DEVELOPMENT OF FUNCTIONALISED RICE STRAW CELLULOSE FOR FLUORIDE REMOVAL IN POTABLE WATER USING RESPONSE SURFACE METHODOLOGY

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College : R.V. College of Engineering, Bengaluru
Branch : Department of Chemical Engineering
Guide(s) : Dr. Jagadish H Patil
Dr. Raviraj Kusanur
Student(s) : Mr. Ajith P Arun
Ms. Niranjana Sreenivasan

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Introduction:

Fluoride contamination in drinking water is a widespread and persistent problem, posing serious risks to public health and water security worldwide. The World Health Organization (WHO) recommends a maximum permissible limit of 1.5 mg/L; however, more than 200 million people are exposed to concentrations exceeding this threshold. While low levels of fluoride are beneficial for dental health, prolonged exposure leads to dental and skeletal fluorosis, along with systemic effects such as kidney dysfunction and neurodevelopmental disturbances. Both geogenic sources, including the dissolution of fluoride-bearing minerals, and anthropogenic activities, such as industrial effluents, contribute significantly to groundwater contamination. Conventional defluoridation methods, including chemical precipitation, ion exchange, reverse osmosis, and electrodialysis, though effective, are often limited by high operational costs, energy requirements, and secondary waste generation. In this context, adsorption has emerged as a promising alternative due to its simplicity, cost-effectiveness, and adaptability to decentralized water treatment systems. The efficiency of adsorption can be further enhanced through the use of low-cost, sustainable, and locally available materials. Agricultural residues have gained considerable attention as eco-friendly adsorbents owing to their abundance, renewability, and presence of functional groups favorable for pollutant binding. Among these, rice straw stands out due to its large global availability and modifiable lignocellulosic structure. Chemical modifications, such as alkali treatment and silica functionalization, significantly enhance its adsorption capacity by introducing active binding sites and improving surface characteristics.

Despite these advantages, systematic studies on NaOH and TEOS co-modified rice straw for fluoride removal remain limited, particularly with respect to process optimization. Furthermore, the application of statistical tools such as response surface methodology (RSM) to optimize adsorption parameters in biomass-based systems is still underexplored. Accordingly, the present study focuses on the development of a sequentially alkali-pretreated and TEOS-functionalized rice straw adsorbent for efficient fluoride removal. The adsorption performance is evaluated under varying physicochemical conditions, and process parameters are optimized using RSM. Additionally, adsorption equilibrium and kinetics studies are conducted to elucidate the underlying removal mechanisms and provide insights for practical water treatment applications.

Objectives:

1. To develop a dual-modified rice straw adsorbent using alkali pretreatment followed by tetraethyl orthosilicate (TEOS) functionalization for enhanced fluoride removal.
2. To characterize the synthesized adsorbent using FTIR, SEM, and EDX to evaluate structural modifications, surface morphology, and elemental composition.
3. To investigate the influence of key operational parameters such as pH, contact time, adsorbent dosage, and initial fluoride concentration on adsorption performance.
4. To optimize the fluoride adsorption process using Response Surface Methodology (RSM) based on Central Composite Design (CCD).
5. To evaluate adsorption behaviour through isotherm and kinetic models to understand the mechanism of fluoride removal.

Methodology:

1. The methodology involves the preparation, modification, characterization, and optimization of a rice straw-based adsorbent for fluoride removal. All chemicals used, including sodium hydroxide ($NaOH$), tetraethyl orthosilicate (TEOS), hydrochloric acid (HCl), ethanol, acetic acid, and sodium fluoride (NaF), were of analytical grade, and deionized water was used for all preparations.
2. Raw rice straw was collected, manually cleaned to remove impurities, washed thoroughly with water, and oven-dried at 70 °C to remove moisture. The dried biomass was chopped, ground using a mechanical grinder, and sieved (40–100 mesh) to obtain a uniform particle size.
3. Alkaline pretreatment was carried out by treating 20 g of rice straw with 10% $NaOH$ solution for 12 hours at room temperature. This treatment removed hemicellulose and partially disrupted lignin–carbohydrate complexes, thereby increasing porosity and exposing cellulose hydroxyl groups. The material was then washed until neutral pH was achieved and dried to prepare it for further modification.

