

Study of Cost Effective Green Natural Adsorbents for the Removal of Fluoride from Water

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www.jrasb.com || Vol. 4 No. 2 (2025): April Issue

Received: 07-05-2025

Revised: 08-05-2025

Accepted: 09-05-2025

ABSTRACT

In the study, access to safe drinking water is not only fundamental to human development and wellbeing but is also recognized as a human right. The provision of safe potable water is considered critical and pivotal to the achievements of overall development, including adequate nutrition, education, gender equality and especially the eradication of poverty in developing countries. Fluoride is one of the water quality parameters of concern, the excess (beyond 1.5 mg/L, the World Health Organization (WHO) guideline value of which contaminates groundwater resources in many parts of the world, and renders it not potable for human consumption, due to the related adverse health effects. Therefore, knowledge of its removal, using the best technique with optimum efficiency is needed. Taking the severity of the problem into consideration, the present study to provide a retrospective approach to the use of effective low -cost adsorbents for the removal of fluoride from water. The defluoridation capacity of certain low-cost natural adsorbents like orange peel, banana peel and coconut jute were added in the list and discussed in detail. The effect of contact time, pH and adsorbent dose were investigated. The adsorption isotherm and kinetics were studied conducting Batch adsorption experiment. Different types of Bio-adsorbents used in this study shows a better adsorption capacity of fluoride. The adsorption removal of fluoride increases with decreases pH value and the maximum fluoride removal occurred at the range pH 2-6. The fluoride removal increases with increases temperature, contact time and adsorbent doses. It was further observed that equilibrium behaviour can be predicted by Langmuir adsorption isotherm.

Keywords- Adsorption isotherms, Drinking Water, Fluoride removal, Kinetic, Natural Adsorbents, Thermodynamic.

I. INTRODUCTION

Water is a universal solvent, dissolving nearly all substances it comes into contact with. The primary need of every human being is Safe drinking water. Pure water is inadequate and is not easily available at all. Water may be contaminated by natural sources or industrial effluents. One such contaminant is fluoride.

The natural presence of fluoride generally occurs through soil rock formation in the form of fluorapatite, geochemical deposits, natural water sources

and earth crust [1-3]. Due to vast rapid urbanization and industrial expansion as well the geochemical dissolution of fluoride-bearing minerals, fluoride concentration is increasing in the environment including water resources. In addition, fluoride found in various industrial activities, especially semiconductor, electroplating, glass, steel, ceramic and fertilizers industries [4-7]. The high concentration in the drinking water leads to the destruction of the enamel of teeth and causes a number of conditions referred to collectively as fluorosis [8-9]. According to WHO standards, in drinking water, the Fluoride should be within a range that slightly varies

above and below 1 mg/L [10]. According to Bureau of Indian Standards, BIS (IS10500:2012), the desirable limit and permissible limit of fluoride in potable water is 1.0 mg/L and 1.5 mg/L respectively [11-12]. The adsorption process is considered one of the most efficient methods for removal of fluoride from drinking water when compared to other techniques which are used for removal of fluoride based on initial cost, flexibility, and simplicity of design, ease of operation and maintenance [13-14].

In the present work, a batch adsorption experiment was performed to study the fluoride removal efficiency and adsorption capacity using natural adsorbents like orange peel, banana peel and coconut jute. However, these materials are available aplenty in this region.

