Investigating the Effect of Operational Parameters on Fluoride Removal Efficiency of GS, MP, and SSP Adsorbents

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Abstract: *This study delves into the efficacy of fluoride removal from water via adsorption employing three distinct adsorbents: GS, MP, and SSP. The investigation explores diverse factors influencing the adsorption process, including initial fluoride concentration, pH, stirring rate, contact time, and temperature. Results indicate that removal efficiency diminishes with escalating initial fluoride concentration, attributable to the finite active sites on the adsorbent surface. Optimal pH conditions emerge as pivotal for effective adsorption, while extreme pH levels may impede the process. Stirring rate and contact time dictate the adsorption kinetics, exhibiting an initial rapid adsorption phase followed by equilibrium. Temperature fluctuations elicit differential impacts on removal efficiency for each adsorbent, underscoring the nuanced role of temperature in the process. In sum, this research furnishes valuable insights for refining fluoride removal from water via adsorption techniques.*

Key words*: Defluorination, fluoride*

1. Introduction:

Freshwater is indispensable for sustaining life on our planet, yet its availability is under threat. Groundwater, a critical source of potable water, is particularly vulnerable to contamination, especially in developing countries such as India, where more than 90% of the population relies on it. Industrialization has led to pollution of groundwater, with fluoride (F-) being a significant concern due to its abundance in the Earth's crust. High concentrations of fluoride pose health risks, necessitating effective defluorination methods. Scientists have explored various techniques including precipitation, membrane processes, ion-exchange, and adsorption to address this issue. Among these, adsorption stands out as a dependable approach, employing materials with strong fluoride-binding capabilities. This research delves into the potential of a specific type of solid waste material for removing fluoride from groundwater. Notably, fluoride exhibits a pronounced affinity for materials like silica, alumina, and calcium, suggesting promising avenues for leveraging these properties in the defluorination process [1,2].

2. Materials and Methods:

2.1 Material Preparation: This section outlines the preparation procedure for three adsorbent materials utilized in fluoride removal [3,4,5].

Sample 1 Groundnut Shell (GS): GS was procured from a local market, presumably due to its high silica content. It underwent thorough washing with de-ionized water to eliminate impurities.

Subsequently, the material was subjected to oven-drying at 110°C for 24 hours to eliminate moisture. Once dried, it was finely ground using a grinding machine and then sieved to achieve particles with a size of 75 micrometres (µm). The prepared material was stored and subjected to another round of washing with de-ionized water followed by oven drying at 110°C for 24 hours (potentially for additional purification).

Sample 2 Marble Powder (MP): MP, presumably rich in calcium, was obtained in powdered form from a nearby market. Similar to Sample 1, it underwent washing with de-ionized water and drying in an oven at 110°C for 24 hours. The dried powder was then sieved to achieve particles with a size of 75 µm. The prepared material underwent storage, followed by another round of washing with de-ionized water and oven drying at 110°C for 24 hours (similar to Sample 1).

Sample 3 Seashell Powder (SSP): Seashells were collected from Chennai, India. Initially, they were crushed using a rammer and a small Mold due to their hardness. The crushed seashells underwent washing with a diluted hydrochloric acid solution (0.01 N HCl) to remove surface contaminants. Following washing, the material was dried in an oven for 3-4 hours at a lower temperature (110°C) compared to the other samples, likely to prevent damage from excessive heat. The dried material was further pulverized using a kitchen mixer grinder. After grinding, it underwent another round of washing with de-ionized water and oven drying at 110°C for 24 hours. Similar to the other samples, the prepared seashell material was stored for future use. The final seashell powder was sieved to achieve particles with a size of 75 µm,

2.2 Instruments and Apparatus

A. Characterization Techniques: Various methods were employed to analyse the GS, MP and SSP and monitor the adsorption process [3,4,5].:

- **Scanning Electron Microscopy (SEM):** Utilized to examine the morphology, or surface features, of the GS powder. SEM provides high-resolution images revealing the size, shape, and texture of the material. Figure 01 likely illustrates the SEM image.
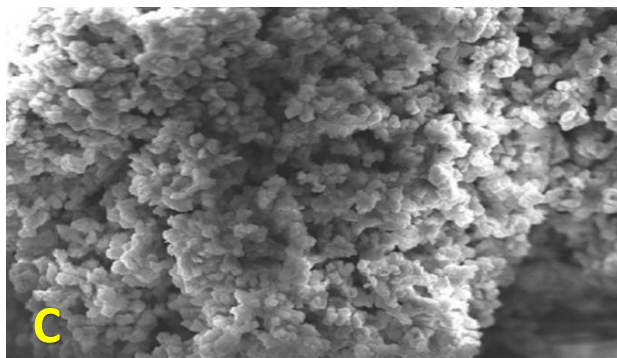