4. Silane functionalization was performed using tetraethyl orthosilicate (TEOS) through a dual-stage sol-gel process. In Stage I, the pretreated biomass was mixed with ethanol, TEOS, and HCl, allowing acid-catalyzed hydrolysis and formation of silanol groups along with initial silica network deposition. In Stage II, further treatment with ethanol, TEOS, and acetic acid promoted condensation reactions, leading to a stable silica coating enriched with Si–OH groups that enhance fluoride adsorption.
5. The modified adsorbent was characterized using FTIR to identify functional groups, SEM to observe surface morphology and structural changes, and EDX to determine elemental composition and confirm fluoride adsorption.
6. Batch adsorption experiments were conducted using fluoride solutions prepared from NaF stock solution (1000 mg/L). Experiments were performed in conical flasks under controlled agitation using an orbital shaker. Key operational parameters such as pH (2–7), adsorbent dosage (0.5–2 g), contact time (30–180 min), and initial fluoride concentration (2–32 mg/L) were systematically varied.
7. Fluoride concentration before and after adsorption was measured using a fluoride ion-selective electrode with TISAB buffer to eliminate interference from competing ions. The percentage removal of fluoride was calculated using initial and equilibrium concentrations.
8. To optimize the adsorption process, Response Surface Methodology (RSM) based on Central Composite Design (CCD) was employed. A total of 30 experimental runs were designed to evaluate the effects and interactions of process variables. Statistical analysis was carried out using ANOVA, and a second-order polynomial model was developed.
9. Three-dimensional response surface plots and contour plots were used to determine optimal conditions for maximum fluoride removal and to understand the interaction between variables.

Result and Conclusion:

1. The synthesized dual-modified rice straw adsorbent demonstrated effective fluoride removal performance, confirming the success of alkali pretreatment and TEOS functionalization. FTIR analysis revealed the presence of silanol (Si–OH) groups and confirmed the removal of hemicellulose, indicating successful surface modification. SEM images showed a transition from smooth fibrous structure to a rough, porous morphology after NaOH treatment and silica coating after TEOS functionalization, enhancing adsorption sites. EDX analysis confirmed the presence of silica and successful adsorption of fluoride through the detection of fluorine after treatment.
2. Batch adsorption studies indicated that pH, adsorbent dosage, contact time, and initial fluoride concentration significantly influenced the removal efficiency. Maximum fluoride removal of approximately 65% was achieved under optimized

acidic conditions. The adsorption equilibrium data closely followed the Langmuir isotherm model with a maximum adsorption capacity of 100 mg/g ($R^2 \approx 0.98$), suggesting monolayer adsorption on a homogeneous surface.

3. Kinetic studies revealed that the adsorption process followed the pseudo-second-order model ($R^2 \approx 0.99$), indicating that chemisorption is the dominant mechanism. The adsorption mechanism involved rapid initial surface adsorption followed by slower intraparticle diffusion and pore filling.
4. Response Surface Methodology (RSM) using Central Composite Design effectively optimized the process parameters and demonstrated strong agreement between predicted and experimental results, validating the statistical model.
5. Overall, the study concludes that TEOS-functionalized rice straw is a cost-effective, sustainable, and efficient adsorbent for fluoride removal. The developed system shows strong potential for application in decentralized water treatment systems, especially in fluoride-affected regions.

