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Fluoride Removal by Spherical Agglomeration Technique Process in Water Using Sunflower Oil as a Sustainable Alternative to *n*-Heptane

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Abstract: Fluoride contamination in water sources presents critical public health challenges, particularly in regions where groundwater exhibits elevated fluoride levels. Chronic exposure can result in dental and skeletal fluorosis, necessitating efficient and sustainable remediation strategies. This study investigates the spherical agglomeration technique (SAT) as an alternative fluoride removal method, assessing the performance of sunflower oil versus n-heptane as humectants and evaluating the synergistic effects of *Agave durangensis* leaf extract. A factorial experimental design optimized dosage parameters in aqueous models and well water samples, ensuring reliable fluoride removal. Sunflower oil significantly outperformed n-heptane, achieving fluoride removal efficiencies of up to 95.19% under optimal conditions (5 mL $_{Hum}$/g $_{TMCs}$ at pH 6.5). Incorporating *A. durangensis* extract sustained high fluoride removal while reducing the required extract dosage to 0.5 g $_{Extr}$/g $_{TMCs}$. When applied to well water samples, the SAT consistently maintained an 88.9% fluoride removal efficiency. Compared to conventional methods such as coagulation–flocculation and adsorption, the SAT demonstrated enhanced effectiveness with a lower environmental footprint. These findings reinforce the viability of sunflower oil and *A. durangensis* extract as eco-friendly alternatives to n-heptane, positioning the SAT as a scalable, cost-effective solution for large-scale fluoride remediation.

Keywords: fluoride removal; spherical agglomeration technique; sunflower oil; *Agave durangensis* extract; sustainable water treatment

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1. Introduction

Access to safe drinking water is essential for human health and sustainable development [1,2]. Globally, over 200 million people are regularly exposed to fluoride-contaminated drinking water, particularly in regions such as India, China, East Africa, and the north-central region of Mexico [3,4]. This widespread exposure represents substantial challenges to both water quality and public health. Fluoride contamination originates from multiple sources, including leaching from mines, industrial activity, and natural contamination from prolonged interactions between groundwater and fluoride-rich rocks, often leading to

elevated fluoride levels that pose significant health risks [5,6]. In this context, their presence in high concentrations can seriously affect ecosystems and human health [7].

Only 0.8% of the world's water is available for human consumption, mainly as groundwater. This limited drinking water supply faces constant threats, including fluoride contamination [5,7–9]. Overexploitation of aquifers, poor recharge, and natural contamination are leading causes of fluorides in the water supply [5,7]. As a result, entire communities are exposed to dangerous levels of fluoride, posing significant public health concerns [6,10]. In addition, aquatic ecosystems can also suffer damage due to the accumulation and biomagnification of fluoride along the food chain, affecting aquatic fauna and flora [11].

Previous studies have explored various methods for fluoride removal, including coagulation–flocculation with aluminum-based salts, adsorption using activated alumina, and membrane filtration [12]. Adsorption is widely recognized as an effective method for fluoride removal, with materials such as activated carbon, activated alumina, and modified adsorbents achieving removal efficiencies between 70 and 99%, depending on the material properties and process conditions. Under optimal conditions, advanced adsorbents, such as metal-oxide-based or composite materials, can achieve removal efficiencies above 90% [12]. Membrane filtration techniques, such as reverse osmosis and nanofiltration, are also commonly employed for fluoride removal. Studies indicate that reverse osmosis can reach removal efficiencies exceeding 95%, making it comparable to the SAT in terms of performance. However, nanofiltration generally exhibits slightly lower efficiencies, typically ranging from 80 to 90%, depending on membrane characteristics and operational conditions [13]. Other techniques, including electrocoagulation and chemical precipitation, have also been used for fluoride removal, with reported efficiencies between 70 and 90%, depending on the reagents used and process parameters. While these methods are effective, they often generate sludge or residues that require additional treatment and disposal. Despite advancements in these technologies, there is still a need to enhance their efficiency, sustainability, and accessibility, particularly in regions where access to safe drinking water remains limited [14].

Considering these limitations, the spherical agglomeration technique (SAT) represents an innovative approach to fluoride removal, facilitating contaminant elimination by promoting the formation of stable solid aggregates within liquid media through hydrophobic interactions [15]. This process operates under well-regulated physicochemical parameters, including temperature, pH, and agitation speed, and comprises four fundamental stages. In the precipitation–adsorption phase, $Ca(OH)_2$ is introduced within a precisely controlled pH range, instigating the formation of colloidal particles by precipitating fluoride as an insoluble compound, thereby significantly enhancing its subsequent removal efficiency [16,17]. Since these particles are naturally hydrophilic, they stay dispersed in aqueous environments and must undergo the hydrophobization stage, which serves as a preconditioning step to facilitate the subsequent wetting (nucleation) phase. In this stage, natural surfactants modify the surface characteristics of the particles, making them hydrophobic and allowing them to self-assemble into hydrophobic nuclei, which form the basis for subsequent particle agglomeration [18]. Once this surface modification occurs, the wetting (nucleation) phase begins, where a suitable humectant, such as n-heptane or vegetable oils, is introduced to enhance the interaction between the newly hydrophobized particles, reinforcing their cohesion and stabilizing the initial hydrophobic aggregates [19]. In the final agglomeration stage, the addition of Ca^{2+} ions induces charge redistribution, minimizing repulsive forces while reinforcing interparticle adhesion, thus ensuring the formation of structurally stable, easily separable aggregates [15]. While n-heptane has conventionally been employed as a wetting agent, there is a growing recognition of vegetable oils as a safer and environmentally sustainable alternative, a hypothesis substantiated by comparative studies

demonstrating their comparable efficacy as binding agents, irrespective of their edible or non-edible nature [20–22]. Although the SAT has already exhibited considerable efficacy in the removal of arsenic and other contaminants, further investigations remain imperative to optimize its environmental and economic feasibility [18]. In this context, vegetable oils emerge as highly promising wetting agents, offering a viable alternative to conventional industrial solvents while aligning with sustainability-driven water treatment strategies [23].

This study aims to address the persistent challenge of fluoride contamination, contributing to sustainable water management by evaluating the efficacy of the SAT in combination with natural agents, particularly *A. durangensis* extract and sunflower oil. Initial experimental comparisons between sunflower oil and n-heptane were undertaken to assess the former's viability as an alternative humectant, with subsequent investigations confirming its superior ability to reduce fluoride concentrations across both aqueous models and well water samples, achieving removal efficiencies of 95.19 and 88.86%, respectively. The transition from industrial to natural wetting agents underscores the potential for developing more effective, environmentally responsible water treatment technologies, thereby minimizing ecological impact and enhancing industrial-scale water purification processes. The findings suggest that natural humectants such as sunflower oil constitute a viable large-scale alternative, offering a cost-effective and ecologically sustainable solution that aligns with contemporary efforts to mitigate the environmental footprint of water treatment.