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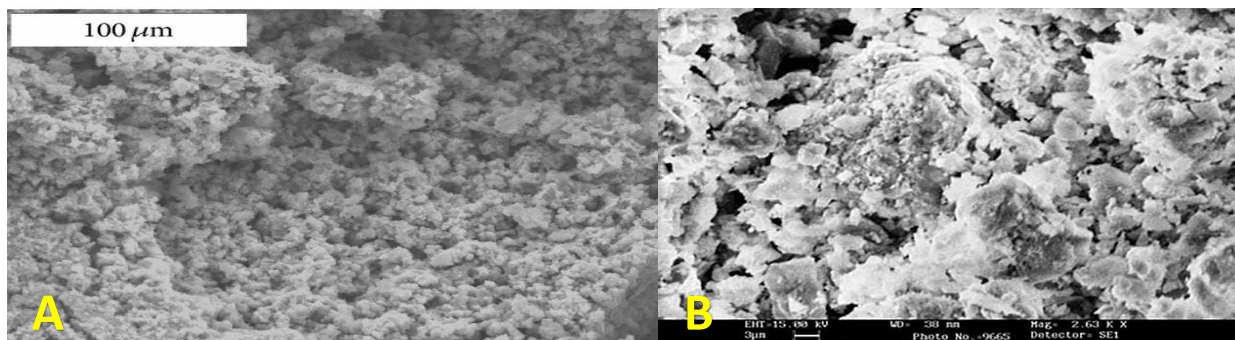
Figure 01: SEM Aanalysis for A:GS, B: MP, and C: SSP

- **Fourier Transform Infrared Spectroscopy (FTIR):** Employed to identify the chemical composition and functional groups present in the GS powder through infrared spectroscopy. A Lab India double beam spectrometer was probably utilized for this purpose. By analysing the infrared light absorbed by the sample, researchers can determine the types of bonds and functional groups present.

- **pH Meter:** Utilized for measuring the acidity or alkalinity (pH) of the solutions utilized in the adsorption experiments. Understanding the pH is crucial as it can significantly influence the adsorption process.

- **Orbital Shaking Incubator:** Provided controlled temperature and shaking conditions during the adsorption experiments, ensuring consistent temperature and agitation, which are often essential for optimal adsorption.

- **SPADNS Method:** Employed for determining the concentration of fluoride ions in the aqueous solutions. The SPADNS method is a well-established analytical technique involving a colorimetric reaction between fluoride and a specific dye.

B. Preparation of Fluoride Solutions: To create solutions with varying fluoride concentrations for the adsorption experiments, a two-step process was followed [3,4,5].:

- **Stock Solution Preparation:** A precise amount of sodium fluoride (NaF), typically 0.22 grams (g), was weighed and dissolved in 1 litre (L) of high-purity water. This high-purity water is often referred to as "double-distilled water" as it has undergone a double distillation process to remove impurities. This concentrated solution is called the "stock solution" and has a known fluoride concentration (likely 100 mg/L based on the mentioned weight and volume).

- **Serial Dilution:** The prepared stock solution was then used to create solutions with lower fluoride concentrations needed for the experiment. This technique, called "serial dilution," involves taking a measured volume of the stock solution and diluting it with a specific amount of additional solvent (usually water) to create a solution with a lower concentration. This process can be repeated to create a series of solutions with different, but known, fluoride concentrations.