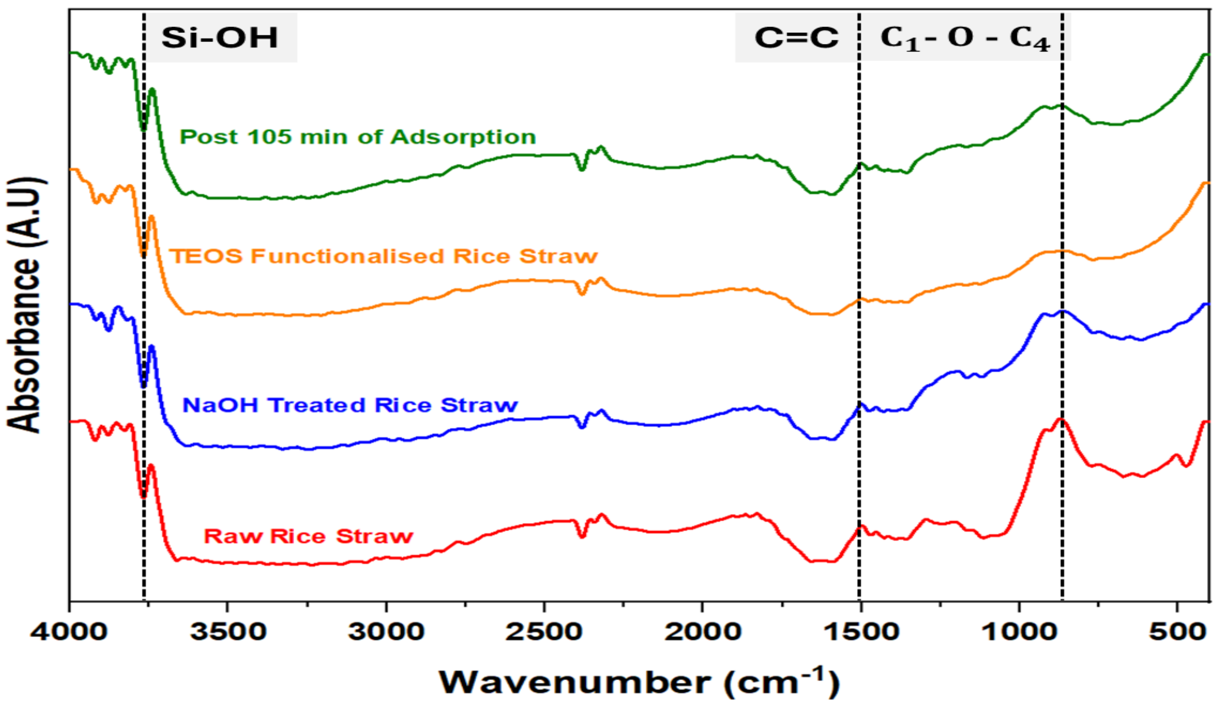

Figure 1: FTIR spectra of rice straw before modification, after modification, and post adsorption.

Stacked Fourier transform infrared (FTIR) spectra of rice straw recorded at different stages of modification and after fluoride adsorption, plotted as absorbance versus wavenumber. The spectra are presented in a stacked format to facilitate visual comparison of major characteristic peaks. Labeled spectral features include Si–OH stretching near 3760 cm^{-1}, C=C stretching around 1510 cm^{-1}, and the β-glycosidic linkage (–C1–O–C4) near 880 cm^{-1}. A common band around 2380 cm^{-1} corresponding to physically adsorbed CO_2 is also visible across the spectra.

