

Original Research

Sustainable and Environmentally Friendly Approaches for Eliminating Alizarin Red S from Contaminated Water Using Hydroxyfluorapatite-Based Biomaterials

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Abstract

This study investigated the use of new bioadsorbent the Hydroxyfluorapatite ($\text{Ca}_{10}(\text{PO}_4)_6\text{OH}_{1.75}\text{F}_{0.25}$, HFA) to eliminate Alizarin Red S (ARS), a harmful water pollutant. Initial batch tests were conducted to evaluate the adsorption process, focusing on both kinetics and equilibrium behavior. Various kinetic models were applied such as: pseudo first-order, pseudo second order, the intraparticle diffusion model and external diffusion model. The modeling results proved that the pseudo-second-order model best matched the experimental data. The data also suggested that both external and internal diffusion resistances significantly influenced the adsorption kinetics. Various isotherm models were



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also tested: Langmuir, Freundlich, Langmuir-Freundlich, Dubinin-Radushkevich, and Redlich-Peterson. The Langmuir-Freundlich model provided the closest fit to the experimental data. Thermodynamic evaluation showed that the adsorption of ARZ is favorable at low temperature; the process was non-spontaneous and exothermic. To optimize the removal process and develop a predictive model for ARS adsorption, the Box-Behnken response surface methodology (RSM) was employed. The results indicated that adsorption was most efficient at pH = 6, an adsorbent dose of 0.2, and an ARZ concentration of 195.83 at room temperature. The maximum adsorption capacity was determined to be 40.75 mg·g⁻¹. The adsorption capacity of HFA was also proved to be effective for real wastewater treatment. Five regeneration cycles had a slight effect on HFA's adsorbent performance. Overall, the findings demonstrate that HFA is a promising material for treating wastewater containing complex pollutant mixtures, offering an effective and reliable solution for dye removal.

Keywords

Adsorption; hydroxyfluorapatite; Alizarin Red S; optimization; modelization

1. Introduction

Currently, environmental concerns are heavily focused on water pollution, which is anticipated to escalate rapidly, posing a significant systemic threat to ecosystems and human health [1]. The primary sources of water contamination stem from human activities related to domestic, industrial, and agricultural sectors [2]. Among these, dyes discharged from industries such as paper manufacturing [3], cosmetics [4], textiles [5], and tanneries [6] are major contributors to water pollution [7]. Recent data estimate that around 80,000 tons of dyes are produced, used, and released into rivers each year, often without any prior treatment [8]. The direct release of these dyes into aquatic environments like lakes, rivers, and ponds threatens aquatic ecosystems due to their toxic and persistent nature [8]. Removing these pollutants remains a complex challenge [9]. Various treatment methods have been explored, including chemical precipitation [10], flocculation [11], ion exchange [12], electrolysis [13], membrane filtration [14], photocatalytic degradation [15, 16], and adsorption techniques [17-19]. Except for adsorption [20], many of these methods are economically inefficient and suffer from drawbacks such as high energy consumption, the use of costly reagents, and the generation of secondary hazardous wastes requiring further treatment [21]. A variety of adsorbents were employed for these objectives, including carbon-containing adsorbents. After waste adsorption, the adsorbed chemical content must be desorbed using a different procedure, or the carbon-based adsorbents must be disposed of in a landfill as hazardous waste. As a result, secondary waste volumes are satisfactorily reduced [22, 23]. Inorganic materials, particularly phosphate-containing rocks rich in apatite which constitutes 60-70% of bone by weight have shown promise due to their excellent biocompatibility and ability to interact with biological systems [24]. In particular, Hydroxyapatite and Fluorapatite are advantageous for water treatment because of their cationic sites, anionic character, and chemical stability [25, 26]. Because of its improved mechanical strength, chemical stability, and biocompatibility, hydroxyfluorapatite (HFA) has better physical and chemical properties than hydroxyapatite and is

therefore more appropriate for use in many environmental fields. Therefore, HFA exhibit enhanced biocompatibility, catalytic activity, and adsorption capacity, making them suitable for applications as biomaterials, catalysts, and adsorbents [27, 28]. To optimize these properties, extensive research has focused on synthesizing HFA with controlled particle size distribution and minimized agglomeration [29]. The incorporation of fluorine reduces crystal size and improves the structural stability of apatite [30]. Studies by Azami et al. [31] and Nikčević et al. [27] demonstrated that HFA $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_{1.5}\text{F}_{0.5}$ (HFA) possesses superior thermal and chemical stability compared to pure hydroxyapatite.

One of the most resilient dyes is the anthraquinone dye Alizarin Red S, which is used in numerous industries. General chemical, physical, and biological processes cannot fully destroy these colors. The intricate architectures of the aromatic rings, which provide excellent physicochemical, thermal, and optical stability, are responsible for this resistance to degradation. As a result, many treatments for these dye-laden effluents are generally insufficient.

An examination of the literature over the past 15 years, specifically regarding Alizarin Red S, has revealed that methods for degrading this dye have largely focused on adsorbents derived from readily available, inexpensive materials. Only a few studies were found to have dealt with the sequestration of Alizarin Red S using non-biomass-based adsorbents [32]. While HAP has been extensively studied as an adsorbent, HFA remains underexplored for dye removal. To the best of our knowledge, no prior studies have systematically investigated the adsorption behavior of ARS onto HFA, making this work novel. Within such a context, this study aims to evaluate the potential of HFA as a novel adsorbent for the removal of ARS from wastewater, investigate the adsorption kinetics, isotherms, and thermodynamics of the process, optimize the adsorption conditions using response surface methodology (RSM), and assess the reusability of HFA for sustainable water treatment applications.

2. Materials and Methods

2.1 Alizarine Red Solution

Alizarin Red S (sodium alizarin sulfonate) was employed as the target molecule in this study. The stock solution was prepared by dissolving a quantity of ARS in distilled water, and the desired concentrations were obtained by simple dilution of the stock solution. The pH was adjusted to a given value by adding HCl (1 N) or NaOH (1 N).

2.2 Hydroxyfluorapatite Preparation

Hydroxyfluorapatite powder (HFA) was synthesized via a wet chemical approach based on the Heughebaert protocol [28]. Initially, Solution A was prepared by dissolving 23.76 g of diammonium hydrogen phosphate, $(\text{NH}_4)_2\text{HPO}_4$ (purity >98%, Carlo Erba) and 0.55 g of ammonium fluoride, NH_4F (purity >98%, Sigma-Aldrich) in 750 mL of distilled water. This mixture was transferred to a 2-liter reactor and brought to a boil with continuous magnetic stirring. In parallel, Solution B was made by dissolving 70.8 g of calcium nitrate tetrahydrate $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (purity >98%, Honeywell) in 750 mL of distilled water. Solution B was then added dropwise to Solution A. The pH was carefully adjusted and maintained between 8 and 9 by periodically introducing concentrated ammonia. Stirring was maintained for an extra three hours to promote complete mixing of the

reagents and allow the reaction to proceed fully. The resulting suspension was filtered, thoroughly washed with hot distilled water, and the collected solid was dried overnight at 70°C. The obtained HAF was characterized using different analytical techniques: Infrared Fourier Transform spectroscopy (FT-IR) instrument (model FTLA2000-102, ABB), an X-ray diffraction (XRD) instrument, a PRO PANalyticalX'pert PRO apparatus (Malverna PANalytical) using a CuK α radiation between 2 θ degrees 20 and 60° with a step of 0.02°/s, and X-ray fluorescence spectroscopy (XRF) (Malverna PANalytical). The specific surface area of the HFAP powder was ascertained utilizing the Brunauer-Emmett-Teller (BET) method with a Belsorp mini X, employing nitrogen gas as the adsorbent.

2.3 Adsorption Study

For kinetic experiments, the prepared solution of ARS was fed into a stirred batch reactor with a volume of 1 L and a controlled temperature. To achieve a uniform dispersion of the adsorbent, the agitation speed has been set constant. A precise amount of HFA was added to the solution as agitation was started. The experiment was made over time to reach equilibrium. Before analysis, samples were filtered using a paper filter and AZR residual concentration was analyzed using a UV-visible spectrophotometer (UV-1900, Shimadzu) at 520 nm.

The treatment of Alizarin Red was also studied under simulated real wastewater conditions. Synthetic wastewater was prepared by combining Alizarin Red with Methylene Blue (cationic) and Congo Red (anionic) at the same concentration to realistically mimic the composition and complexity of industrial effluents, ensuring reproducibility of the experimental conditions. The amount absorbed was calculated using the following equation:

$$q_t = \frac{C_0 - C_f}{m} \times V \quad (\text{Eq. 1})$$

q_t : Total adsorbed quantity (mg·g⁻¹) at time t ; C_0 : Initial dye concentration (mg·L⁻¹); C_f : ARS concentration (mg·L⁻¹) at equilibrium; m : adsorbent mass (g); V : Adsorbate volume (L).

2.3.1 Effect of the Adsorbent Dose

To better understand the interactions between the pollutant and the adsorption sites present in the adsorbent, a systematic investigation is needed. Various adsorbent doses (0.1 g, 0.2 g, 0.3 g, 0.4 g, and 0.5 g) were tested. The adsorbent was put in contact with 50 mL of an ARS solution at a 50 ppm concentration. The agitation is maintained at a constant speed for 60 minutes (the HFA equilibrium time) at room temperature and natural pH.