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2.3 Adsorption Experiment and Analysis: In-depth investigations were conducted on GS, MP, and SSP materials to analyse their effectiveness in removing fluoride from aqueous solutions. Numerous experiments were carried out to examine the impact of pH, adsorbent dose, kinetics, and thermodynamic parameters. The pH varied between 2 to 12, while the adsorbent dose ranged from 0.5 to 5.5 grams per 100 millilitres, with a particle size less than 75 micrometres. Contact times spanned from 15 minutes to 1440 minutes, initial fluoride concentrations ranged from 0 to 16 milligrams per litre, and temperatures were assessed at 293K, 303K, and 313K. Each study utilized 250 millilitres conical flasks containing 100 millilitres of a fluoride solution at 10 milligrams per litre, which were then subjected to orbital shaking incubation at 150 rotations per minute for 24 hours at 303 ± 1 Kelvin. The resultant solids were separated via normal filtration processes, and the fluoride solution's concentration was determined using a double beam spectrophotometer. Each experiment was conducted thrice to ensure accuracy, and the average values were recorded. The amount of fluoride adsorbed per unit adsorbent was calculated using the mass balance concept[3,4,5]..

3. Results and Discussion

3.1 Effect of Adsorbent Dose: Experimental investigations were conducted to assess the impact of adsorbent doses on fluoride removal for GS, MP, and SSP. The doses ranged from 0.5 to 5.5 g/L, maintaining a pH of 7, an initial fluoride concentration of 10 mg/L, and a contact time of 24 hours. Figure-02 illustrates the effect of adsorbent dose on fluoride removal percentage. Results indicate that as the dose increases, there is a proportional rise in fluoride adsorption. The augmentation in surface area enhances removal efficiency due to the availability of additional active sites for solution adsorption. GS exhibited a 91.36% fluoride removal rate at a dose of 4.5 g/L at a temperature of 30°C. Similarly, MP demonstrated a 90% removal rate at the same dose and temperature conditions, leading to the selection of 4.5 g/L for further investigations. For SSP, maximum removal efficiency was observed at 91% with a dose of 4 g/L at room temperature. Further investigations revealed no significant alterations, prompting the selection of 4 g/L for subsequent studies.
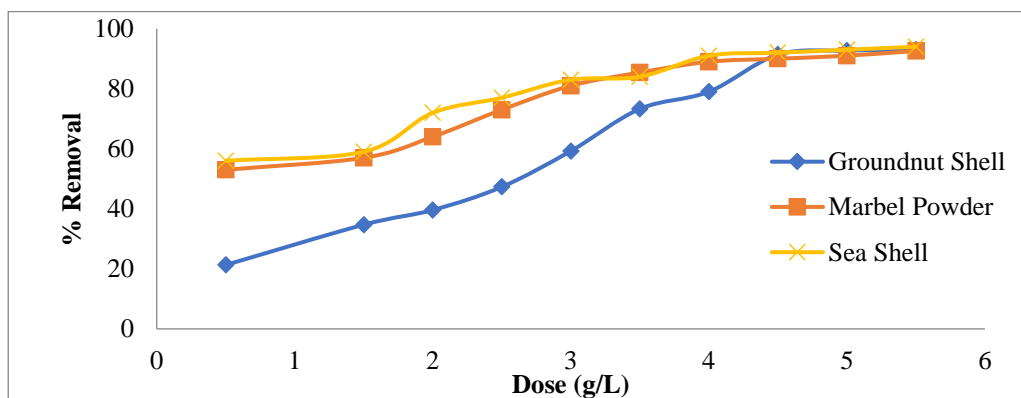

Figure-02, Effect of adsorbent dose on fluoride

3.2 Effect of pH: The impact of solution pH on the capacity of fluoride adsorption was explored across all three adsorbents (GS, MP, and SSP). Experiments were conducted over a broad pH spectrum, typically ranging from 2 to 14. pH adjustments were achieved by adding either 0.5 N HCl (for acidic conditions) or 0.1 N NaOH (for alkaline conditions) to 1 litre of a prepared 10 mg/L fluoride solution. Each experiment maintained a 24-hour contact time with a specific adsorbent dose.

- **GS:** The effect of pH on GS's fluoride removal percentage is depicted in figure-03. Removal efficiency increased with rising pH until reaching an optimal value around pH 7-8. Subsequently, removal declined due to competition between fluoride ions and abundant OH- ions for adsorption sites. Hence, pH 7 (neutral) was selected for further GS studies, given its highest observed removal efficiency.

- **MP:** Similarly, the influence of pH on MP's fluoride removal is presented in figure-03. The removal percentage also escalated with increasing pH, peaking between pH 9.2 and 10.4. This trend can be attributed to the competition between fluoride and OH- ions at higher pH levels. Consequently, pH 9.2 was chosen for subsequent experiments involving MP.