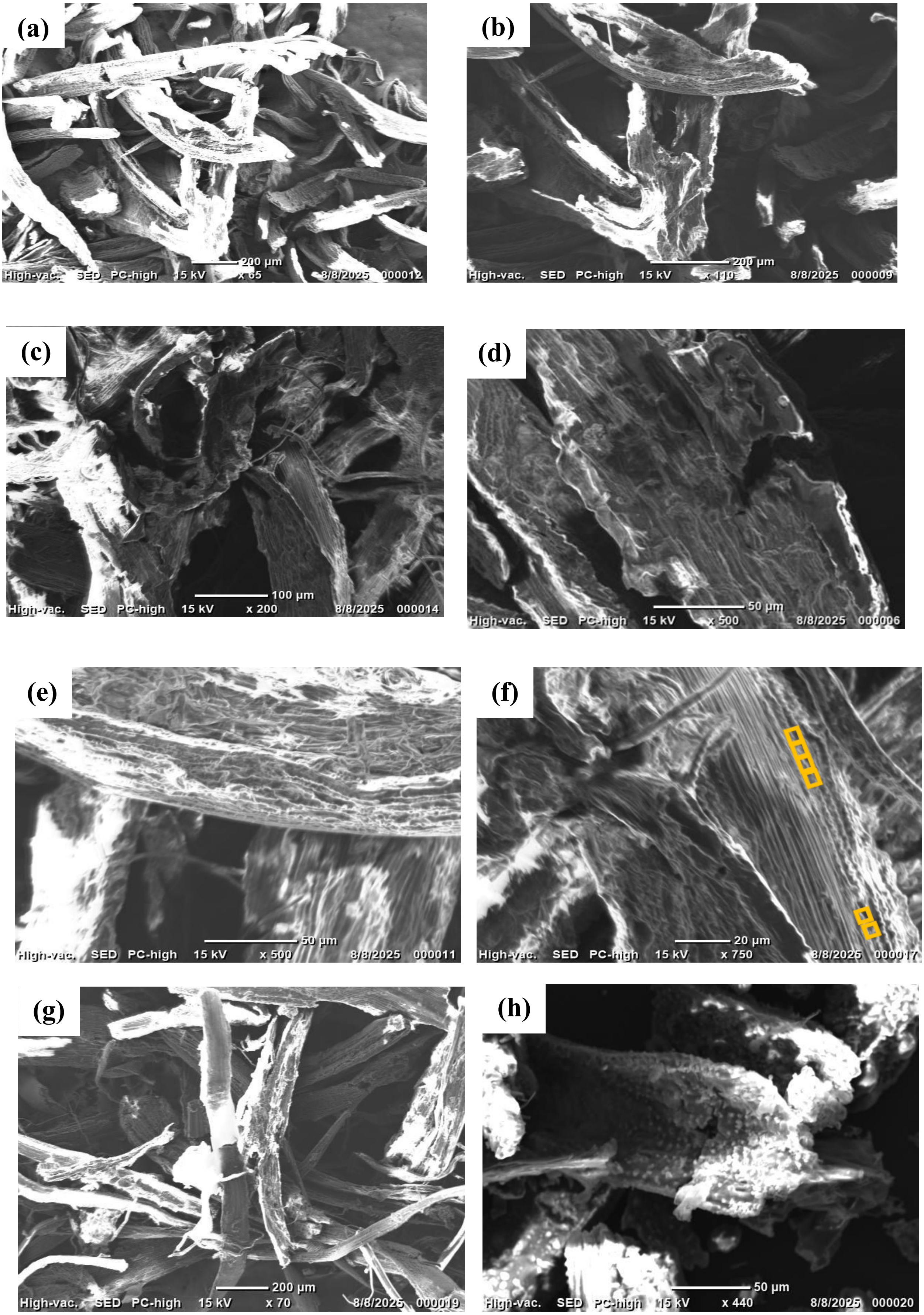

Figure 2: The SEM images of (a-b) raw rice straw (c-d) NaOH treated rice straw (e-f) TEOS functionalized rice straw (nodules are highlighted in yellow) (g-h) modified rice straw post fluoride adsorption

Scanning electron microscopy (SEM) images illustrating the morphological evolution of rice straw across different treatment and adsorption stages. Panels (a) and (b) show raw rice straw with fibrous, sheet-like bundles, relatively smooth external surfaces, and compact fibre cross-sections. Panels (c) and (d) display NaOH-treated rice straw with increased surface roughness, fibrillation, longitudinal cracks, partially separated fibres, and visible grooves and channels along the fibre length. Panels (e) and (f) present TEOS-modified rice straw exhibiting a thin surface coating with granular deposits, including fine spherical nodules and thin film-like structures distributed across the fibrils. Panels (g) and (h) show rice straw after fluoride adsorption, where granular clusters are observed embedded within or fused to the fibril matrix, with pore entrances appearing partially covered.

$$\begin{aligned}\text{Fluoride adsorprtion (\%)} \\ &= -23.82 + 29.27(\mathrm{A}) - 11.14\,(\mathrm{B}) - 0.28(\mathrm{C}) + 0.33\,(\mathrm{D}) - 3.36(\mathrm{A}^2) \\ &+ 10.73(\mathrm{B}^2) + 0.026(\mathrm{C}^2) - 0.00085\,(\mathrm{D}^2) - 1.21(\mathrm{AB}) - 0.031\,(\mathrm{AC}) \\ &- 0.015(\mathrm{AD}) - 0.06(\mathrm{BC}) - 0.01(\mathrm{BD}) - 0.0008(\mathrm{CD})\end{aligned}$$

Table 1: Analysis of variance (ANOVA) for CCD design with experimental responses.