2.3.2 Effect of the Initial Concentration

To study the effect of initial dye concentration, the pollutant concentration was varied (25-200 mg·L⁻¹). The agitation speed was set to a constant. Then, a certain amount of HFA was introduced into the reactor. Over time, measurements of two milliliters have been made until equilibrium. Samples were filtered and diluted before analysis.

2.3.3 Effect of pH

Batch adsorption experiments have been conducted with the determined stability domain to assess the impact of pH on ARS adsorption. The adsorption process was carried out in well-closed flasks of 100 mL, 50 mL of the solution with a 50 ppm concentration at room temperature (25°C), and 0.3 g of the adsorbent mass.

2.4 Isotherm Study

Adsorption systems rely heavily on adsorption isotherms, which are essential for describing the interactive behavior between the adsorbent (HFA) and the adsorbate (ARS). They are frequently used to assess an adsorbent's capacity. The following experimental methodology was used to study adsorption isotherms: in 100 mL glass flasks containing 50 mL of solution with initial ARS concentrations ranging from 5 to 300 mg·L⁻¹, 0.35 g of HFA was added. These flasks were then placed on a rotating agitator that maintained a steady temperature until equilibrium was reached. The concentration of the pollutant remaining in solution at equilibrium was analyzed to determine the adsorption capacity and to facilitate subsequent modeling of the adsorption mechanism. After this equilibrium is reached, 10 mL of the solution was filtered and then centrifuged for 10 minutes to remove any fine particles that may have come to the surface due to attrition during agitation. The amount that was adsorbed was calculated using a material balance by comparing the residual concentration of the sample to the beginning concentration, which was determined by UV-visible spectrophotometer analysis.

A thermodynamic study was performed in a thermostatic reactor at 25°C, 40°C, and 60°C. An ARS solution containing 100 mL and an initial concentration fixed at 200 mg·L⁻¹ was mixed with 0.7 g of adsorbent. The adsorption process takes place at the solution's natural pH.

2.5 Experience Design Optimization

Current work is focused on a three-level Box-Behnken (BBD) design using the Response Surface Methodology (RSM) to optimize the adsorbed amount of ARS on HAF. The statistical analysis software [Design Expert software version 2013] was used to determine the importance of each factor, interaction, and quadratic term in the optimization process.

2.5.1 Process Factors and Levels

The different factors with different levels are presented in Table 1.

Table 1 Process factors with different levels.

Factors	Code	Level (-1)	Level (0)	Level (+1)
ARS Concentration (mg/L)	X ₁	50	125	200
pH	X ₂	6	8	10
Adsorbent dose (g)	X ₃	0.2	0.35	0.5

2.5.2 Experimental Design

To optimize the amount of ARS ions adsorbed, a study was conducted according to the following experimental protocol:

Glass flasks with an initially fixed concentration of ARS (50, 125, and 200 mg·L⁻¹) and pH (6, 8, and 10) were placed in contact with adsorbent masses (0.2, 0.35, and 0.5 g). These bottles were then placed on a rotating agitator, where the temperature is kept constant until equilibrium. Then, a well-determined volume of solution was filtered and analyzed by the UV-visible spectrophotometer.

2.5.3 Real Water Contained ARS Treatment

The wastewater containing ARS was treated with HFAP to evaluate the adsorption of ARS in real wastewater conditions. This mixture, containing ARS and other components, including various ions (both cations and anions), was brought into contact with the adsorbent to assess its potential for removing the dye. The synthetic mixture can interact with the ARS dye and modify its behavior with respect to the adsorbent material, thereby affecting sorption performance. Competitive adsorption kinetics was achieved by charging the reactor with the pollutant solution at a fixed speed at ambient temperature. A well-determined amount of HFA (1 g) is introduced into the reactor, which corresponds to the zero time of the experiments. Samples (2 mL) were taken over time. Before any analysis, these samples are filtered through a 0.45 µm syringe filter. The analyses were measured using the total organic carbon (TOC) apparatus (Duo, Pharma) (multi N/C 2100 S).

3. Results and Discussion

3.1 XRD, FTIR, and XRF Characterization of Hydroxyfluorapatite

Figure 1 displays a diffraction pattern of the synthesized HFA according to the experimental procedure described above. The XRD pattern shows diffraction lines characteristic of the combination of hydroxyapatite and fluorapatite, as reported in standards and in the literature. All the major peaks (for $2\theta = 25.95, 32.04, 33.02, 34.07, 39.98, 47.06, 49.67, \text{ and } 53.26$) match exactly with the reference, and consequently, this material is confirmed to be HFA minerals formed by a single apatite phase [33]. The infrared spectrum depicted in Figure 2 presents typical HFA absorption bands. Namely, the bands attributed to PO_4^{3-} . The characteristic absorption bands are detected in the ranges of $1087\text{--}1022\text{ cm}^{-1}$, 951 cm^{-1} , $594\text{--}560\text{ cm}^{-1}$, and at 454 cm^{-1} . Additionally, a band near 3531 cm^{-1} is assigned to the stretching vibration of hydroxide ions (OH^-). The chemical analysis findings of the HFA are compiled in Table 2. The Ca/P ratio is equivalent to 1.67 for stoichiometric apatites. By comparing the synthesized powers, one can establish the stoichiometry of the HFA. Furthermore, the analyzed quantities of calcium, phosphate, and fluoride exhibit ratios comparable to those in the initial reagents. Therefore, the chemical formula produced after synthesizing the powders is nearly identical to the hypothetical formulas estimated before dissolving the reactants. The measured specific surface area of the HFA powder was $36\text{ m}^2\cdot\text{g}^{-1}$, and the porosity was nearly 23%.

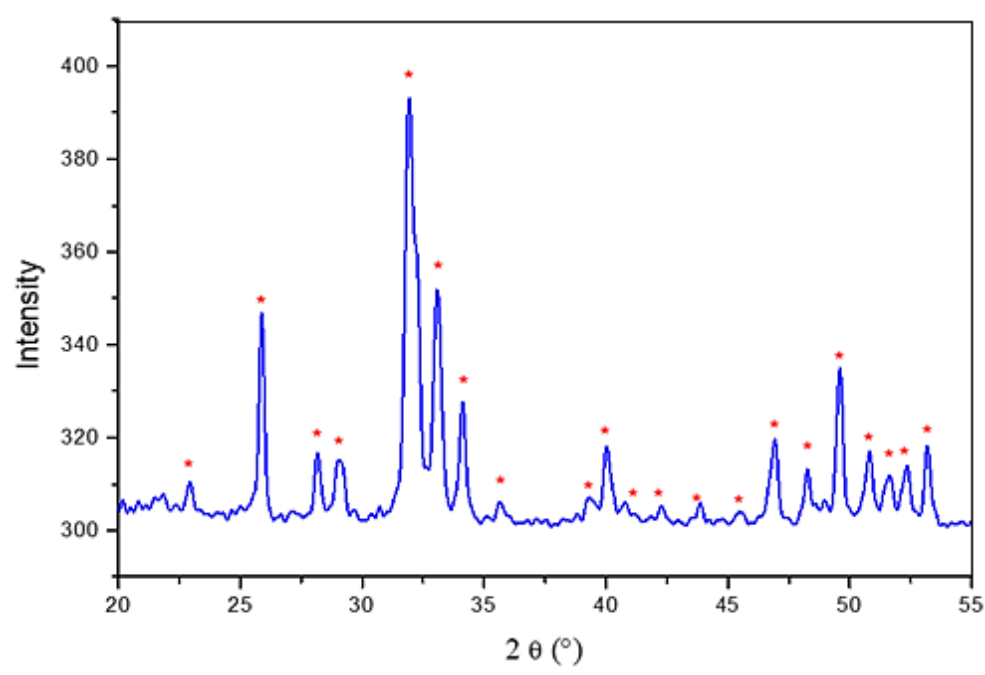


Figure 1 XRD diffractogram of synthesized HFA.

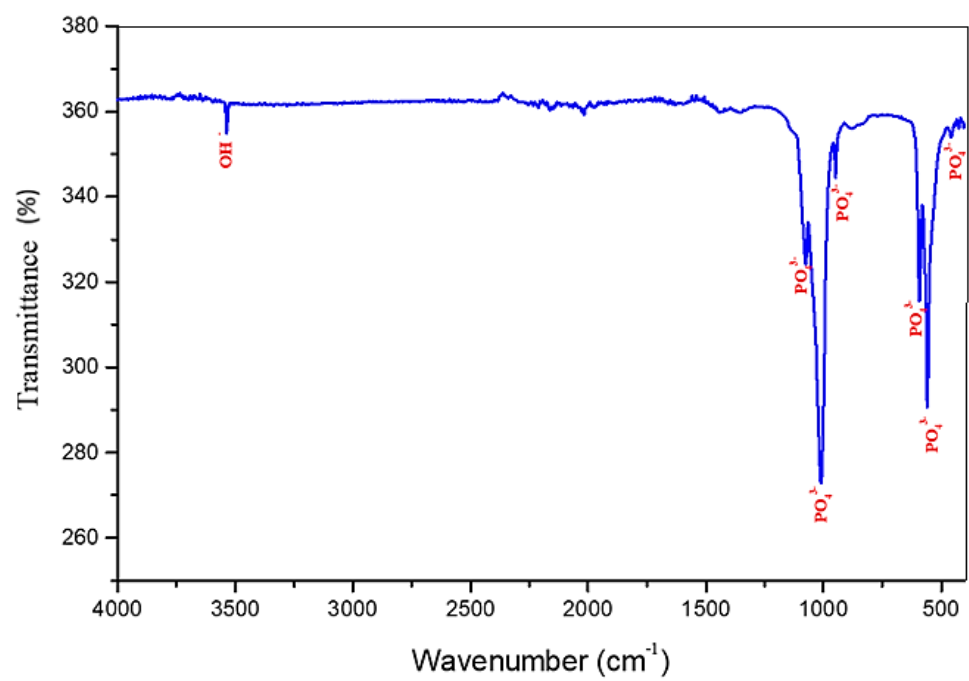


Figure 2 FTIR spectra of synthesized HFA.