- **SSP:** The removal percentage likewise rose with increasing pH, reaching a maximum between pH 7.8 and 8 as shown in figure-03. This trend, attributed to the competition between fluoride and OH- ions at higher pH values, led to the selection of pH 7.8 for further experiments involving SSP.
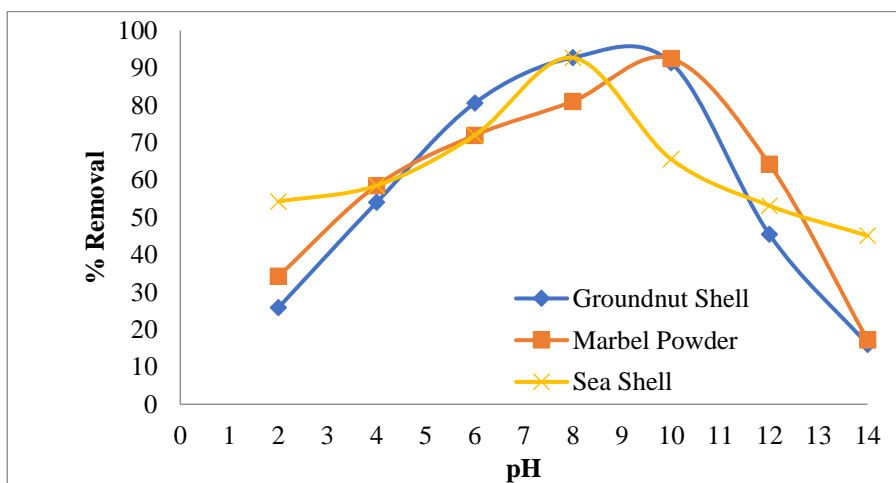

Figure-03, Effect of pH

3.3 Effect of Stirring Rate: The influence of stirring rate on fluoride adsorption was investigated for all three adsorbents (GS, MP, and SSP) using similar experimental conditions. The stirring speed was varied from 20 to 200 rpm, while the following parameters were held constant: The previously determined optimal pH value for each adsorbent was used (pH 7.0 for GS, pH 9.2 for MP, and pH 7.8 for SSP). A consistent adsorbent dose of 4.5 g/L was employed for all experiments. A standard contact time of 24 hours was maintained. The relationship between stirring rate and fluoride removal percentage was observed for each adsorbent. A general trend emerged across all three materials: as the stirring rate increased, the percentage of fluoride removal also increased up to a certain point. This can

be attributed to enhanced mixing and mass transfer between the adsorbent particles and the fluoride solution at higher stirring rates.

- **GS:** Figure-04 depicts the effect of stirring rate on GS. The removal efficiency reached 90% at a stirring speed of 150 rpm. Beyond this point, no significant improvement in removal was observed. Therefore, 150 rpm was chosen as the optimal stirring rate for GS.

- **MP:** Similar to GS, the effect of stirring rate on MP's removal efficiency is shown in figure-04. In this case, 90.70% removal was achieved at 140 rpm. Further increases in stirring rate did not yield a significant benefit. Consequently, 140 rpm was selected as the optimal stirring rate for MP.

- **SSP:** While the provided content mentions investigating stirring rate for SSP, the optimal rpm is 125 as shown in figure-04. However, it's likely that SSP follows a similar trend as GS and MP, where removal efficiency increases with stirring rate until a plateau is reached.
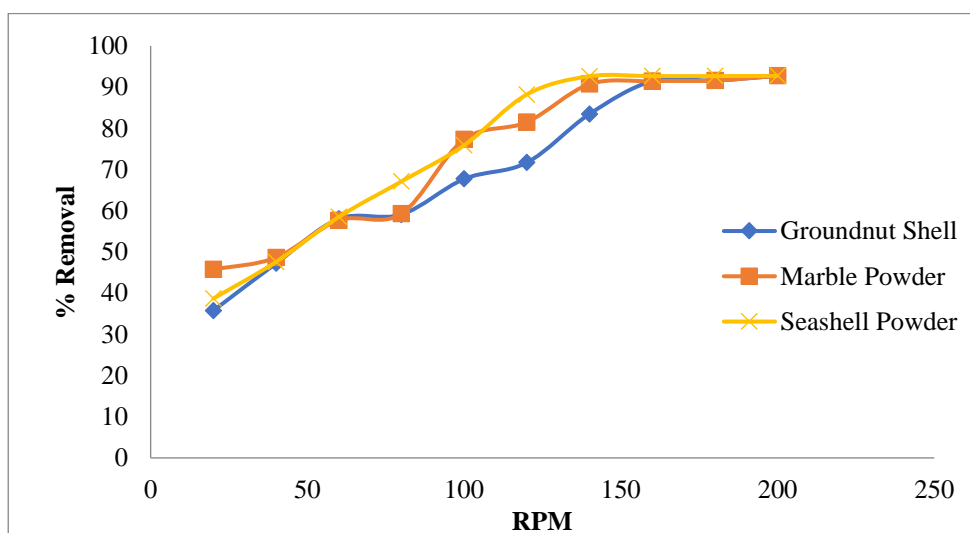