2. Materials and Methods

2.1. Reagents and Equipment

Fluoride removal studies utilized a meticulously prepared fluoride solution with a concentration of 5.0 mg L^{-1}, prepared from a 1000 mg L^{-1} fluoride standard (HANNA Instruments, Woons., USA.) and deionized water to ensure optimal precision. Freshly prepared aluminum hydroxide ($Al(OH)_3$) was synthesized for the adsorption studies and the SAT precipitation stage through the reaction between $AlCl_3$ (Fermont, CAS No. 10025-77-1 MEX) and $Ca(OH)_2$ (Jalmek, CAS No. 1305-62-0 CDMX, MEX.). During the hydrophobization phase, *Agave durangensis* Gentry (*A. durangensis*) extract underwent preparation through ethanolic extraction [18], employing ≥99.5% absolute ethyl alcohol (Fermont, CAS No. 64-17-5, Mty, MEX.). The wetting and agglomeration stages incorporated commercial sunflower oil, n-heptane (SIGMA CHEMICAL), and $CaCl_2$ (Fermont, CAS No. 10043-52-4, Mty, MEX.), with all reagents meeting analytical-grade standards and exceeding 99% purity. Samples and standard solutions underwent dilution in a 1:1 ratio with the buffer. The fluoride concentration underwent measurement using an ORION VERSA STAR PRO multiparameter meter (Thermo Fisher Scientific Inc., Walth., USA) equipped with a specific ion electrode (ORION 9609NWP) and a total ionic strength adjustment buffer (TISAB with CDTA, Orion 940909).

2.2. Application of the Spherical Agglomeration Technique (SAT)

Fluoride removal experiments took place at room temperature (20 ± 3 °C), using 500 mL baffled vessels and 3.5 × 2.5 cm stainless steel stirrers, in 250 mL of solution at 22 °C and with constant stirring at 600 rpm [17]. The first stage of the SAT, precipitation–adsorption, lasted 15 min, adding $AlCl_3$ and $Ca(OH)_2$ and adjusting to pH 6.5 with the latter reagent to obtain freshly prepared aluminum hydroxide precipitates ($Al(OH)_3$), which adsorb fluoride. A dose of 1 g L^{-1} of $Al(OH)_3$ was added. Optimal precipitation occurs after adding $Ca(OH)_2$ until the specified pH is reached [24,27]. The solids formed, resulting from the reaction between $AlCl_3$, $Ca(OH)_2$, and the adsorbed fluoride, were called "Total Mixture Components" (TMCs). The hydrophobization stage (second stage) proceeds without interruption to the reaction, with the surfactant *A. durangensis* leaf extract added at

doses of 0, 0.25, 0.5, 0.75, or 1.0 g $_{Ext}$/g $_{TMCs}$ for aqueous models and 0.25, 0.5, or 0.75 g $_{Ext}$/g $_{TMCs}$ for well water. In the wetting stage (third stage), the process involved applying either n-heptane or sunflower oil as wetting agents to coat the hydrophobic colloids formed in the second stage, selecting the most effective option. The experimental design determined the appropriate doses, using 2.5, 5.0, 6.3, 7.5, or 10 mL $_{Hum}$/g $_{TMCs}$. [15,25]. Finally, the crystal nucleus growth stage (agglomeration stage) took place as a result of the addition of 10 mL of 1 M $CaCl_2$ solution per mole of fluoride present in the aqueous solution [23]. After the process, Whatman #40 filter paper was used to retain the agglomerates from the solution, and fluoride concentrations in the filtered aqueous medium were quantified using a specific ion electrode, adhering to NMX-AA-051-SCFI-2001 standards [26]. Figure 1 illustrates the system implemented, showing the jar test setup used in the experiments.

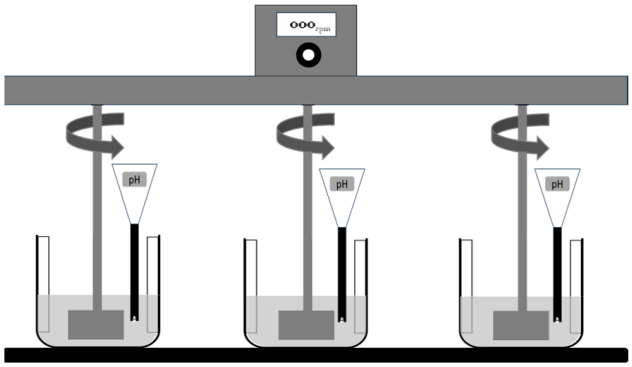


Figure 1. Schematic representation of the jar test system implemented for fluoride removal using the SAT process.

2.3. Experimental Design for Fluoride Removal in Aqueous Models and Groundwater

A 5 × 2 factorial design served to evaluate the effect of humectant type on fluoride removal efficiency. This factorial design enabled a comparative analysis of how effectively sunflower oil and n-heptane stabilize agglomerates and contribute to fluoride removal. The final fluoride concentration in solution was the response variable, measured after the agglomeration process.

The second experimental phase employed a 5 × 4 factorial design to evaluate the interaction between surfactant and humectant dosages. The independent variables included surfactant dosage (0.25, 0.50, 0.75, 1.00, and 1.25 g $_{Ext}$/g $_{TMCs}$) and humectant dosage (2.5, 5.0, 7.5, and 10.0 mL $_{Hum}$/g $_{TMCs}$). The experimental conditions remained consistent with those established in the previous stage, the combined effects of humectant and surfactant concentrations on fluoride removal, its effectiveness, and the development of stable hydrophobic agglomerates underwent careful evaluation using this factorial design. The application of statistical analysis to the collected results (as described in Section 2.5) enabled the identification of significant variable interactions, ensuring a precise assessment of sunflower oil's effectiveness in fluoride removal.

2.4. Fluoride Removal from Well Water by SAT

The groundwater utilized in this study was obtained from Durango, Dgo., Mexico (Durango City), and was characterized by fluoride concentrations surpassing both national and international regulatory thresholds. Alongside fluoride, the water contains various dissolved ions, including bicarbonates, sulfates, and calcium, which may significantly influence the adsorption dynamics [4]. A bibliographic analysis of water samples from the Valle del Guadiana aquifer from Durango City provided the basis for determining the fluoride concentration in aqueous models. The aquifer exhibits fluoride concentrations that exceed the limits established by the Mexican NOM-127-SSA1-1994 requirements (>1.5 mg L^{-1}) as

well as those recommended by the World Health Organization (WHO). A bibliographic analysis of historical and recent data (2014–2024) from Aguas del Municipio de Durango (AMD) identified the wells with the highest fluoride concentrations, ranging from 2.8 to 5.2 mg L^{-1}. These levels are attributed to the natural interaction of groundwater with fluoride-rich geological formations. For this study, synthetic water models (aqueous models) were prepared using a 1000 mg L^{-1} fluoride standard in deionized water to simulate the fluoride levels found in the most contaminated well in Durango City. The fluoride content of the solution was verified through multiple measurements using an ORION VERSA STAR PRO multiparameter meter (Thermo Fisher Scientific Inc., Walth., USA) equipped with a specific ion electrode (ORION 9609NWP) to guarantee consistency and accuracy. The aqueous models served in factorial experimental designs to improve the SAT parameters for fluoride removal, maintaining consistency with real environmental conditions; finally, the analysis of residual fluoride concentrations in treated water determined the effectiveness of the optimized SAT in fluoride removal.