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	6218.13	14	444.15	67.87	< 0.0001	significant
A-pH	2465.66	1	2465.66	376.78	< 0.0001	
B-Adsorbent dose	655.10	1	655.10	100.11	< 0.0001	
C-Initial Fluoride Concentration	433.85	1	433.85	66.30	< 0.0001	
D-Contact time	340.95	1	340.95	52.10	< 0.0001	
AB	83.13	1	83.13	12.70	0.0028	
AC	22.16	1	22.16	3.39	0.0856	
AD	133.34	1	133.34	20.38	0.0004	
BC	7.49	1	7.49	1.15	0.3015	
BD	5.89	1	5.89	0.9005	0.3577	
CD	12.80	1	12.80	1.96	0.1823	
A^2	1146.31	1	1146.31	175.17	< 0.0001	
B^2	94.39	1	94.39	14.42	0.0018	
C^2	94.08	1	94.08	14.38	0.0018	
D^2	58.93	1	58.93	9.01	0.0090	
Residual	98.16	15	6.54			
Lack of Fit	85.36	10	8.54	3.33	0.0980	not significant
Pure Error	12.80	5	2.56			
Cor Total	6316.29	29				

Table summarizing the analysis of variance results for the central composite design model used to evaluate fluoride adsorption. The table includes the overall model, individual factors namely pH, adsorbent dose, initial fluoride concentration, and contact time, along with their interaction terms and quadratic terms. For each source, the sum of squares, degrees of freedom, mean square, F-value, and p-value are reported. The overall model is statistically significant with a p-value less than 0.0001, while the lack of fit is reported as not significant. Residual, pure error, and total variation components are also presented.