Table 2 XRF analysis converted n number of atoms per unit cell in mmol·g⁻¹ of HFA.

Element X	Ca	P	F	Ca/P
Number of atoms	9.94	5.96	0.48	1.66

3.2 Adsorption Study

3.2.1 Effect of pH

As shown in Figure 3, the decrease in the adsorbed amount of Alizarin Red as the pH increases from 6 to 12, from 6.45 to 4.035 $\text{mg}\cdot\text{g}^{-1}$, can be explained by the combined effects of pH on both the surface charge of hydroxyfluorohydroxyapatite and the speciation of the dye. At moderately acidic to neutral pH, the apatite surface is partially protonated, leading to the presence of positively charged surface sites, particularly exposed Ca^{2+} ions, which promote the adsorption of weakly ionized or mono-anionic forms of Alizarin Red through electrostatic attraction and surface complexation mechanisms. In contrast, under alkaline conditions, the progressive deprotonation of surface hydroxyl groups results in a negatively charged surface, leading to electrostatic repulsion with the highly anionic species of Alizarin Red formed due to the deprotonation of its phenolic groups. In addition, the increased concentration of OH^- ions at high pH leads to competition for active adsorption sites, especially calcium sites, and weakens hydrogen-bonding interactions. Moreover, the strong ionization of Alizarin Red in alkaline media enhances its solubility in water, thereby reducing its affinity for the adsorbent surface. Similar trends have been reported for the adsorption of anthraquinone dyes onto apatite-based materials, confirming that electrostatic interactions and dye speciation play a key role in the adsorption mechanism [34, 35].

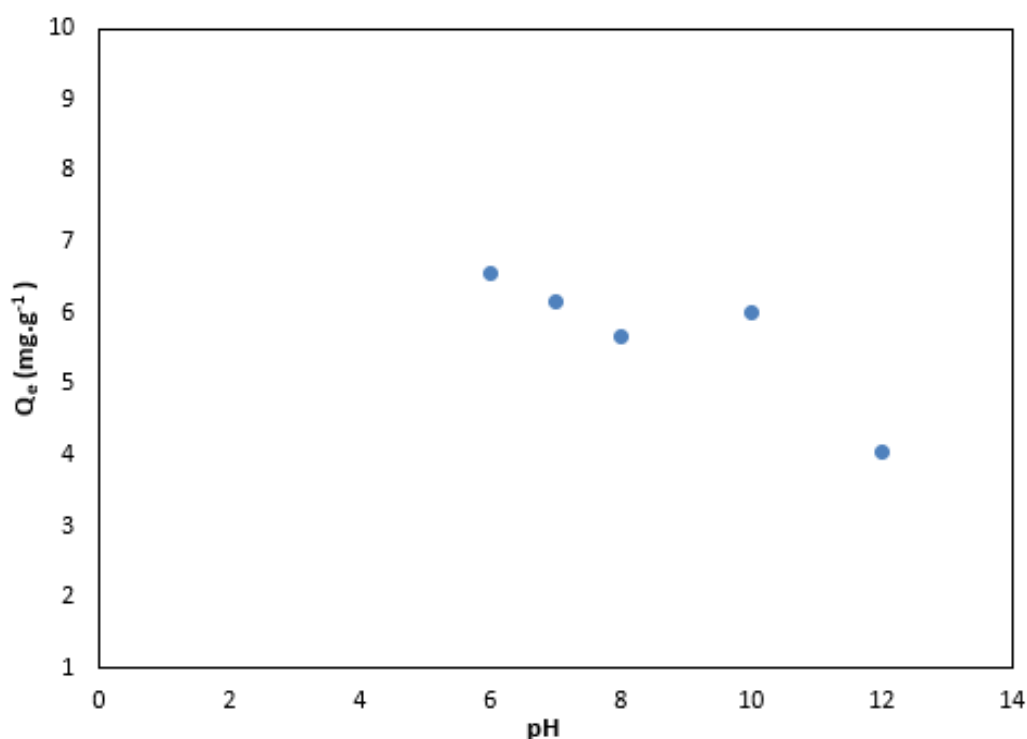


Figure 3 pH effect ($C_i = 50$ ppm; $T = 25^\circ\text{C}$; $m = 0.35$ g).

3.2.2 Effect of Adsorbent Dose

The determination of the adsorbent dose effect is a key parameter. The effect of the adsorbent mass on the HFA adsorption capacity of the ARS dye is shown in Figure 4. Increasing the adsorbent dose from 0.1 to 0.5 $\text{mg}\cdot\text{L}^{-1}$ decreases the adsorption capacity from 10.53 to 4.47 $\text{mg}\cdot\text{g}^{-1}$. It can be

concluded that increasing the dosage of adsorbents increases the number of unsaturated sites. Furthermore, the adsorption capacity formula explains this decrease. A mass of 0.1 g indeed absorbs a significant amount of adsorbent, but the level (balance) is achieved at a mass equal to 0.35 g. This mass will be able to fix the maximum of ARS ions. The adsorption capacity of the material strictly follows the obtained SSA and porosity values.

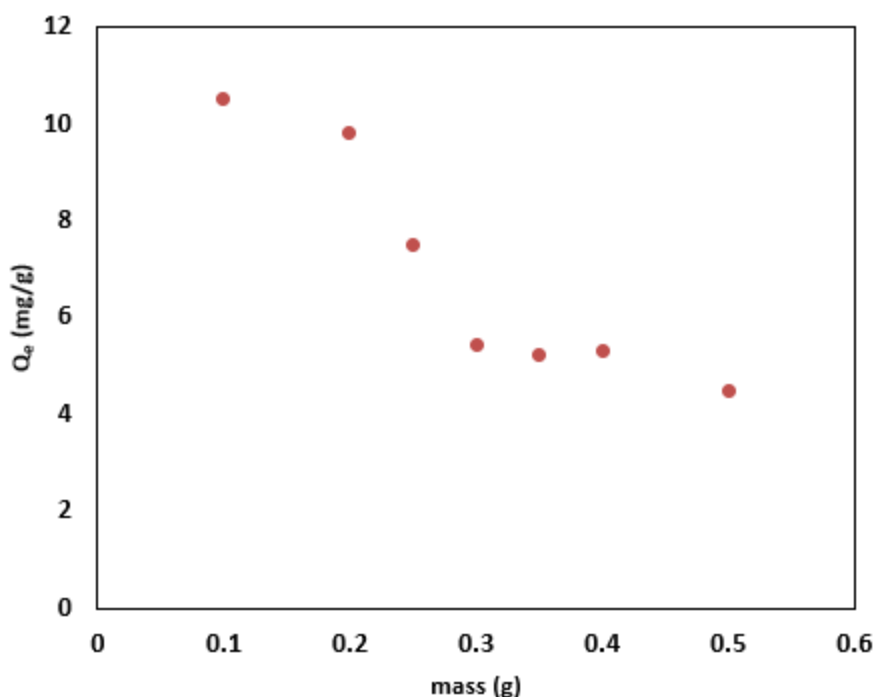


Figure 4 Adsorbents' dose effect ($C_i = 50$ ppm; 300 rpm; $T = 25^\circ\text{C}$; $\text{pH} = 6$).

3.2.3 Determination of Equilibrium Time

Determining the contact time required to reach adsorption equilibrium is a fundamental step in kinetic studies. The effect of contact time on ARS (Acid Red 97) adsorption onto HFA was investigated. As shown in Figure 5, the adsorption capacity for ARS ions increases with contact time until a saturation plateau is reached, indicating equilibrium. This trend is driven by the diffusion of ions to the available adsorption sites. The process exhibits rapid initial kinetics, with the majority of adsorption occurring within the first 30 minutes, yielding a capacity of $6.15 \text{ mg}\cdot\text{g}^{-1}$. This suggests a high initial availability of active surface sites. The capacity increased only slightly to $6.44 \text{ mg}\cdot\text{g}^{-1}$ when the contact time was extended to 60 minutes, confirming that equilibrium is effectively attained at this point. Therefore, a contact time of 60 minutes was selected for all subsequent experiments.