2.5. Statistical Analysis

An ANOVA test evaluated the assumptions of homogeneity, independence, and normality of variance to confirm the statistical reliability of the experimental data. This analysis verified the model's accuracy, robustness, and suitability for describing the SAT within the established operating limits. Additionally, ANOVA quantified the variance attributed to the independent variables and determined their statistical significance in fluoride removal.

The evaluation of the model's goodness of fit involved estimating Pearson's determination coefficient (R^2) using Statistica 7 for Windows [28]. A high R^2 value indicated strong predictive reliability, validating the model's ability to represent the experimental relationships effectively. The application of Fisher's least significant difference (LSD) test enabled the identification of statistically significant differences among extract dosages (EDs), humectant dosages (HDs), and their interaction effects. The experimental data validated the development of a quadratic response surface model to describe the relationships between independent variables (ED and HD) and fluoride concentration (dependent variable), facilitating a predictive understanding of the system's behavior and the optimization of operational conditions.

3. Results and Discussion

3.1. Determination of Fluoride Concentration Used in Aqueous Models

The fluoride concentration in the most contaminated wells in the northeastern region supplying the city of Durango, based on data from Aguas del Municipio de Durango (AMD), is consistently beyond the maximum permissible limits (MPLs) established by Mexican regulations and WHO recommendations. The data registered a peak value of 8.2 mg L^{-1} in 2014, aligning with previous studies [29,30], which is consistent with other studies conducted in the field; nonetheless, fluoride concentrations consistently exceed established regulatory limits, indicating a persistent deviation from permissible standards. The Seminario well (No. 50), recorded in bibliographical sources with the highest fluoride levels (5.3–8.2 mg L^{-1}), served as the sample source for this study, measuring a fluoride concentration of 5.0 mg L^{-1}, comparable to the amount reported by AMD data. Based on this concentration, fluoride aqueous models provided a controlled medium for fluoride removal studies with the SAT, identifying the key removal parameters for this element.

3.2. Fluoride Removal in Aqueous Models by SAT Application

3.2.1. Comparison Between n-Heptane and Sunflower Oil as Humectant Agent

A comparison of n-heptane and sunflower oil during the third stage of the SAT demonstrated that both humectants effectively improve fluoride removal by promoting interfacial adhesion and enabling stable particle clustering (Table 1). N-heptane achieved removal rates ranging from 91.85 to 93.40%, while sunflower oil exhibited removal rates of approximately 92.53 to 95.19%. The increased efficiency is attributed to sunflower oil's ability to form stronger hydrophobic layers, which enhance the encapsulation of fluoride-adsorbed colloids within agglomerates while minimizing reagent wastage. The optimized SAT using sunflower oil achieved a final fluoride concentration of 0.26 mg L^{-1}, well below WHO and Mexican NOM-SSA-127-2021 limits (1.0 mg L^{-1}). Unlike conventional adsorption and coagulation-flocculation methods, which typically require multiple treatment stages, the SAT offers a single-step, low-waste alternative, making it particularly suitable for decentralized water treatment facilities. This efficiency highlights the practical application of the SAT in rural or resource-limited areas, where access to complex treatment infrastructure is restricted. Additional studies validate that vegetable oils exhibiting amphiphilic characteristics act as efficient binding agents in agglomeration processes, facilitating significant fluoride removal efficiencies [31,32]. As a result, the interaction between the oil's hydrophobic regions and adsorbent particles enhances fluoride capture, reinforcing its viability as a sustainable and practical alternative to n-heptane, particularly at moderate dosages.

Table 1. Comparison of fluoride removal efficiency between n-heptane and sunflower oil during the third stage of the SAT process.

n-Heptane		
Humectant Dosage (mL_{Hum}/g_{TMCs})	**pH_{final}**	**$[F^-]_{final}$ (mg L^{-1})**
2.5	7.04	0.43 * ± 0.04
5	7.1	0.44 * ± 0.02
6.3	7.11	0.42 * ± 0.02
7.5	7.09	0.41 * ± 0.03
10	7.11	0.36 * ± 0.02
Sunflower Oil		
Humectant Dosage (mL_{Hum}/g_{TMCs})	**pH_{final}**	**$[F^-]_{final}$ (mg L^{-1})**
2.5	7.1	0.27 * ± 0.01
5	7.15	0.26 * ± 0.01
6.3	7.04	0.40 * ± 0.02
7.5	7.12	0.36 * ± 0.01
10	7.05	0.30 * ± 0.02

Initial fluoride concentration: 5.0 mg L^{-1}. * Values below NOM-SSA-127-SSA1–2021 (1.0 mg L^{-1}); pH between 6.5 and 8.

On the other hand, the first stage of the SAT, which involves the adsorption of fluoride onto freshly prepared $Al(OH)_3$, is key for the effectiveness of the whole process. This phase involves the electrostatic interactions that occur between the negatively charged fluoride ions and the positively charged aluminum species, which promote the immobilization of fluoride. At the same time, hydrophobic interactions contribute to the stability of the complex. Previous studies indicate that the integration of modified diatomite with $Al(OH)_3$

achieves removal efficiencies greater than 88%, highlighting the importance of effective adsorbent design in fluoride capture [33]. Similarly, adsorption-based methods have achieved fluoride removal rates of up to 89% [34,35], which remains lower than the 95.2% efficiency attained in this study. Other research on seashell-derived adsorbents reported a removal efficiency of 92% [36], while aluminum/alumina composite systems reached 92.6% at pH 6.5 [37]. These findings highlight the critical role of strong electrostatic interactions and hydrophobic mechanisms in enhancing the adsorption capacity of $Al(OH)_3$ during the initial SAT stage, contributing to its superior performance in fluoride removal.