II. MATERIALS AND METHOD

'Pyrex' quality Corning glassware and analytical reagent grade(AR) chemicals were used. The glassware was soaked in a 5.0 mg/L of Fluoride solution to minimize the possibility of absorption of fluoride for overnight. The glassware was washed off with nitric acid (HNO₃) and distilled water before use. First, a stock solution of 100 mg F/L was prepared by dissolving an appropriate amount of sodium fluoride (NaF) in distilled water and desired concentrations of working solutions were then prepared from stock solution. Sulphuric acid (0.1N) and sodium hydroxide (0.1 N) were used for adjusting the pH values either too acidic or alkaline conditions. Locally available natural adsorbents such as orange peel, banana peel, and coconut jute were collected from markets and campus surroundings. The adsorbents were first cleaned with deionized water and then subjected to a 24-hour air-drying process in an oven set at 100–120 °C. After drying, the materials were crushed using a jaw crusher and screened through an ASTM 50-mesh screen. The crushed material was further sieved using IS sieves 150 µm and 300 µm size and the material passing through 150 µm and retained on 300 µm which has a geometric mean size (Gm) of 212 µm was used to obtain uniform particle sizes for adsorption studies in all experiments. For the convenience, we abbreviated the adsorbents, Banana Peel as BP-1, Orange Peel as OP-2, and Coconut Jute as CJ-3.

Batch adsorption studies were conducted towards contact time, adsorbent doses, pH etc. The stock solution was prepared by dissolving exactly 100 mg of sodium fluoride (NaF) in distilled water. Solutions for the experiment were prepared by dilution from the standard stock solution all studies were carried out with initial fluoride concentration solution in temperature-controlled bath with a shaker. The adsorption isotherm at pH 6.90 ± 0.10 was studied by varying the initial fluoride concentration from 5 to 100 mg/L. The effect of pH was investigated by adjusting the pH from 2 to 12

using 0.1 M NaOH and HCl solutions under an initial fluoride concentration of 10 mg/L. A kinetic study at pH 6.90 ± 0.10 was carried out at different time intervals with an initial fluoride concentration of 10 mg/L. Finally, the effects of a number of various competing for ions (F⁻, Cl⁻, NO₃⁻, CO₃²⁻, SO₄²⁻ and PO₄³⁻) were observed using, 20- 200 mg/L solutions at pH 6.90 ± 0.10 over 1 hour.

III. RESULTS AND DISCUSSION

3.1 Effect of pH on Fluoride Adsorption

The pH of the solution significantly influences the adsorption efficiency of fluoride ions. The experimental results demonstrated that fluoride removal increased as pH decreased, with maximum adsorption observed in the pH range of 2 to 6. Beyond pH 6, the removal efficiency declined due to the increased competition between hydroxide ions (OH⁻) and fluoride ions (F⁻) for active adsorption sites. The maximum fluoride removal of 85.3% was observed at pH 4, whereas at pH 9, the removal efficiency dropped to 41.7%.

These findings align with previous studies which reported similar trends in pH-dependent fluoride adsorption [15]. The decrease in adsorption at high pH values can be attributed to the increased electrostatic repulsion between negatively charged fluoride ions and the deprotonated adsorbent surface.

3.2 Effect of Adsorbent Dose

The impact of adsorbent dose on fluoride removal efficiency was evaluated by varying the adsorbent concentration from 0.2 to 2.4 g/100 mL. The fluoride removal efficiency increased with higher adsorbent doses due to the availability of more active adsorption sites. The highest fluoride removal of 92.1% was observed at an adsorbent dose of 2.0 g/100 mL. However, a further increase in dose beyond this point resulted in negligible improvement in fluoride removal, likely due to the saturation of adsorption sites and particle aggregation.

Comparatively, orange peel-based adsorbents exhibited higher fluoride removal capacity than banana peel and coconut jute, with maximum adsorption capacities ($q_{\max}$) of 12.5 mg/g, 10.8 mg/g, and 9.6 mg/g, respectively. The adsorption parameter for fluoride of various adsorbents were listed in table. 1.

Table 1. Fluoride adsorption parameters of various adsorbents.

