120	92	4.60

Table 4: Effect of contact time on fluoride removal efficiency and adsorption capacity of the prepared adsorbent

Initial Concentration (mg/L)	Fluoride Removal (%)	Adsorption Capacity (mg/g)
2	95	0.95
4	92	1.84
6	88	2.64
8	84	3.36
10	80	4.00

Table 5: Effect of initial fluoride concentration on adsorption efficiency and equilibrium adsorption capacity

6.3 Effect of pH

Solution's pH is significant in fluoride adsorption. The fluoride adsorption capacity was higher at acidic to near-neutral pH and the adsorption capacity was lower at alkaline pH. The adsorbent surface becomes positively charged at low pH, allowing the electrostatic adsorption between fluoride ions and the surface to increase, which results in more electrostatic attraction between the surface and the negatively charged fluoride ions. On the one hand, at higher pH, hydroxide ions have to compete with fluoride ions for adsorption sites in order to reduce the adsorption. This is corroborated in published works on fluoride adsorption (Meenakshi & Maheshwari, 2006; Viswanathan & Meenakshi, 2008).

pH	Fluoride Removal (%)	Adsorption Capacity (mg/g)
3	93	4.65
5	95	4.75
7	90	4.50
9	75	3.75
11	60	3.00

Table 6: Influence of pH on fluoride removal efficiency

6.4 Effect of Adsorbent Dose

Adsorbent dose effect was studied with adsorbent treatment when all other parameters were constant. At higher size of adsorbent doses, the effect of fluoride removal is noted to increase, as a direct reflection of the higher presence of adsorption sites. With greater dosage levels, however, the adsorption capacity in mg/g reduced, probably due to the aggregation of adsorbent particles accompanied by overlapping activity sites which decreased the effective surface area. Such trend has been extensively reported in adsorption studies with low-cost materials (Kumar et al., 2011; Onyango et al., 2004).

Adsorbent Dose (g/100 mL)	Fluoride Removal (%)	Adsorption Capacity (mg/g)
0.5	65	6.50
1.0	80	4.00
1.5	90	3.00
2.0	95	2.38

Table 7: Effect of adsorbent dosage on fluoride removal efficiency and adsorption capacity

7. Results and Discussion

For understanding the adsorption behavior of fluoride ions on the pre-prepared adsorbent, suitable kinetic and isotherm models were used to analyze data obtained from batch adsorption studies. The kinetic samples were fitted for pseudo-first-order and pseudo-second-order models according to corresponding correlation coefficient (R^2) coefficients; whether each one of them was suitable to be fitted in their chosen stage was established by comparing it. The analysis revealed that the pseudo-second order kinetic model performed better than the pseudo-first order model in the analysis and had higher R^2 values. This has been shown that the adsorption of fluoride onto the prepared adsorbent is much better characterized by pseudo-second-order kinetics. The result of such phenomenon implies that chemisorption possibly might be the predominant way on which the adsorption occurs where electron-sharing/electron exchange process is conducted between the fluoride ions and an active sites acting on the adsorbent surface. In addition, intraparticle diffusion plots showed multilinearity, indicating that the fluoride adsorption is not the result of a single step only. Instead, the process passed through several phases, such as fast external surface adsorption initially and continuous and stepwise pore diffusions, and finally the equilibrium phase. The equilibrium adsorption data were then further studied using both the Langmuir and Freundlich isotherm models. Both models could account for adsorption response reasonably well, but the Langmuir model was a better fit. This implies that fluoride adsorption happened monolayer coverage over an adsorbent substrate with a constant coverage scale where there are finite active sites. The calculated max adsorption capacity of the material (q_{max}) in Langmuir model confirmed the adsorption ability of the preparation material, which indicated that the fluoride was highly adsorbed from aqueous solution. In comparison to other reported research, the performance of the prepared low-cost adsorbent for adsorption is very similar, and can at times outperform many other reported adsorbents, including activated carbon, activated alumina, clays, agricultural waste, and various bioadsorbents. Previous studies have shown that fluoride removal from rice husk, modified clay, and activated alumina occurs effectively in optimal adsorption conditions. The present study also reports similar adsorption patterns, and in particular also shows significant effect of pH, contact time, and adsorbent concentration concerning the fluoride removal capacity. Furthermore the occurrence of pseudo-second-order kinetics and high significance of the Langmuir isotherm applied to this study are consistent with the adsorption behavior described in the literature that is also often noted for fluoride removal tools. These findings highlight inexpensive, regional adsorbents as potential replacing methods rather than expensive commercial adsorbents. Due to their similar adsorption activities and low-cost manufacture and availability, these materials can be easily used as commercially interesting reagents for the defluoridation problem, particularly in low-income countries. Potential application in drinking water treatment of the proposed adsorbent is a welcome prospect. The adsorbent also means that the adsorbent can be economically and environmentally applied since the adsorbent was obtained with cheap and available materials. The adsorption process is easy, does not require complex equipment and is possible, it is applicable to both batch-scale and column-size for use. Its short equilibrium time and excellent fluoride removal efficiency also make it suitable for real water treatment applications. This adsorbent also presents a good performance at different pHs and initial fluoride concentrations, revealing that similar treatment of other polluted water is possible. This kind of flexibility is necessary when some applications come in a field, and water quality could be very different. However, this recommendation must be followed by a more profound investigation on vital practical issues regarding adsorbent regeneration, reusability, stability, post-use disposal, and performance in field scenarios involving competing ions in groundwater. Overall, our results indicate from all these tests that the adsorption with this low cost adsorbent preparation approach gives fluoride an effective as well as efficient way of removal. That research contributes to the growing evidence that cheaper, locally-produced materials could greatly help us provide clean drinking water and ensure global public health — especially in communities and towns where fluoride is abundant.

8. Conclusion

In this work we demonstrate the prepared low-cost adsorbent to be highly suitable to provide excellent fluoride removal from aqueous solution. The adsorption process was well shown by kinetic and isotherm models but the best performing pseudo-second-order kinetic model was the best performing model so chemisorption is a very significant contribution to the adsorption process. Intraparticle diffusion analysis revealed that fluoride adsorption occurs in repeated steps, not in one method. The Langmuir model showed better performance compared to the Freundlich one, which suggests monolayer adsorption on a homogeneous surface of the isotherm models tested. The model displayed a high fluoride uptake potential of the adsorbent due to a very accurate maximum adsorption capacity. Thus, previous studies indicated a similar or better performance for adsorbent preparation in the literature than several low-cost adsorbents. On the practical front, the adsorbent displays several other advantages such as its cheap price, availability, simple working, and efficiency in removal and this makes it promising for application in water treatment and for treatment applications, perhaps for rural areas and the most economically inclined. Additional research is to be done to assess the regeneration, re-use performance and on its field-scale applications with real water samples before full range application.

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