All treatments consistently met the established regulatory standards, including NOM-SSA-127-2021 and WHO guidelines [2022], which set a maximum allowable fluoride concentration of 1.0 mg L^{-1} and a permissible pH range of 6.5–8.0. Throughout all tests, fluoride concentrations varying from 0.25 to 0.44 mg L^{-1} and pH measurements between 7.04 and 7.25 demonstrated compliance with the established guidelines (Table 1). The results align with previous studies [38,39], which demonstrate that vegetable-oil-based humectants performed similarly to n-heptane in reducing interfacial tension and enhancing emulsification. Amphiphilic compounds are crucial for creating stable agglomerates with carbonaceous particles, facilitating effective fluoride encapsulation in aqueous environments. The mechanism relies on the formation of stable agglomerates via hydrophobic interactions, with amphiphilic compounds facilitating the encapsulation of colloids that include adsorbed fluoride. This process reduces the redispersion of contaminants by promoting coalescence between the surfactant–oil matrix and colloidal particles [40]. While n-heptane achieved similar results, the negligible performance differences highlight sunflower oil as a sustainable, cost-effective alternative, particularly when the amphiphilic properties of the surfactant–humectant are optimized.

Likewise, Table 1 highlights the effective removal of fluoride using *A. durangensis* extract (0.5 g $_{Ext}$/g $_{TMCs}$) as a biosurfactant and sunflower oil as the humectant. Emulsion stability is crucial for ensuring uniform dispersion of the biosurfactant and enhancing its interaction with fluoride ions, consistent with prior findings [41]. The hydrophilic–lipophilic balance (HLB) is a key determinant of system stability, with unsaturated fatty acids playing a crucial role in modifying interfacial properties [42]. Under optimal conditions, the fluoride concentration achieved a minimum of 0.26 mg L^{-1} with the application of 5 mL $_{Hum}$/g $_{TMCs}$ of sunflower oil; by contrast, a concentration of 0.27 mg L^{-1} was obtained with 2.5 mL $_{Hum}$/g $_{TMCs}$ of n-heptane. The pH of the treated water remained within 7.0–7.25, complying with both NOM-SSA-127-2021 and WHO standards, ensuring its safety for use. The findings underscore the critical role of optimizing surfactant–humectant interactions, driven by hydrophobic and emulsification mechanisms, in enhancing fluoride removal efficiency while adhering to regulatory standards. Sunflower oil demonstrates superior performance compared to n-heptane, consistently achieving lower final fluoride concentrations and ensuring compliance with established guidelines. Moreover, sunflower oil's lower environmental impact and cost-effectiveness position it as a viable alternative for large-scale water treatment applications.

3.2.2. SAT Optimization for Fluoride Removal in Aqueous Models, Using Different Surfactant and Humectant Doses

Table 2 presents fluoride removal resulting in final concentrations ranging from 0.26 to 0.67 mg L^{-1} of final fluoride concentration (86.6 to 94.8% removal), highlighting the effectiveness of the SAT under optimized humectant and surfactant conditions. The lowest final fluoride concentration observed resulted in 0.26 mg L^{-1}; this was achieved using 0.50 g $_{Ext}$/g $_{TMCs}$ of *A. durangensis* extract as a surfactant and 5.0 mL $_{Hum}$/g $_{TMCs}$ of sunflower oil as a humectant. These findings comply with the NOM-SSA-127-2021 standard, which sets a maximum fluoride concentration of 1.0 mg L^{-1} and mandates

a final pH of approximately 7.0, further validating the SAT's suitability for drinking water treatment.

Table 2. Fluoride removal efficiency under optimized humectant and surfactant conditions using SAT process.

Surfactant Dosage (g_{Ext}/g_{TMCs})	Humectant Dosage (mL_{Hum}/g_{TMCs})	pH_{final}	$[F^-]_{final}$ (mg L^{-1})
1	2.5	7.14 *	0.61 * ± 0.01
0.75	2.5	7.12 *	0.34 * ± 0.03
0.5	2.5	7.10 *	0.27 * ± 0.01
0.25	2.5	7.14 *	0.41 * ± 0.02
0	2.5	7.0 *	0.67 * ± 0.01
1	5	7.2 *	0.37 * ± 0.01
0.75	5	7.25 *	0.38 * ± 0.01
0.5	5	7.15 *	0.26 * ± 0.04
0.25	5	7.12 *	0.45 * ± 0.02
0	5	7.14 *	0.67 * ± 0.01
1	7.5	7.0 *	0.51 * ± 0.01
0.75	7.5	7.0 *	0.28 * ± 0.02
0.5	7.5	7.12 *	0.36 * ± 0.02
0.25	7.5	7.15 *	0.50 * ± 0.02
0	7.5	7.11 *	0.68 * ± 0.02
1	10	7.1 *	0.31 * ± 0.01
0.75	10	7.09 *	0.30 * ± 0.01
0.5	10	7.05 *	0.30 * ± 0.01
0.25	10	7.0 *	0.57 * ± 0.01
0	10	7.04 *	0.65 * ± 0.02

Initial fluoride concentration: 5.0 mg L^{-1}. * Values below NOM-SSA-127-SSA1–2021 (1.0 mg L^{-1}); pH between 6.5 and 8.

The effectiveness of the SAT is primarily attributed to the precipitation–adsorption mechanism, in which fluoride ions are adsorbed onto $Al(OH)_3$ via the regulated formation of aluminum colloids. This is consistent with earlier investigations showing fluoride removal efficiencies surpassing 85% when utilizing metal–organic framework (MOF) adsorbents [42]. The removal percentages achieved, which range from 94 to 97%, are similar to those documented in membrane-based processes [43,44]. Similarly, the adsorption of fluoride through calcium- and zirconium-modified acid-activated alumina (CAZ) in batch reactors has shown an 85.8% removal rate [45]. The SAT also achieved higher efficiency than the 89.0% obtained using graphene-nanostructure-supported manganese oxide (GO-MnO_2) under similar pH conditions [46].

On the other hand, the process modified the hydrophobic affinity of the precipitated colloidal particles by introducing *A. durangensis* leaf extract, which facilitated the transition toward agglomeration. Prior research indicates that optimized micellar and bridging liquid ultrafiltration techniques can reach removal efficiencies of 95% [47,48]. In this stage, fluoride-laden particles aggregate, forming stable nuclei that initiate the nucleation of hydrophobic colloidal clusters, ultimately leading to spherical agglomerates. This process is in agreement with coagulation–flocculation methodologies, where fluoride removal rates above 99% have been documented [49,50]. The mechanism involves the incorporation of fluoride ions into the metal hydroxide phase ($Al(OH)_3$), followed by co-precipitation and subsequent separation through filtration [51].

The addition of $CaCl_2$ in a 1:1 molar ratio enhanced particle cohesion by creating bridges with hydroxyl groups on the hydrophilic segment of the surfactant, thus strengthening the agglomeration process. This interaction strengthens structural integrity and in-

creases the efficiency of the agglomeration phase, as evidenced by previous studies [15,52]. By stabilizing the agglomerated particles, $CaCl_2$ enhances the overall performance of the SAT, ensuring reliable removal efficiency under the specified conditions. The findings underscore the effectiveness of the SAT in fluoride remediation, showcasing its promise as a dependable approach for treating potable water.