Serial No.	Adsorbent	Maximum Adsorption Capacity (q_m , mg/g)	% Removal	Distribution Coefficient (K_d)	Optimal pH Range	Optimal Adsorbent Dose (g/100 mL)
1	BP-1	10.8	92.1	9.3	2-6	2

2	OP-2	12.5	85.3	10.5	2-6	2
3	CJ-3	9.6	80.5	8.7	2-6	2

3.3 Adsorption Kinetics

The kinetics of fluoride adsorption were analyzed using pseudo-first-order and pseudo-second-order models. The results showed that adsorption followed the pseudo-second-order kinetic model, with a high correlation coefficient ($R^2 = 0.98$) for all adsorbents. The calculated rate constant (k_2) values for orange peel, banana peel, and coconut jute were 0.015, 0.012, and 0.010 $\text{g mg}^{-1} \text{min}^{-1}$, respectively. The experimental equilibrium adsorption capacity ($q_{e, \text{exp}}$) was found to be 11.9 mg/g , 10.4 mg/g , and 9.2 mg/g , closely matching the theoretical values ($q_{e, \text{cal}}$), confirming the validity of the model. Kinetic study of fluoride adsorption of various adsorbent has been shown in Table 2.

Table 2. Kinetic study of F^- adsorption of various adsorbents.

Serial No.	Adsorbent	Pseudo-first-order R^2	Pseudo-second-order R^2	Intraparticle Diffusion R^2	Rate Constant (k_2 , $\text{g mg}^{-1} \text{min}^{-1}$)
1	BP-1	0.92	0.98	0.95	0.012
2	OP-2	0.94	0.99	0.96	0.015
3	CJ-3	0.91	0.98	0.94	0.01

3.4 Adsorption Isotherm Analysis

The equilibrium adsorption data were analyzed using Langmuir and Freundlich isotherms. The Langmuir model provided a better fit than the Freundlich model, with R^2 values of 0.98, 0.96, and 0.94 for orange peel, banana peel, and coconut jute, respectively. The monolayer adsorption capacities (q_{max}) derived from the Langmuir model were 12.5 mg/g , 10.8 mg/g , and 9.6 mg/g . These values indicate strong fluoride binding on homogeneous adsorbent surfaces, as supported by previous studies [16-17].

3.5 Thermodynamic Analysis

The thermodynamic parameters, including Gibbs free energy (ΔG), enthalpy (ΔH), and entropy (ΔS), were calculated to assess the feasibility and nature of the adsorption process. The negative ΔG values (-8.21, -6.94, and -6.41 kJ/mol for orange peel, banana peel, and coconut jute, respectively) indicate that the adsorption process is spontaneous. The positive ΔH values (+24.3 kJ/mol , +21.7 kJ/mol , and +19.5 kJ/mol) confirm that the process is endothermic, meaning adsorption efficiency improves at higher temperatures.

3.6 Adsorption Mechanism

The adsorption process was evaluated using the intraparticle diffusion model. The multilinearity of the Weber-Morris plot suggests that adsorption occurs in two phases:

- Surface adsorption (initial fast phase)
- Intraparticle diffusion (gradual phase)

Since the plot did not pass through the origin, film diffusion also played a role in the adsorption mechanism. The adsorption was controlled by a combination of external mass transfer and intraparticle diffusion rather than a single rate-limiting step.

3.7 Limitations and Future Research

While the study demonstrated promising fluoride removal efficiency, there are some limitations which must be acknowledged. Batch studies do not reflect real-world continuous flow conditions; future studies should focus on column adsorption. Competing ions in groundwater (e.g., Cl^- , NO_3^- , SO_4^{2-}) may interfere with fluoride adsorption, requiring further investigation. Adsorbent regeneration and reuse feasibility need to be explored to determine long-term applicability.

IV. CONCLUSION

The study confirmed that natural bio-adsorbents effectively remove fluoride from water, with orange peel exhibiting the highest adsorption capacity. Adsorption followed the Langmuir isotherm and pseudo-second-order kinetics, and thermodynamic analysis confirmed that the process was spontaneous and endothermic. Future research should focus on continuous flow adsorption, regeneration studies, and field-scale implementation to enhance practical applications. Different types of Bio-adsorbents used in this study shows a better adsorption capacity of fluoride. The adsorption removal of fluoride increases with decreases pH value and the maximum fluoride removal occurred at the pH range 2-6. Fluoride removal efficiency increases with higher temperature, extended contact time, and increased adsorbent dosage. The adsorption equilibrium was best described by the Langmuir isotherm, indicating monolayer adsorption on homogeneous sites.

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