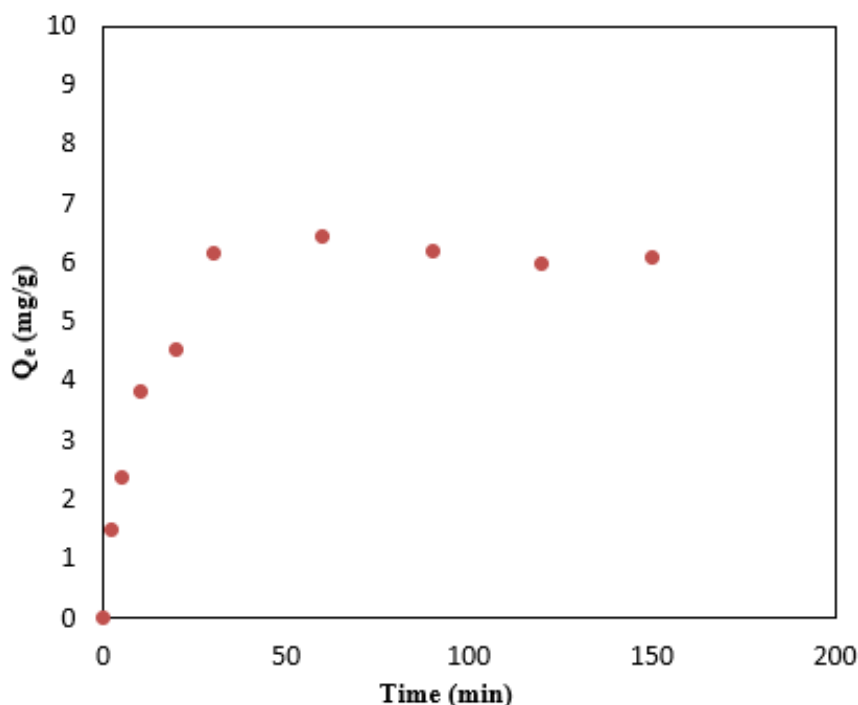


Figure 5 Effect of balance time ($C_i = 50$ ppm; 300 rpm; $m = 0.35$; $T = 25^\circ\text{C}$; $\text{pH} = 6$).

3.2.4 Effect of the Initial Dye Concentration

The impact of increasing the initial dye concentration on adsorption behavior was examined. The results are presented in Figure 6, where the adsorption process exhibits a rapid initial phase. This rapid uptake is attributed to a high concentration gradient between the solution and the adsorbent surface, as well as a high initial availability of unoccupied active sites, which together provide a strong driving force to overcome mass transfer resistance [36]. In the subsequent phase, the adsorption rate decreases as the available sites are occupied, gradually approaching equilibrium. The equilibrium adsorption capacity increased from $3.12 \text{ mg}\cdot\text{g}^{-1}$ at an initial concentration of $25 \text{ mg}\cdot\text{L}^{-1}$ to $32.78 \text{ mg}\cdot\text{g}^{-1}$ at $200 \text{ mg}\cdot\text{L}^{-1}$. This significant rise is due to the increased number of dye ions in solution, which enhances the probability of collision and interaction with the adsorbent's active sites. In addition, as the initial concentration of Alizarin Red increases, the driving force for mass transfer from the solution to the adsorbent surface increases, resulting in higher adsorption capacities. However, this increase continues only until the active sites of the adsorbent become saturated.

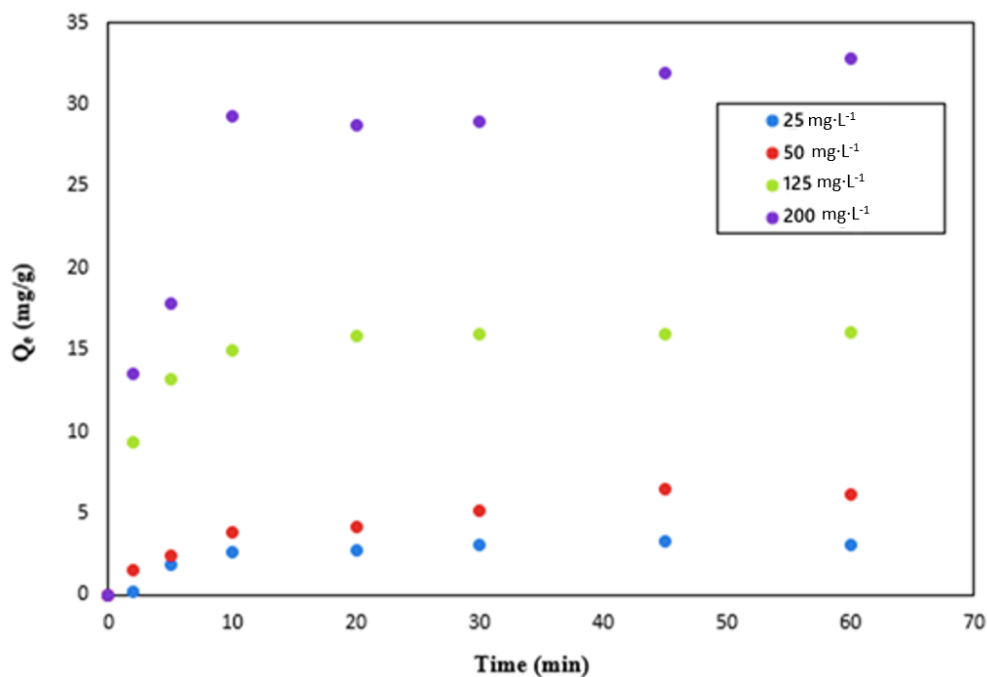


Figure 6 Initial concentration effect for ARS adsorption on HFA ($t = 60$ min; 300 rpm; $m = 0.35$; $\text{pH} = 6$; $T = 25^\circ\text{C}$).

3.3 Isotherm and Thermodynamic Study

An adsorption isotherm was established by varying the initial dye concentration in the range 5-150 $\text{mg}\cdot\text{L}^{-1}$ in aqueous solution, with the temperature constant at 25°C . Figure 7 shows the results of the established isotherm and the dynamic balance and affinity between adsorbent and adsorbate. The adsorption isotherms exhibit a sharp initial rise at low solution concentrations, followed by a plateau at higher concentrations, indicating surface saturation.

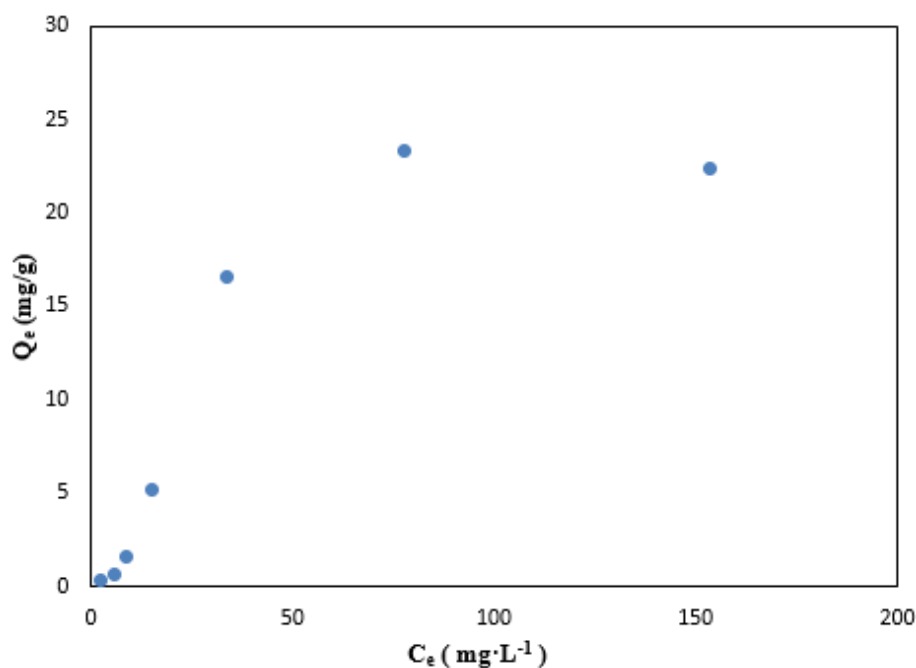


Figure 7 Adsorption isotherms ($T = 25^\circ\text{C}$; $m = 0.35$; $\text{pH} = 6$).

The examination of the thermodynamic process behavior is necessary to determine the temperature dependence and spontaneity of the adsorption. In this context, the effect of temperature on ARS adsorption on HFA was examined. The standard enthalpy change (ΔH°) and standard entropy change (ΔS°) were determined from the slope and intercept, respectively, of the linear plot of $\ln(K_d)$ versus $1/T$ (Van't Hoff plot), presented in Figure 8.

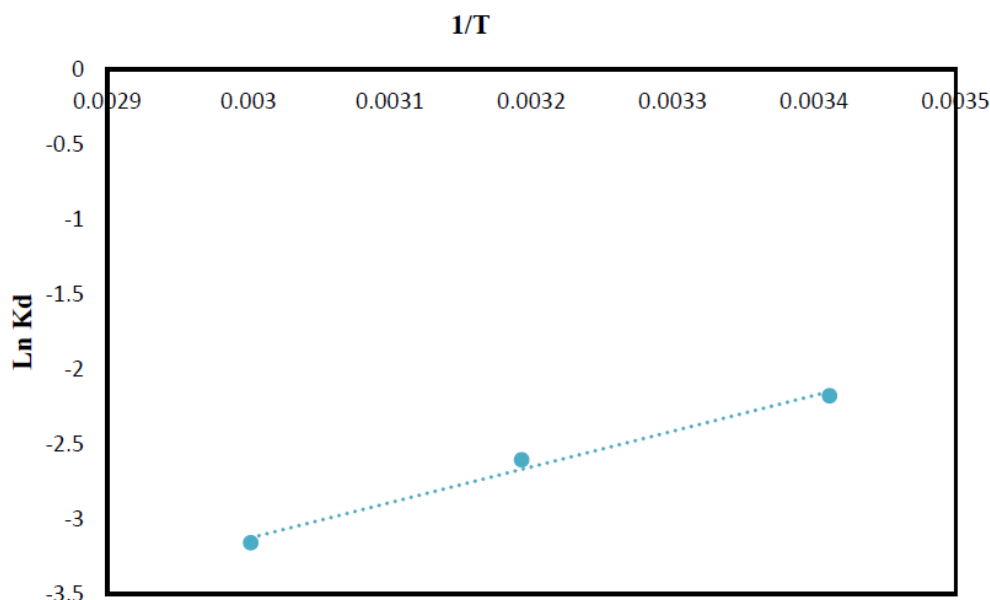


Figure 8 Van't Hoff plot for ARS adsorption onto HFA.