3.3. Removal of Fluoride from Well Water Using the Spherical Agglomeration Technique

3.3.1. Groundwater Sampling and Analysis in the City of Durango, Mexico

A bibliographic review of data provided by Aguas del Municipio de Durango (AMD) and previous studies indicated significant variations in fluoride concentrations among urban wells of Durango City. Concentrations observed varied between 2.8 and 5.2 mg L^{-1}, surpassing the allowable limits set by the Mexican NOM-127-SSA1-2021 standard as well as those established by the World Health Organization (WHO). Among the wells analyzed, Well No. 50, commonly known as 'El Seminario', exhibited the highest fluoride concentrations, prompting an in situ sampling campaign to validate these reported levels. The bibliographic findings led to an in situ sampling campaign to validate the reported concentrations. The analysis of samples from Well No. 50 revealed a fluoride concentration of 5.0 ± 0.1 mg L^{-1}. This value aligns with historical data, reinforcing the classification of the well as the most fluoride-contaminated source in the urban water supply. The natural leaching of fluoride-rich geological formations into the groundwater caused the increased fluoride concentrations, a phenomenon attributed to the geochemical characteristics of the region and recognized as a major factor influencing local water quality [4,29,30]. The analysis resulted in the development of aqueous models intended to replicate fluoride concentrations in Well No. 50 (a solution of 5.0 mg L^{-1} fluoride concentration). This facilitated controlled experimentation by employing the SAT to enhance fluoride removal, ensuring that remediation strategies align with real-world conditions.

3.3.2. Efficiency of Fluoride Removal from Well Water by the SAT Process

As shown in Table 3, the SAT effectively removed fluoride from well water, which demonstrates the significance of sunflower oil as a humectant in achieving regulatory compliance (Table 3). The results indicate that the overall removal efficiency is primarily attributed to the encapsulation of colloidal particles throughout the process, enhanced by the strong hydrophobic affinity and lipophilic interactions between hydrophobized colloids and sunflower oil [53,54]. Stable agglomeration is further promoted through prior particle hydrophobization via surfactant application, which enhances surface hydrophobicity and strengthens interaction with the humectant [55]. The combined impact of surfactants and humectants in the SAT is essential for maximizing fluoride removal, as it improves particle adhesion and agglomeration, resulting in more effective separation.

The results from the groundwater study demonstrate significant fluoride removal using the SAT, with removal efficiencies ranging from 85.5 to 88.9%. Final fluoride concentrations of 0.55 to 0.71 mg L^{-1} were obtained, demonstrating greater fluoride reduction than previously reported methods. For instance, an online coagulation–adsorption process achieved 83% fluoride removal in groundwater [54], while electrocoagulation with zero-valent iron (Fe^0) reached 85% removal [56]. The findings indicate that achieving fluoride concentrations within regulatory limits is feasible with an aluminum hydroxide dosage of 30 g $Al(OH)_3$/g F^-_{Tot}, in combination with a humectant (sunflower oil) dosage of 9.0 mL $_{Hum}$/g $_{TMCs}$. In contrast, aqueous models achieved over 90% removal using lower adsorbent and humectant doses. This variation arises from the complex and heterogeneous composition of well water, where competing ions and organic matter reduce adsorption efficiency by occupying active adsorption sites [57].

Table 3. Fluoride removal efficiency in well water using the SAT process with sunflower oil as humectant.

Surfactant Dosage (g_{Ext}/g_{TMCs})	Humectant Dosage (mL_{Hum}/g_{TMCs})	pH_{final}	$[F^-]_{final}$ (mg L^{-1})
0.25	2.5	7.0 *	0.63 * ± 0.02
0.25	5	7.03 *	0.66 * ± 0.01
0.25	7.5	7.05 *	0.67 * ± 0.01
0.5	2.5	7.07 *	0.71 * ± 0.02
0.5	5	7.03 *	0.68 * ± 0.01
0.5	7.5	7.02 *	0.61 * ± 0.02
0.75	2.5	7.03 *	0.64 * ± 0.01
0.75	5	7.0 *	0.58 * ± 0.01
0.75	7.5	7.04 *	0.55 * ± 0.02

Initial fluoride concentration: 5.0 ± 0.1 mg L^{-1}, as found in well No. 50. * Values below NOM-SSA-127-SSA1–2021 (1.0 mg L^{-1}); pH between 6.5 and 8.

These findings are consistent with electrocoagulation studies that reported an 85.6% fluoride removal rate [57]. The presence of competing ions in groundwater, such as bicarbonates and sulfates, affects fluoride adsorption capacity, necessitating higher adsorbent and humectant doses compared to controlled aqueous systems. The interaction between surfactants and humectants in the SAT ensures that fluoride removal is maintained despite these interferences. The improved agglomeration and stabilization mechanisms improve fluoride separation, demonstrating the SAT's robustness in real-world water treatment applications by ensuring efficiency despite water matrix complexities.

Furthermore, these findings underscore the potential of the SAT as a scalable and adaptable method for fluoride mitigation in various water sources. The technique's ability to achieve regulatory fluoride limits highlights its applicability in large-scale water treatment processes. The incorporation of surfactants and humectants in the SAT significantly enhances agglomeration efficiency while enabling the reduction of fluoride concentrations to achieve regulatory-compliant levels in just one treatment. This advantage positions the SAT as a competitive alternative to conventional methods, particularly in areas with high fluoride contamination and limited access to advanced water treatment infrastructure.

3.4. Statistical Analysis and Data Interpretation

3.4.1. Statistical Analysis for Sunflower Oil and n-Heptane Treatment in Aqueous Models

The analysis of variance (ANOVA) conducted in a 5 × 2 experimental design evaluated the fluoride removal efficacy utilizing two humectants: n-heptane (derived from hydrocarbons) and sunflower oil (derived from vegetables). The results revealed significant differences in removal efficiency based on the type of humectant and the administered dosage (2.5, 5, 6.3, 7.5, and 10 mL $_{Hum}/g_{TMCs}$). The results indicated that sunflower oil surpassed n-heptane in fluoride removal in aqueous models; they also suggested that sunflower oil is a viable alternative to n-heptane and improves fluoride removal effectiveness, corroborating a previous study that identified it as a suitable alternative for agglomerate formation in spherical agglomeration procedures (Table S1 in the Supplementary Materials).

The general linear model employed in this experimental design met the criteria of normality, independence, and homogeneity of variance, with a coefficient of determination (R^2) of 0.9342, indicating its reliability at a 95% confidence level.

Fisher's LSD test indicated that the 10 mL $_{Hum}/g_{TMCs}$ dose of n-heptane resulted in a fluoride removal of 93.40%, with a residual concentration of 0.36 mg L^{-1} (Table S2 in the Supplementary Materials). In the use of sunflower oil, the 5 mL $_{Hum}/g_{TMCs}$ dosage achieved the maximum efficacy, yielding a removal efficiency of 95.19% and a residual

concentration of 0.26 mg L^{-1}. Sunflower oil demonstrated greater effectiveness than n-heptane throughout all tested doses, offering an excellent alternative in the humectation process within the SAT (Figure 2).