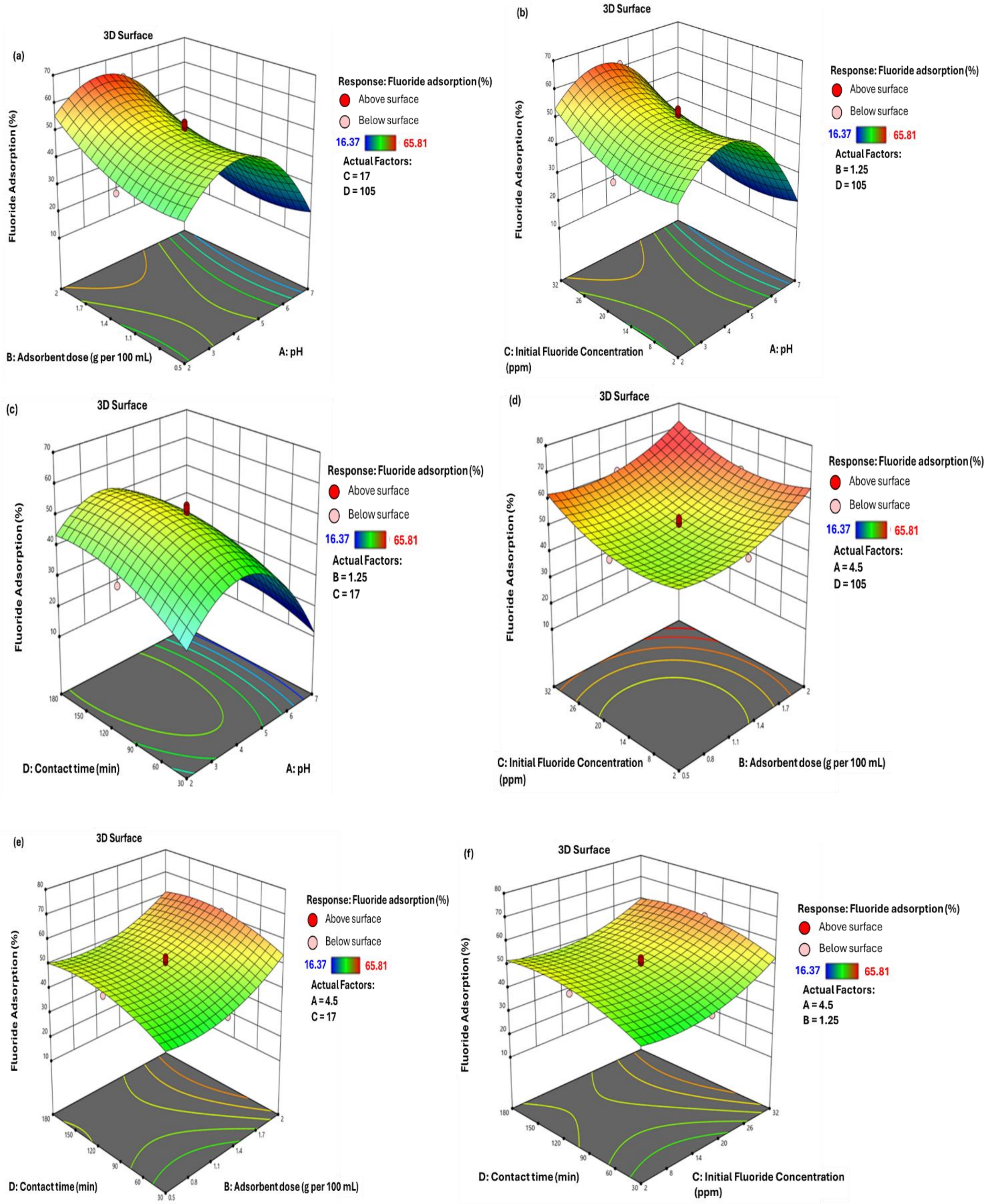

Figure 3: 3D response surface analysis of fluoride adsorption by TEOS modified rice straw showing interaction between (a) pH and adsorbent dose (b) pH and initial fluoride concentration (c) pH and contact time (d) initial fluoride concentration and adsorbent dose (e) contact time and adsorbent dose (f) contact time and initial fluoride concentration.

Three-dimensional response surface plots illustrating the interaction effects of process variables on fluoride adsorption. **Figure 3(a)** shows the combined effect of solution pH (A) and adsorbent dose (B) on fluoride removal, with initial fluoride concentration fixed at 17 ppm and contact time fixed at 105 min. The curved surface indicates a significant interaction between pH and adsorbent dose, with fluoride removal exceeding 60% at low pH values of 2–3 and increasing adsorbent dose, while removal efficiency declines at pH values above 6 regardless of adsorbent dose. **Figure 3(b)** illustrates the combined effect of solution pH and contact time on fluoride removal efficiency, showing higher removal at pH 2–3 with increasing contact time until a plateau is reached at approximately 120–150 min, while near-neutral pH results in consistently low removal irrespective of contact time. **Figure 3(c)** presents the interaction between solution pH and contact time, with adsorbent dose fixed at 1.25 g per 100 mL and initial fluoride concentration fixed at 17 ppm, indicating increased fluoride removal with extended contact time, decreased efficiency as pH approaches neutral values, and maximum removal of approximately 65% under acidic conditions at contact times of 150–180 min. **Figure 3(d)** depicts the combined effect of initial fluoride concentration (C) and adsorbent dose (B) on fluoride removal at constant solution pH of 4 and contact time of 105 min, showing reduced removal efficiency at higher fluoride concentrations, particularly at low adsorbent doses, and improved adsorption with increasing adsorbent dose, with adsorption tending to plateau at very high concentrations. **Figure 3(e)** illustrates the interaction between adsorbent dose (B) and contact time (D) at fixed solution pH of 4.5 and initial fluoride concentration of 17 ppm, showing steady improvement in fluoride removal with increasing adsorbent dose and contact time, followed by a plateau beyond approximately 150–180 min, indicating the attainment of equilibrium conditions.

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Future Scope:

The future scope of this project includes:

1. Enhancement of adsorption performance through advanced modifications such as metal or hybrid functionalization, along with evaluation under real groundwater conditions containing competing ions.
2. Investigation of adsorbent regeneration, reusability, and long-term stability to ensure sustainable and cost-effective operation.
3. Scale-up of the process through fixed-bed column studies and development of continuous treatment systems for practical applications.
4. Integration of the developed adsorbent into decentralized water treatment units and exploration of its applicability for the removal of other contaminants, such as heavy metals and dyes.