The thermodynamic adsorption parameters collected in Table 3 were determined from experiments conducted at different temperatures. The negative values of ΔH° and ΔS° confirm that the adsorption process is exothermic and results in a more ordered arrangement of dye molecules at the adsorbent surface. Furthermore, the positive value of ΔG° indicates that the adsorption is non-spontaneous under the studied conditions.

Table 3 Thermodynamic parameters of ARS adsorption by HFA.

	ΔH° (kJ·mol ⁻¹)	ΔG° (kJ·mol ⁻¹)	ΔS° (kJ·K ⁻¹ ·mol ⁻¹)
	-19.80	5.31	-0.085
HFA		6.78	
		8.75	

3.4 Treatment of Real Water Containing ARS

This section evaluates the treatment of a real effluent containing ARS, demonstrating the adsorbent's potential retention and the time-based pollutant removal rate under conditions relevant to wastewater treatment, with a retention rate calculated according to the following equation:

$$R\% = \frac{TOC^0 - TOC}{TOC^0} \quad (\text{Eq. 2})$$

Figure 9 demonstrates the significant retention potential of the HFA adsorbent, which effectively fixed 78% of contaminants, confirming its efficacy for this application.

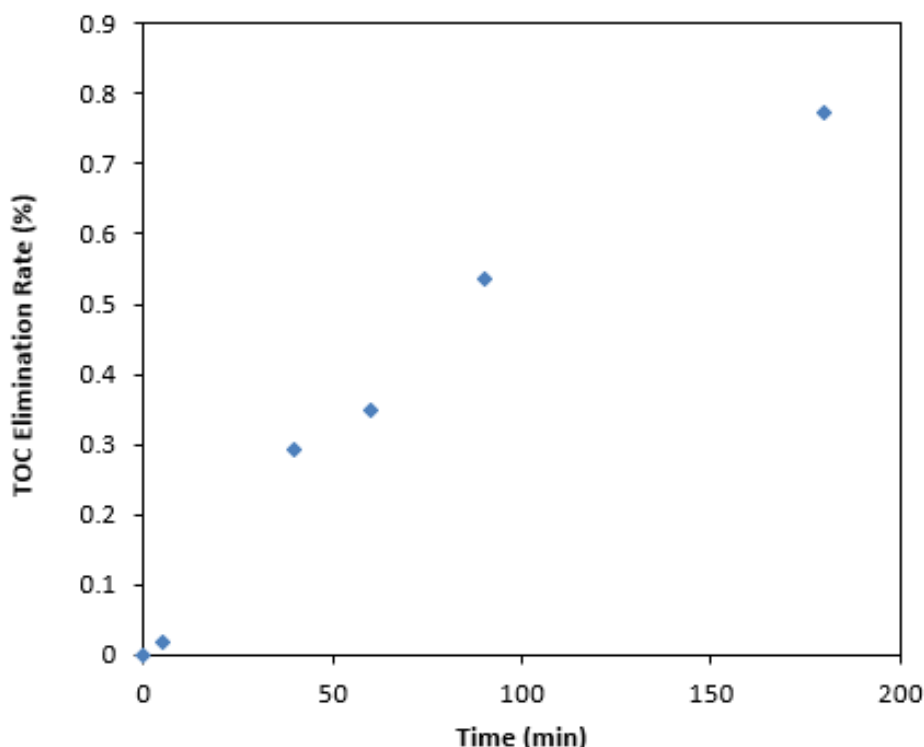


Figure 9 Treatment of a real mixture by HFA.

3.5 Optimization of Treatment Conditions by Experimental Design

3.5.1 Statistical Analysis of the Experimental Results

A Box-Behnken design (BBD) was employed to statistically determine optimal operating conditions and to evaluate the influence of three independent variables: pH, adsorbent mass (m), and initial dye concentration (ARS) on the adsorption capacity of HFA for ARS dye. Fifteen experimental runs were conducted to study the effects of these factors. The results of the experimental design matrix are presented in Table 4 and Table 5. Based on the collected data, a quadratic model was selected as the final predictive model. Statistical analysis confirmed the model's significance, with a high model F-value of 39.51, indicating it is statistically adequate. Model terms with p-values less than 0.05 are considered significant; in this case, the linear terms (A, B, C), the interaction terms (AB, AC), and the quadratic terms (A^2 , C^2) were identified as significant. Conversely, terms with p-values greater than 0.10 were considered non-significant.

Table 4 Plan Matrix of Box–Behnken for retention of ARS by HFA.

		A	B	C	Experimental response	Predicted Response
Std	Run	[ARS] mg·L ⁻¹	pH	m g	Q _{exp} mg·g ⁻¹	Q _{predic} mg·g ⁻¹
2	1	200	6	0.35	31.6	30.8
1	2	50	6	0.35	5.98	4.21
7	3	50	8	0.5	2.5	3.31
10	4	125	10	0.2	19.5455	18.58
4	5	200	10	0.35	8.95	10.72
14	6	125	8	0.35	15.32	14.65
15	7	125	8	0.35	14.35	14.65
9	8	125	6	0.2	27.8	29.41
8	9	200	8	0.5	14.905	14.75
5	10	50	8	0.2	8.15	8.31
12	11	125	10	0.5	10.67	9.06
13	12	125	8	0.35	14.28	14.65
3	13	50	10	0.35	3.2	4.00
6	14	200	8	0.2	31	30.19
11	15	125	6	0.5	17.5455	18.50

Table 5 Analysis of variance results (ANOVA) for response surface.

Source	Sum Square	Df	Average Square	Value of F	Value of p	
Model	1186.00	9	131.78	39.51	0.0004	Significant
A-C	554.86	1	554.86	166.34	<0.0001	
B-pH	205.64	1	205.64	61.65	0.0005	
C-m	208.85	1	208.85	62.61	0.0005	
AB	98.70	1	98.70	29.59	0.0028	
AC	27.27	1	27.27	8.18	0.0354	
BC	0.4755	1	0.4755	0.1425	0.7213	
A ²	44.83	1	44.83	13.44	0.0145	
B ²	5.93	1	5.93	1.78	0.2400	
C ²	32.64	1	32.64	9.79	0.0260	
Residual	16.68	5	3.34			
Lack of Fit	16.00	3	5.33	15.79	0.0602	Not significant
Pure Error	0.6758	2	0.3379			
Cor Total	1202.67	14				

$$R^2 = 0.9861; R^2 \text{ Adjusted} = 0.9612; R^2 \text{ predicted} = 0.7858.$$

The projected R^2 coefficient of 0.7858 is in reasonable harmony with the adjusted R^2 , which is 0.9612, i.e., the difference is less than 0.2. A ratio greater than 4 is desirable. Our report of 18,431 indicates that the signal is adequate. Hence, this model can be used to navigate the design space. The response ($Y = Q_e$ adsorbed from the dye) was obtained using a square equation:

$$Y = 14.65 + 8.32X_1 - 5.07X_2 - 5.10X_3 - 4.96X_1X_2 - 2.61X_1X_3 + 0.34X_2X_3 - 3.48(X_1)^2 + 1.26(X_2)^2 + 2.97(X_3)^2 \quad (\text{Eq. 3})$$

Based on the ANOVA and according to the results mentioned in Table 5, the second-order polynomial model is identified with the statistical significance adjustment as follows:

$$Y = 14.65 + 8.32X_1 - 5.07X_2 - 5.10X_3 - 4.96X_1X_2 - 2.61X_1X_3 - 3.48X_1^2 + 2.97X_3^2 \quad (\text{Eq. 4})$$

The analysis of model coefficients elucidates the significant individual and interactive effects of the parameters studied on adsorption performance. The positive coefficient for initial concentration ($a_1 = +8.32$) confirms a direct proportionality, where an increase in concentration promotes a higher adsorbed quantity, aligning with prior findings on mass transfer driving forces. Conversely, both solution pH ($a_2 = -5.07$) and adsorbent dose ($a_3 = -5.10$) exhibit significant negative coefficients, indicating an inverse relationship with the adsorption capacity. This suggests that lower pH and a smaller adsorbent dose are favorable within the studied range, the latter likely due to site saturation or aggregation effects at higher masses. Furthermore, significant negative interaction effects are observed between concentration and pH ($a_{12} = -4.96$) and between concentration and adsorbent dose ($a_{13} = -2.61$). These antagonistic interactions imply that the positive effect of increasing concentration is substantially diminished at higher pH levels or with larger adsorbent doses, highlighting the complex, interdependent nature of the process optimization. A crucial diagnostic tool for assessing the predictive efficacy of the constructed model is residual analysis, which examines the difference between the model-predicted and experimentally obtained responses [37]. The normality of the residuals for ARS dye removal was examined in this work to evaluate the suitability of the updated Box-Behnken Design (BBD) model. Figure 10, which shows the normal probability plot of the residuals, visually illustrates this diagnostic assessment. The model's statistical dependability is validated by the data points' tight alignment with the theoretical straight line, which demonstrates a normal distribution.