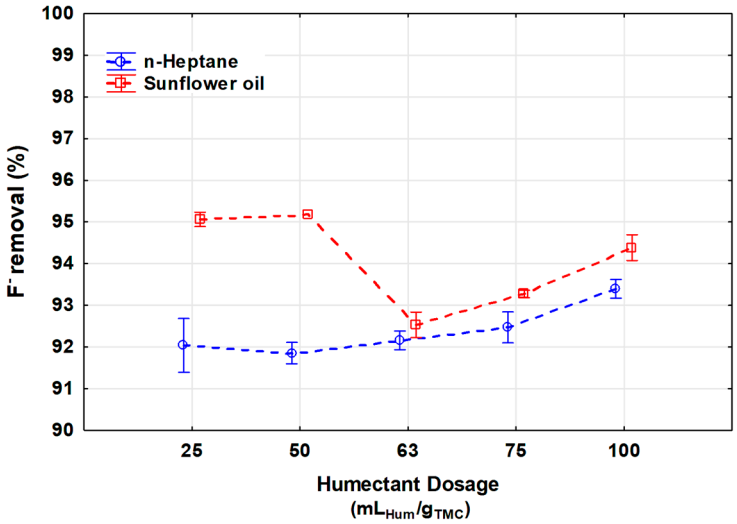


Figure 2. Comparison of fluoride removal efficiency between sunflower oil and n-heptane as humectants in SAT.

3.4.2. Statistical Analysis for Fluoride Removal in Aqueous Models

The experimental design for fluoride removal in aqueous models utilized a 5 × 4 factorial approach, evaluating the interaction between five surfactant dosages (0.1, 0.3, 0.5, 1.0, and 2.0 g $_{Ext}$/g $_{TMCs}$) and four humectant dosages (1.5, 3.0, 5.0, and 7.5 mL $_{Hum}$/g $_{TMCs}$). An analysis of variance (ANOVA) determined the significance of the primary influences and their interaction on fluoride removal efficiency. The findings demonstrated that both the surfactant dosage ($p < 0.001$) and the humectant dosage ($p < 0.01$) showed statistically significant impacts on fluoride removal. A notable interaction effect ($p < 0.05$) became evident, indicating that optimal performance depended on the combined dosages rather than on either variable independently (Table S3 in the Supplementary Materials). Tests for homogeneity, independence, and normality validated the ANOVA results, supporting that the assumptions were satisfied and confirming the reliability of the results. The response surface exhibited a non-linear trend, with removal efficiency increasing up to an optimal dosage of 0.5 g $_{Ext}$/g $_{TMCs}$ of surfactant and 7.5 mL $_{Hum}$/g $_{TMCs}$ of humectant. Beyond these optimal dosages, the efficiency stabilized, indicating saturation effects. A least significant difference (LSD) test evaluated specific dosage combinations to enhance the accuracy of the findings (Table S4 in the Supplementary Materials). The test demonstrated that the optimal dosage resulted in significantly higher fluoride removal compared to both lower and higher dosages ($p < 0.05$), corroborating the interaction results from the ANOVA. The statistical studies confirmed that precise control of reagent doses is a requirement for optimizing fluoride removal efficiency. The factorial design provided reliable insights into the synergistic effects of surfactant and humectant dosages, establishing a solid basis for the development of the SAT process in well water treatment applications.

3.4.3. Response Surface Graph for Fluoride Removal in Aqueous Models

The response surface illustrated in Figure 2 demonstrates how fluoride removal efficiency varies with different dosages of the surfactant and humectant in aqueous models using the SAT. The non-linear response indicates significant interactions between *A. durangensis* extract (surfactant) and sunflower oil (humectant). The mathematical model illustrated in Equation (1) determines the response surface behavior displayed in Figure 3,

capturing the complex interaction between surfactant and humectant concentrations; additionally, the ideal parameters, as specified in Equation (1), involved 0.5 g $_{Ext}$/g $_{TMCs}$ of ED and 7.5 mL $_{Hum}$/g $_{TMCs}$ of HD, achieving a maximum fluoride removal of 95.19%.

$$\%F^{-}{}_{Removal} = 89.2945 + (17.9153 \times ED) - (0.3442 \times HD) + (17.4956 \times ED^2) + (0.636 \times ED \times HD) + (0.0049 \times HD^2) \quad (1)$$

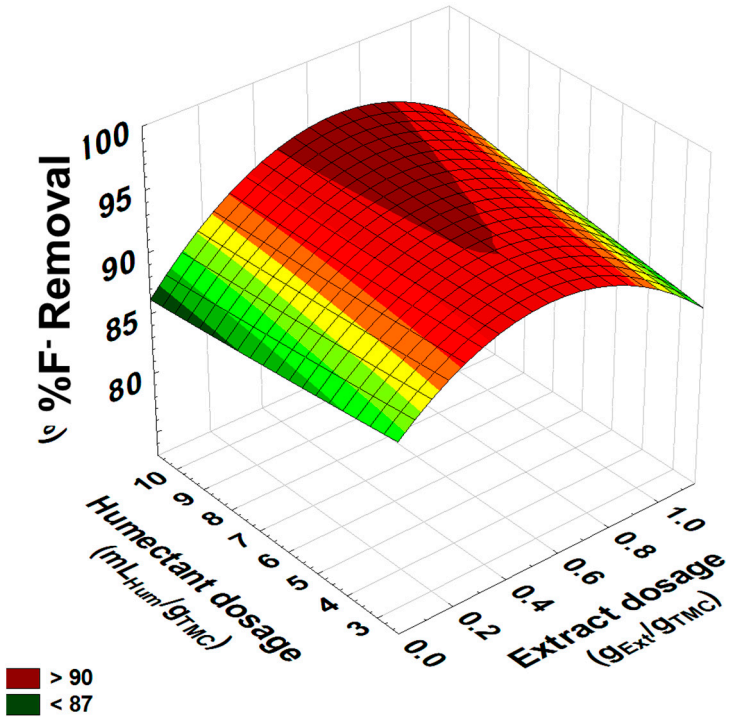


Figure 3. Response surface for the percentage removal of F^{-} present in groundwater using sunflower oil as a wetting agent in the SAT.

The response surface trends indicate that insufficient hydrophobization and humectation hinder stable agglomerate formation, thereby reducing effectiveness. Excessive dosages lead to reagent inefficiency, as saturation effects reduce cohesion within the system. Moreover, excessive surfactant dosages induce micellization, destabilizing hydrophobic aggregates and in that way inhibiting fluoride entrapment. Likewise, excess humectant alters interfacial tension, further disrupting the aggregation mechanism essential for fluoride removal.