Figure-04, Effect of stirring rate (RPM)

3.4 Effect of Contact Time: The evaluation of contact time's impact on fluoride removal efficiency was conducted across all three adsorbents (GS, MP, and SSP). Experiments were performed under the following conditions: varying contact time from 15 minutes to 1440 minutes (24 hours) to observe adsorption progression, utilizing a specific dose of each adsorbent (4.5 g/L for GS, MP, and SSP), employing optimal pH values (pH 7.0 for GS and pH 9.2 for MP), and utilizing stirring rates (150 rpm for GS, 140 rpm for MP, and 125 rpm for SSP). The experiments were executed at three different temperatures: 293 K, 303 K, and 313 K. A common trend was observed across all adsorbents, where initially, fluoride removal percentage increased rapidly due to the abundance of vacant adsorption sites on the adsorbent surface. However, as time progressed, the removal rate gradually decelerated until reaching an equilibrium point, indicating saturation of available adsorption sites.

- **GS:** The impact of contact time on GS is depicted in figure-05, at room temperature (293 K), rapid removal was observed, reaching approximately 90.53% within 360 minutes. Similar behaviour was observed at higher temperatures (303 K and 313 K), with equilibrium attained at shorter contact times (240 minutes and 120 minutes, respectively).

- **MP:** Similar to GS, the influence of contact time on MP's removal efficiency is illustrated in figure-05, at room temperature (293 K), around 90.47% removal was achieved within 480 minutes. Higher temperatures (303 K and 313 K) also exhibited a faster initial removal rate, with equilibrium reached at 360 minutes.

- **SSP:** For SSP, the optimal contact time was determined under similar conditions as shown in figure-05. The trend mirrored that of GS and MP, with a rapid initial rise in removal percentage followed by a plateau at equilibrium. At room temperature (293 K), approximately 91.57% removal was achieved within 240 minutes. Faster initial removal at higher temperatures (303 K and 313 K) was also observed.
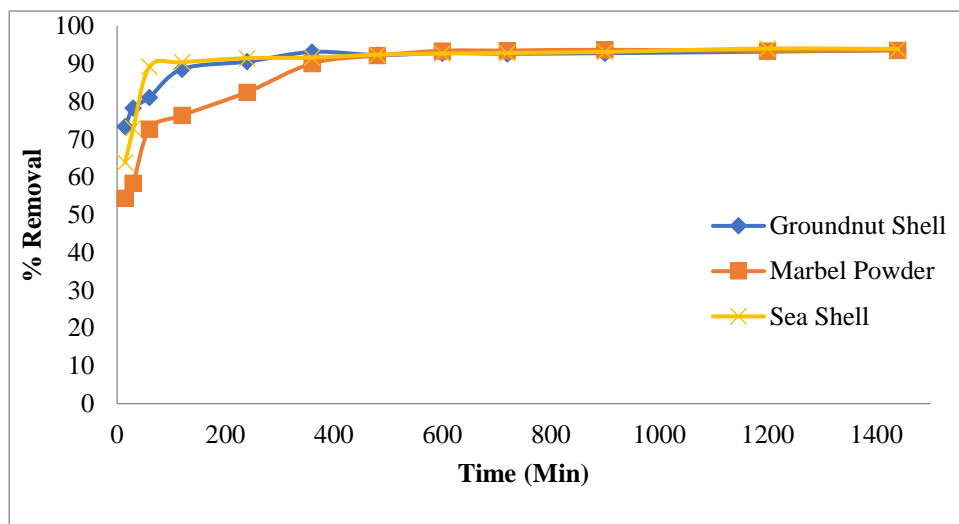