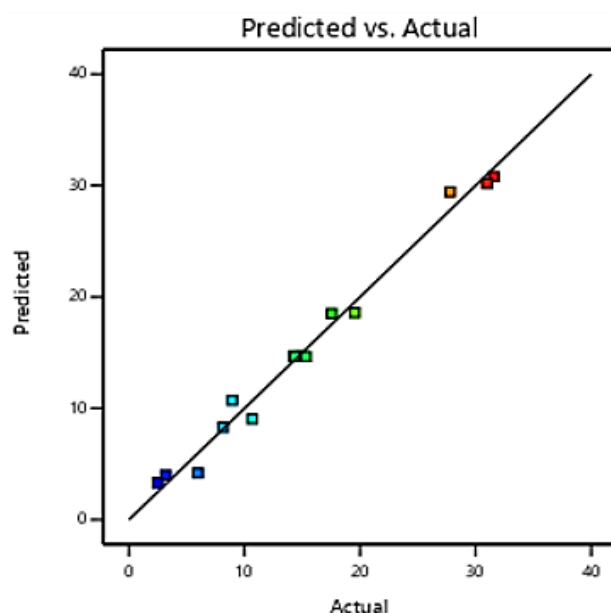


Figure 10 Values predicted by the model VS experimental values of the HFA.

From Figure 11, it can be concluded that the residual distribution is perfect, with the points appearing significantly close to a straight line. This result indicates that residues are correctly presumed and separated. In addition, the actual and expected values were similar, as confirmed by statistical analysis, supporting the BBD model.

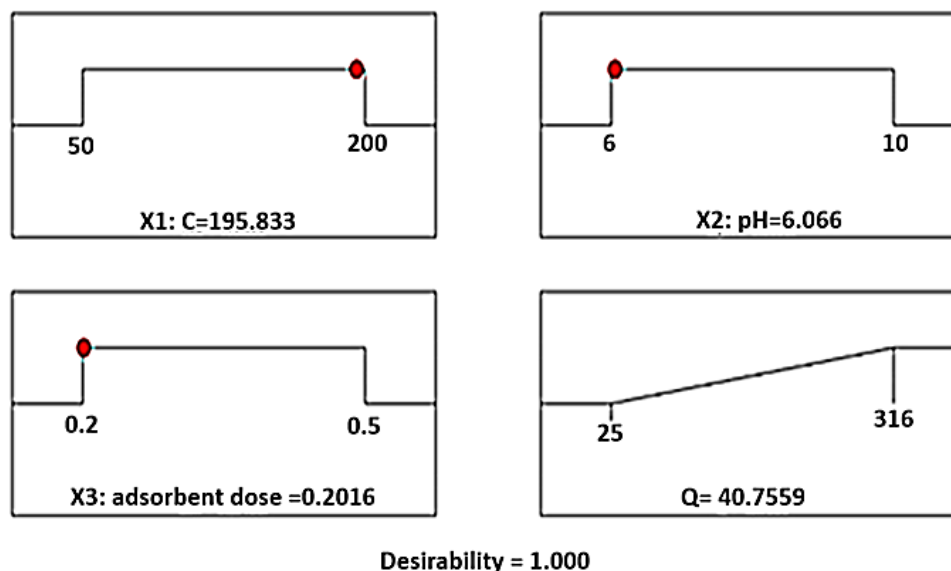


Figure 11 Desirability and optimal condition of HFA by ARS adsorption.

3.5.2 Desirability Study

The desirability function approach was used to determine the ideal input variable values to achieve the best performance levels for one or more responses. Every answer during optimization, (Y_i) is transformed into the unique desirability function (d_i). The ideal reaction is represented by a value of 1, and this function ranges from 0 to 1.

The intermediate values indicated results that were, in general, acceptable. To study numerical optimization and the response that reaches its optimum, a minimum and a maximum level for each input variable must be given. The independent variables under their optimal response surface methodology with the desirability function are shown in Figure 11.

It can be noted that all these optimal values are accurate within the given range of operational parameters and are attributed to a desirability value of 1. The optimum conditions generated are as follows: Initial concentration of ARS = 195.83 $\text{mg}\cdot\text{L}^{-1}$; Adsorbent dose = 0.20 g; Medium pH = 6.06. These conditions were maintained as constant throughout the study, except when a specific parameter was deliberately varied to isolate its effect.

3.5.3 3D Response Surface Plots

Based on the constructed regression model, three-dimensional response surface plots, two-dimensional contour plots, and interaction effect diagrams were created to clarify the interactive impacts of the process factors on adsorption capacity. The 3D response surface (Figure 12) for the adsorbed ARS quantity, with the three factors studied (pH, initial ARS concentration, and adsorbent dosage), was used to better explain the relationship among these factors and to assess the optimal conditions for each variable to achieve maximum adsorption. From Figure 12(a), the

adsorption capability was greatly impacted by the interplay between pH and Alizarin Red S (ARS) concentration. Adsorption capacity showed a direct correlation with ARS concentration, rising as the dye concentration in solution increased, as seen in the related response surface plots. On the other hand, adsorption capacity declined significantly as the solution pH increased, indicating an inverse relationship with pH. This opposing pattern points to a competitive interaction in which pH controls the dye's ionization state and the adsorbent's surface charge, hence regulating the adsorption efficiency even at increasing contaminant loads. Figure 12(b) shows that pH and adsorbent dosage have a simultaneous detrimental effect on adsorption capacity. Adsorption efficiency decreased as the adsorbent mass increased. At the same time, capacity decreased as pH increased. The combination of low pH and low adsorbent dosage was thus shown to be the most advantageous for adsorption. This pattern implies that medium pH creates ideal electrostatic circumstances for absorption, whereas the adsorbent's active sites are used more effectively at lower doses. The data in Figure 12(c) clearly show that the interaction between the adsorbent dosage and the ARS concentration was significant. Higher concentrations and smaller adsorbent doses produced greater adsorption capability. The greater quantity of ARS at the adsorption site causes the adsorbent particle to become overloaded, which explains this observation.

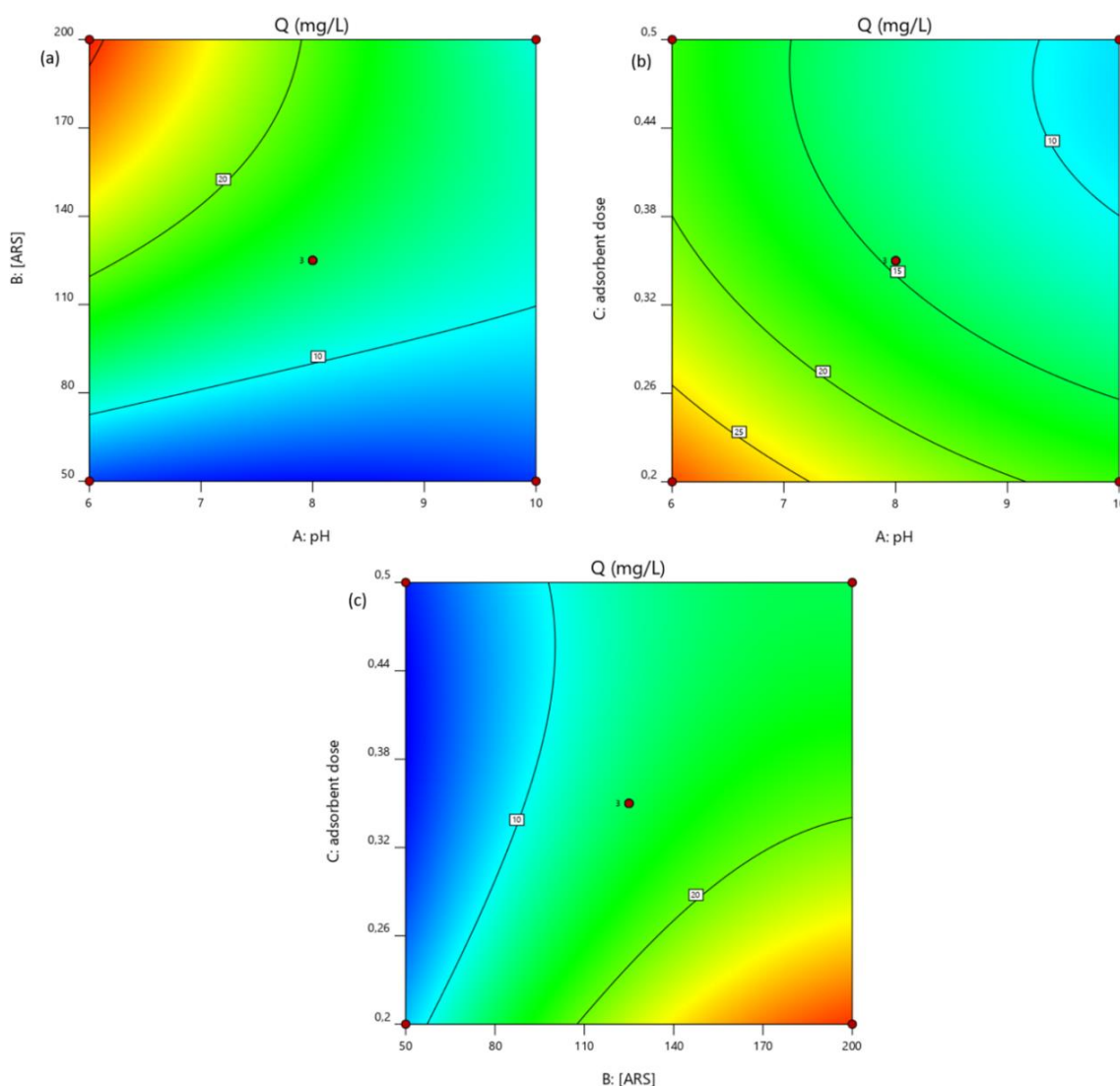


Figure 12 Interaction between the adsorption parameters for HFA.