In contrast to these results, coagulation–flocculation processes employing aluminum salts have demonstrated removal efficiencies between 89% and 92% under optimal conditions [5]. Similarly, surfactant-modified zeolites have been reported to achieve fluoride removal efficiencies close to 90% [58], while biosurfactant-based adsorption methods have attained efficiencies of up to 93% [59]. However, the superior removal performance observed in this study can be attributed to the specific mechanisms involved in the SAT, which integrates hydrophobization and kinetic collisions to generate stable agglomerates, enhancing fluoride encapsulation and separation [23]. In contrast, coagulation–flocculation primarily relies on charge neutralization and particle bridging, which can be less effective for fluoride ions in certain water matrices [60]. Adsorption-based techniques, while effective, are inherently limited by the adsorbents' surface area, porosity, and eventual saturation, which can impede long-term efficiency [58].

The SAT represents a highly efficient approach to fluoride removal, primarily due to its ability to rapidly form hydrophobic agglomerates. This efficiency is enhanced by the synergistic effect of surfactants and humectants, which improve surface interactions and minimize reagent wastage. Consequently, the SAT is particularly advantageous in scenarios with elevated fluoride concentrations, such as those reported in Durango. The

application of biosurfactants in fluoride removal has demonstrated comparable advantages, underscoring the significant role of amphiphilic compounds in enhancing fluoride removal. Conversely, coagulation–flocculation methods necessitate higher chemical dosages and generate considerable sludge, reducing their viability in high-contaminant environments. Meanwhile, adsorption techniques employing modified adsorbents often experience challenges related to material saturation and limited reusability.

The enhanced efficiency of the SAT is primarily due to the physicochemical mechanisms governing the formation of stable agglomerates. Surfactants lower interfacial tension, facilitating the aggregation of fluoride-laden particles, while humectants optimize moisture retention, improving particle cohesion. This dual-action process not only enhances fluoride capture but also mitigates reagent loss, making it a more sustainable alternative. Notably, biosurfactant-based methods operate under similar principles, where amphiphilic molecules mediate the adsorption and separation of fluoride from aqueous solutions [61]. However, coagulation–flocculation remains dependent on charge interactions, which can be less efficient in matrices with variable ionic compositions. Additionally, the substantial sludge generation further limits its application in large-scale treatments [62]. Similarly, adsorption-based techniques, despite their initial effectiveness, are constrained by the saturation of active sites and the declining adsorption capacity over time [63].

3.4.4. Statistical Analysis for Fluoride Removal in Well Water

The analysis of variance (ANOVA) conducted on a 3 × 2 randomized block factorial design in triplicate using well water indicates significant differences in fluoride removal via the SAT (Table S5 in the Supplementary Materials), affected by surfactant doses (0.25, 0.5, 0.75 g $_{Ext}$/g $_{TMCs}$) and humectant doses (2.5, 5, 7.5 mL $_{Hum}$/g $_{TMCs}$), as well as the interaction between both of these variables, at a 95% confidence interval ($p < 0.05$).

The model's validation, via residual analysis of the general linear model, confirms that the assumptions of normality, independence, and homogeneity of variance are satisfied. A coefficient of determination (R^2) of 0.9693 demonstrates a strong model fit, indicating high predictive reliability ($p < 0.05$). The homogeneity, independence, and normality of variance tests confirm the normality of the distribution and the homogeneity of variances, with p-values over 0.05, supporting the robustness of the factorial design. The least significant difference test (Fisher's LSD) indicates significant differences between the means of final fluoride concentrations for both the surfactant (*A. durangensis* extract) and humectant (sunflower oil) dosages (Table S6 in the Supplementary Materials). Optimal fluoride removal is achieved with 0.75 g Ext/g TMCs of ED and 7.5 mL Hum/g TMCs of HD, resulting in residual fluoride concentrations of 0.56, 0.59, and 0.61 mg L^{-1}, corresponding to removals above 87%. All treatments administered remained within the maximum allowable limits set by NOM-127-SSA1-2021 and WHO guidelines, confirming the efficacy of the experimental design and the chemicals employed for fluoride removal in well water by the SAT. The results suggest that both *A. durangensis* extract and sunflower oil effectively remove fluoride from well water by the SAT, utilizing particular dosage combinations that optimize performance and adhere to established water quality criteria.

3.4.5. Response Surface Graph for Fluoride Removal in Well Water

The response surface figure describes the system's dynamics under different surfactant and humectant doses, validating significant trends noted in fluoride removal efficiency. The mathematical representation in Equation (2) describes this behavior, highlighting the interactions among the reagents and correlating with the graphical trends observed in Figure 4. The response surface demonstrates that fluoride removal efficiency increases with rising ED and HD up to an optimal point, beyond which a plateau effect is observed.

This trend suggests that excessive reagent concentrations may not further enhance removal efficiency due to micellar saturation and competitive ion effects. Experimental results indicate that the optimized parameters of the SAT effectively enhance a significant fluoride removal from well water. A removal efficiency of 88.86% was achieved with a surfactant dosage of 0.75 g $_{Ext}$/g $_{TMCs}$ and a humectant dosage of 7.5 mL $_{Hum}$/g $_{TMCs}$; in this way, the treatment resulted in a final fluoride concentration of 0.55 mg L^{-1}, which was significantly lower than the maximum permissible limit (MPL) of 1.0 mg L^{-1} set by the World Health Organization (WHO) and the Mexican NOM-127-SSA1-2021 standards. The results indicate the effectiveness of the SAT in ensuring compliance with regulatory standards under various reagent conditions, reinforcing the predictive capabilities of the response surface model.

$$\%F^{-}{}_{Removal} = 90.5481 - (16.2222 \times ED) - (0.4356 \times HD) + (13.5111 \times ED^2) + (1.04 \times ED \times HD) + (0.0124 \times HD^2) \quad (2)$$

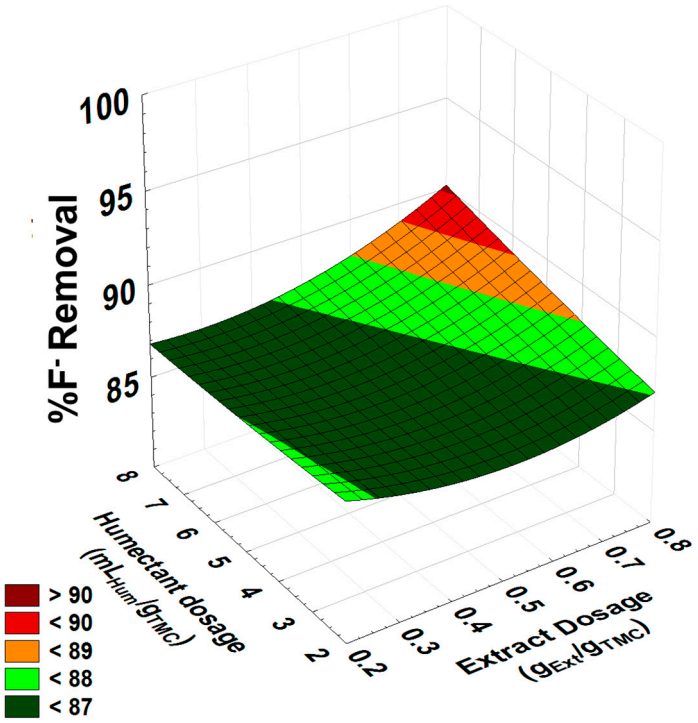


Figure 4. Response surface for the percentage removal of F^- present in well water using sunflower oil as a wetting agent in the SAT.