Figure-05, Effect of Contact Time

3.5 Effect of Temperature: The effect of temperature on removal efficiency varied depending on the adsorbent.

- **GS and MP:** Figure-06 depict the effect of temperature for GS and MP. In these cases, an increase in temperature generally led to a slight increase in removal efficiency. This might be due to two opposing factors: Increased mobility of fluoride ions at higher temperatures, potentially enhancing their interaction with the adsorbent. Possible decrease in the forces holding fluoride ions onto the adsorbent surface at higher temperatures. The net effect of these factors appears to be a slight increase in removal for GS and MP.

- **SSP:** For SSP, the effect of temperature was studied with varying adsorbent doses (4.5mg/l). Figure-06 shows a trend of increasing removal percentage with increasing temperature up to 313

K. This suggests that the positive effect of increased mobility dominates in SSP. However, the provided content mentions that sorption is generally an exothermic process, implying a decrease in removal with increasing temperature. More information about SSP's specific behaviour is needed to fully understand the interplay between temperature and adsorption for this material.
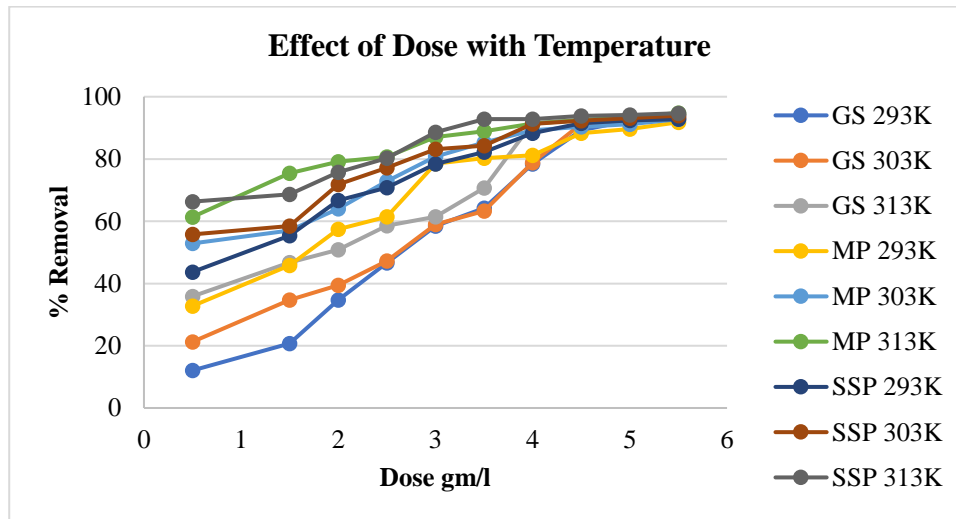

Figure-06, Effect of Temperature

4. **Conclusion:** The theory of adsorption suggests that molecules (adsorbates) can accumulate on the surface of another material (adsorbent) due to physical or chemical interactions. This process depends on various factors studied in this research [6]:

   a. **Limited Active Sites:** The removal efficiency decreases with increasing initial fluoride concentration because there are a finite number of active sites on the adsorbent surface available for capturing fluoride ions.

   b. **pH Dependence:** The optimal pH suggests that appropriate surface charge conditions on the adsorbent are crucial for effective adsorption. High or low pH might introduce competition from other ions or weaken the interaction between fluoride and the adsorbent.

   c. **Mass Transfer and Equilibrium:** Stirring rate and contact time influence the rate of adsorption. Initially, rapid adsorption occurs as fluoride ions readily encounter available sites. As time progresses, the rate slows down until an equilibrium is reached, where the rate of adsorption equals the rate of desorption.

   d. **Temperature Effects:** The observed variations in removal efficiency with temperature for different adsorbents highlight the complexity of temperature's role. It can influence both the mobility of fluoride ions and the strength of adsorption forces. Further investigation is needed to fully understand these interactions for SSP.

In conclusion, the findings of this research support the theoretical principles of adsorption. By optimizing various parameters like pH, stirring rate, contact time, and potentially temperature (for specific adsorbents),

efficient removal of fluoride from water can be achieved using GS, MP, and SSP. This knowledge can be valuable for developing practical and effective water treatment strategies.

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