3.6 Modeling of Experimental Conditions

3.6.1 Pseudo-First and Pseudo-Second Order Models

Adsorption kinetics is one of the most important characteristics that govern the rate of absorption of the solute; it represents the adsorbent's absorptive efficiency and, therefore, determines its potential applications. The kinetic parameters obtained for the adsorption process were analyzed by mathematical models. The modeling of adsorption kinetics by pseudo-first-order and pseudo-second-order models is illustrated in Table 6 for the different operating conditions studied.

Table 6 Parameters for modeling the kinetics of ARS adsorption by Hydroxyfluorapatite.

ARS concentration	Pseudo-first Order Model				Pseudo-second order Model			
	Q_{exp} ($mg \cdot g^{-1}$)	K_2 ($g \cdot mg \cdot min^{-1}$)	Q_{cal} ($mg \cdot g^{-1}$)	R^2	Q_{exp} ($mg \cdot g^{-1}$)	K_2 ($g \cdot mg \cdot min^{-1}$)	Q_{cal} ($mg \cdot g^{-1}$)	R^2
C = 50 $mg \cdot L^{-1}$	6.440	0.048	4.76	0.857	6.440	0.182	5.48	0.952
C = 125 $mg \cdot L^{-1}$	19.196	0.157	15.61	0.943	19.196	0.048	20.6	0.910
C = 200 $mg \cdot L^{-1}$	32.786	0.068	31.54	0.670	32.786	0.033	33.3	0.882

According to Table 6, the pseudo-second order regression coefficient for the adsorption of ARS on the HFA is close to the unit, indicating better compliance with experimental results compared to the pseudo-first order model. On the other hand, the value of the experimental adsorption capacity (Q_{exp}) is more consistent with the calculated adsorption capacity (Q_{cal}) from the pseudo-second order kinetic model.

In addition, a systematic decrease in k_2 was observed with increasing initial adsorbate concentration. This is consistent with experimental data. This decrease is because higher concentrations require longer treatment times to reach equilibrium [38]. Therefore, the chemical adsorption process can be involved during the adsorption mechanism [39].

3.6.2 Intra-Particle Diffusion Model

The intraparticle diffusion model was linearized by plotting the adsorbed quantity, q_t , as a function of the square root of time, $t^{0.5}$, under various operating conditions (Figure 13). According to this model, if intraparticle diffusion were the sole rate-limiting step, the plot would yield a straight line passing through the origin. This is not observed in the present system; instead, the plot exhibits multi-linear segments, indicating that the adsorption process occurs in two successive stages. The first linear segment represents the initial stage of instantaneous or external surface adsorption, governed by rapid diffusion through macropores. The second segment corresponds to a slower, progressive adsorption stage controlled by diffusion into mesopores [40]. Finally, the plateau region signifies the attainment of equilibrium, where intraparticle diffusion slows significantly due to solute depletion in the bulk solution [40]. These results demonstrate that, while intraparticle diffusion is a major mechanism, external film diffusion also contributes to the overall adsorption kinetics.

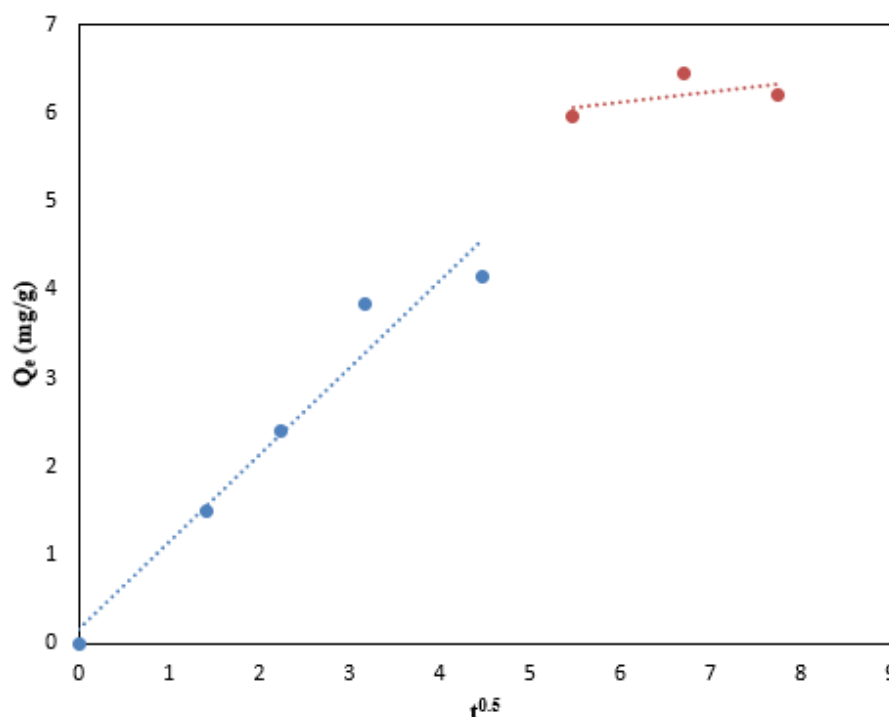


Figure 13 The intraparticle diffusion model for adsorption of ARS by HFA ($C_i = 50$ ppm; $m = 0.35$ g; $T = 25^\circ\text{C}$; $\text{pH} = 6$).

3.6.3 Diffusion Model in Liquid Film

Film diffusion is one of the transfer stages during the adsorption process. To assess the existence of this resistance, the external film model is used. From Figure 14, the linear trajectory of $-\ln(1 - F)$ versus time (t), which passes through the origin, confirms that the diffusion pattern within the liquid film aligns with the experimental adsorption data for ARS on both adsorbents. This alignment demonstrates that mass transfer across the boundary layer is a determining factor in ARS retention, thereby corroborating earlier findings.

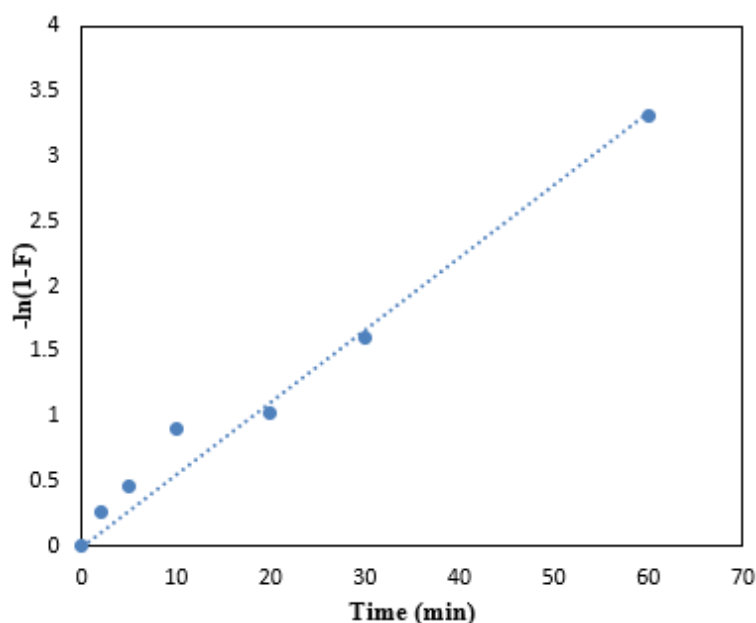


Figure 14 Linearization of the diffusion pattern in the external HFA film ($C_i = 50$ ppm; $m = 0.35$ g; $T = 25^\circ\text{C}$; $\text{pH} = 6$).

Additional insights from the intraparticle diffusion model and the film diffusion mode indicate that the adsorption mechanism involves a combination of surface interactions, such as electrostatic attraction and hydrogen bonding, along with potential weak chemical interactions. Therefore, the adsorption process is better described as a mixed mechanism rather than purely chemisorptive.

3.6.4 Validation of Adsorption Isotherm Models

The study of adsorption equilibrium isotherms is based on the determination of the capacity and nature of the adsorption mechanism and the assessment of the adsorbent-adsorbate affinity. To describe the phenomenon of ARS adsorption, different models have been applied, namely the Langmuir, Freundlich, Langmuir-Freundlich, Temkin, Dubinin-Radushkevich, and Redlich-Peterson models.