A notable observation is the absence of saturation effects, even at elevated reagent doses. This behavior is largely due to the complex composition of well water, which contains high concentrations of dissolved ions and organic compounds. Specifically, competitive ions such as bicarbonates and sulfates interfere with micelle formation in surfactants, thereby hindering the development of stable hydrophobic aggregates. This inhibition arises from electrostatic interactions that lower the effective concentration of surfactant monomers necessary for micelle formation. Similarly, humectant saturation is constrained as the hydrophobic chains of oil molecules fail to establish nucleation points due to disruption from other dissolved species. The disruption of these aggregation processes prevents the formation of a uniform hydrophobic phase, preserving available binding sites and enhancing hydrophobic interactions within the agglomeration system. Consequently, fluoride removal efficiency remains high even at elevated reagent concentrations [64].

Further supporting this observation, it has been documented that competitive ions impede adsorption onto reactive surfaces by altering electrostatic interactions, effectively reducing available active sites [65]. Additionally, hydrophobic aggregation processes are

highly sensitive to the ionic composition of water matrices, as variations in ionic strength can modify interfacial tension and disrupt aggregate stability [66]. These findings highlight the necessity of understanding water chemistry when optimizing reagent doses in natural water treatment applications.

Comparatively, findings from arsenic removal via the SAT indicate that increasing surfactant and humectant concentrations enhances removal efficiency without reaching saturation, a phenomenon attributed to the persistence of competitive anions that modify adsorption equilibria [67]. This suggests that the efficiency of hydrophobic interactions in multi-contaminant systems is influenced by the specific ionic environment, requiring tailored reagent dosages to achieve optimal removal across various species. The complexity of such interactions underscores the importance of designing treatment protocols that account for both competitive effects and the physicochemical nature of contaminants in well water systems. The relevance of these findings extends beyond fluoride removal, as they provide insight into broader treatment strategies applicable to a range of contaminants in complex aqueous environments.

The results indicate that optimizing the dosages of both surfactants and humectants in the SAT leads to higher fluoride removal rates, all while adhering to regulatory standards. The method's adaptability to diverse water matrices suggests its potential for large-scale water treatment applications. Moreover, the identified trends underscore the impact of competitive interactions on system dynamics, inhibiting saturation and maintaining removal efficiency. Sunflower oil proved more effective than n-heptane as a humectant, improving fluoride removal efficiency while mitigating environmental impact. The interaction between fluoride and multiple dissolved ions in water, such as bicarbonates and sulfates, could influence removal efficiency, underscoring the necessity for further research on chemical dynamics related to complex water matrices. Further research should explore the use of alternative biosurfactants to enhance process sustainability and fluoride removal efficiency. Despite its proven efficacy, the SAT faces challenges related to the long-term stability of humectants and biosurfactants across varying water conditions. Moreover, the integration of the SAT with hybrid treatment systems, including membrane filtration or electrocoagulation, has the potential to enhance its adaptability for different water sources. Scaling up the SAT process presents both opportunities and challenges, necessitating thorough evaluation for effective implementation. Key factors to consider include optimizing reaction kinetics, maintaining process efficiency at larger scales, and addressing operational constraints such as reagent consumption and waste management. Furthermore, variations in water composition across different scales may impact fluoride removal efficiency, emphasizing the need for adaptive process modifications. Conducting pilot-scale studies is crucial for assessing real-world performance and identifying potential limitations before full-scale deployment. Future research should prioritize cost-effective strategies to enhance scalability while maintaining environmental sustainability and regulatory compliance.

4. Conclusions

This study demonstrates the efficacy of the SAT process as a viable and sustainable method for fluoride removal, achieving efficiencies of 95.19% in aqueous models and 88.86% in well water, by incorporating *A. durangensis* extract as a surfactant and sunflower oil as a humectant. Response surface analysis identified optimal reagent dosages (0.5 g_{Ext}/g_{TMCs} surfactant and 7.5 mL_{Hum}/g_{TMCs} humectant) as crucial for maximizing fluoride removal efficiency. The results highlight the potential of the use of agents of natural origin (surfactant and humectant), offering an eco-friendly alternative to industrial-based solvents while maintaining comparable or superior performance to n-heptane. Through hydrophobic interactions and kinetic aggregation, the SAT process promotes stable agglomerates,

which induces the encapsulation and subsequent separation of fluoride-adsorbed colloids, significantly improving fluoride removal efficiency. The substitution of n-heptane with sunflower oil further improves fluoride removal efficacy, particularly in areas such as Durango, Mexico, where elevated fluoride concentrations pose significant public health concerns. Although these results validate the SAT as an economically feasible remediation method, further research at the pilot scale is essential to fully evaluate operational parameters, stability, and economic feasibility. Additionally, future studies should examine the SAT's applicability to other metallic and non-metallic contaminants, explore its integration into hybrid treatment systems for enhanced versatility across different water matrices, and validate its performance at the pilot scale by assessing operational parameters, long-term stability, and economic feasibility before broader implementation.

Supplementary Materials: The following supporting information can be downloaded at https://www.mdpi.com/article/10.3390/pr13030913/s1: Table S1. ANOVA results for the residual fluoride concentration in the 5 × 2 factorial arrangement design (comparison between n-heptane and sunflower oil). Table S2. Least significant difference analysis comparing humectant types (n-heptane and sunflower oil) at different dosages for fluoride removal using the SAT aqueous models. Table S3. ANOVA results for the residual fluoride concentration in the 5 × 4 factorial arrangement design in aqueous models. Table S4. Least significant difference analysis of humectant and surfactant dosage interaction in fluoride removal using SAT in aqueous models. Table S5. ANOVA results for the residual fluoride concentration in the 3^2 factorial arrangement design applied to well water. Table S6. Least significant difference analysis of humectant and surfactant dosage interaction in fluoride removal using SAT in well water.

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Abbreviations

The following abbreviations are used in this manuscript:

ANOVA	Analysis of variance
ED	Extract dosage (mL_{Ext}/g_{TMCs})
F^-	Fluoride ion
HD	Humectant dosage (mL_{Hum}/g_{TMCs})

TMCs	Total Mixture Components (formed by the reaction between $AlCl_3$, $Ca(OH)_2$)
R^2	Pearson determination coefficient
SAT	Spherical agglomeration technique

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