The Langmuir isotherm confirmed that, in the absence of interactions between adsorbed molecules, ARS absorption was achieved on a homogeneous surface through monolayer sorption. The following equation is the linear form of the Langmuir isotherm equation [41]:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m} \quad (\text{Eq. 5})$$

where q_e and q_m are the equilibrium adsorption capacities and the maximum monolayer adsorption capacity ($\text{mg}\cdot\text{g}^{-1}$) respectively, K_L is the Langmuir constant ($\text{L}\cdot\text{g}^{-1}$), and C_e is the solute's equilibrium concentration ($\text{mg}\cdot\text{L}^{-1}$). The Freundlich isotherm model is applied when non-ideal sorption takes place on heterogeneous surfaces, and the following is the linear version of the equation [41]:

$$q_e = K_F C_e^{1/n} \quad (\text{Eq. 6})$$

where C_e is the solute concentration at equilibrium ($\text{mg}\cdot\text{L}^{-1}$), n is a constant, K_F is the Frischen constant ($\text{L}\cdot\text{g}^{-1}$), and q_e is the capacity at equilibrium ($\text{mg}\cdot\text{g}^{-1}$). The solute-adsorbent pair determines the Freundlich constants (K_F and n). Adsorption is advantageous when n is between 1 and 10. Conversely, an unfavorable adsorption is indicated when the value of n is smaller than 1.

The thermodynamic conditions of the adsorption process can be specified using Temkin's model. Temkin postulates that the heat of absorption will decrease linearly with recovery rate. In chemical adsorption, Temkin's equation is relevant.

The following equation represents this model [41]:

$$q_e = B_T \times \ln(K_T C_e) \quad (\text{Eq. 7})$$

where B_T is the Temkin constant, which is associated with the heat of sorption ($\text{J}\cdot\text{mol}^{-1}$). An empirical model that is frequently used to determine the adsorption mechanism with Gaussian energy distribution onto heterogeneous surfaces is the Dubinin-Radushkevich adsorption isotherm model. It is typically used to differentiate between chemical and physical adsorption. The following is the expression for the Dubinin-Radushkevich model [41]:

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \quad (\text{Eq. 8})$$

$$\varepsilon = RT \ln \left(1 + \frac{1}{e} \right) \quad (\text{Eq. 9})$$

The Redlich–Peterson model is a combination of the Langmuir and the Freundlich models into a single one. It proposes an empirical equation that can describe adsorption equilibrium over a wide range of concentrations in both heterogeneous and homogeneous systems. At low surface coverage, the Redlich–Peterson equation reduces to the Freundlich isotherm at high adsorbate concentrations, and to the Langmuir isotherm when $\beta = 1$. The equation is given by Eq. 10 [41]:

$$q_e = \frac{K_R C_e}{1 + \alpha \times C_e^\beta} \quad (\text{Eq. 10})$$

With K_R is the Redlich–Peterson isotherm constant ($\text{L}\cdot\text{g}^{-1}$); α_R is the Redlich–Peterson isotherm constant ($\text{L}\cdot\text{mg}^{-1}$); and β is an exponent ranging between 0 and 1.

The Langmuir–Freundlich isotherm was initially proposed for gas adsorption on heterogeneous solids; however, it has also been developed and widely used for liquid adsorption on heterogeneous solids. This model is given by the following equation [42]:

$$q_e = \frac{K_{LF} \times C_e^{1/n}}{1 + K_{LF} \times C_e^{1/n}} \quad (\text{Eq. 11})$$

With K_{LF} : Langmuir-Freundlich Constant.

The fitting of the experimental results by the models is given in Figure 15. The results of non-linear modeling of isotherms are summarized in Table 7. From the data in this table and the determination of the regression coefficient, as well as the calculated RMSE error of experimental conditions, it can be concluded that:

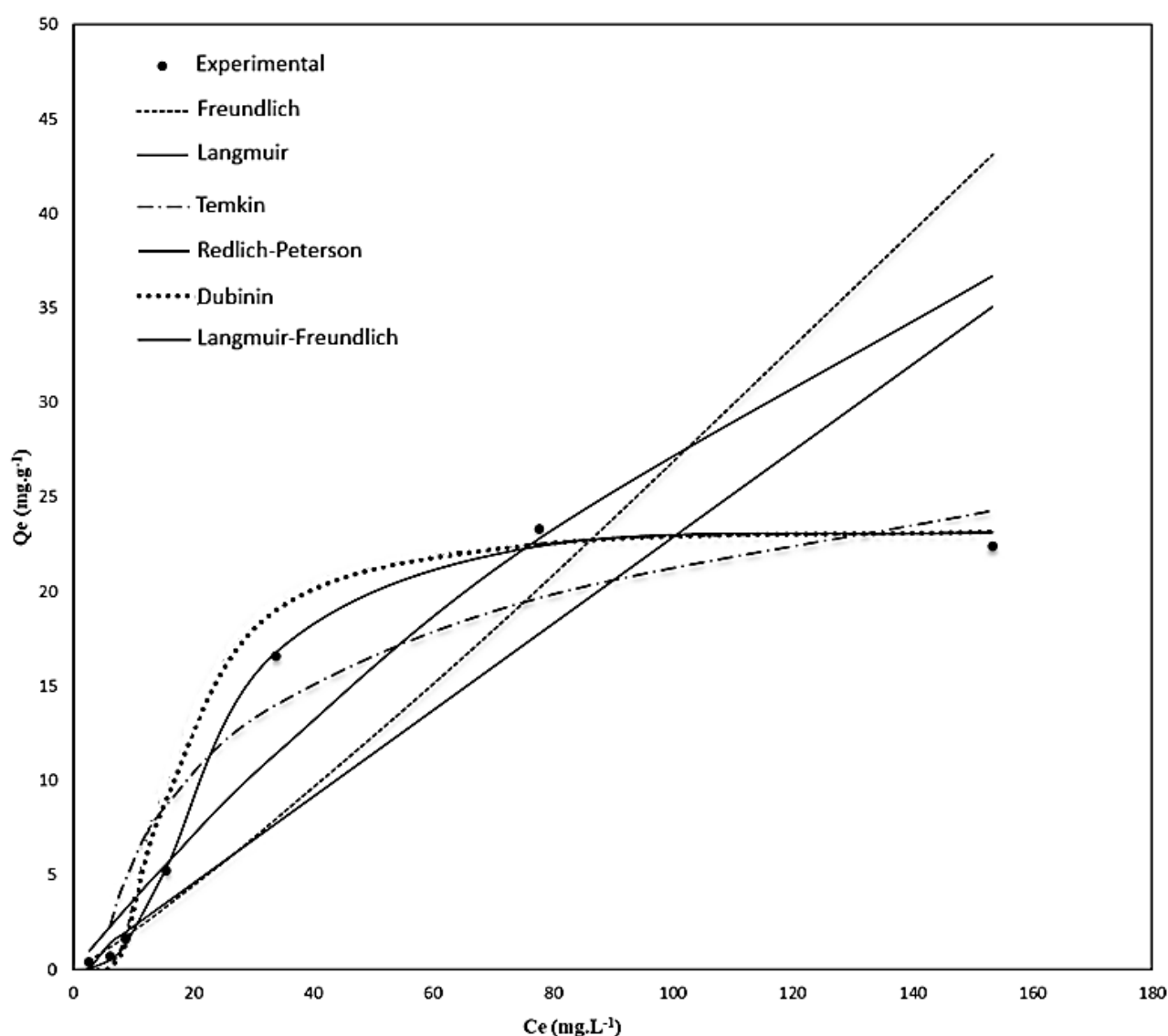


Figure 15 Isotherm modeling of ARS adsorption on HFA ($m = 0.35$; $T = 25^{\circ}\text{C}$; $\text{pH} = 6$).

Table 7 Parameters' of adsorption isotherm models.

Model	Parameter Value
Langmuir	
$Q_{\max}$ ($\text{mg}\cdot\text{g}^{-1}$)	98.04
K_L ($\text{L}\cdot\text{mol}^{-1}$)	3.9E(-3)
R^2	0.923
Freundlich	
n	8.95E-1
K_F ($\text{mg}\cdot\text{g}^{-1}$)	1.56E-1
R^2	0.914
Langmuir-Freundlich	
$Q_{\max}$ ($\text{mg}\cdot\text{g}^{-1}$)	23.26
K_{L-F} ($\text{L}\cdot\text{mg}^{-1}$)	1.56E-4
N_{L-F}	2.75
R^2	0.998
RMSE	0.64
Temkin	
A ($\text{L}\cdot\text{mg}^{-1}$)	0.23
B	6.78
R^2	0.902
Dubinin-Radushkevich	
q_m ($\text{mg}\cdot\text{g}^{-1}$)	23.26
β ($\text{mol}^2\cdot\text{kJ}^{-2}$)	4E-5
RMSE	2.03
R^2	0.974
Redlich-Peterson	
K_R ($\text{L}\cdot\text{g}^{-1}$)	0.14
α_R ($\text{L}\cdot\text{mg}^{-1}$)	7.1E-8
B	0.09
R^2	0.908
RMSE	2.92

The Langmuir model fits the experimental results, with a regression coefficient of 0.923. This empirical model demonstrates that adsorption is homogeneous, occurs in a single adsorption layer, and that all active sites have an affinity for the adsorbate [43]. The Freundlich model is also considered validated and can describe the phenomenon of this study with a regression coefficient equal to 0.914. This empirical model provides insights into the idea about the reversibility and heterogeneity of the adsorbent surfaces and that the phenomenon is not limited to the formation of a single layer but multi-layer adsorption is also possible [44].

Under these conditions, the combination of the two models, Langmuir and the Langmuir-Freundlich model, was used to improve model validation. The modeling results show that the regression coefficient is 0.998. So, this model is the most appropriate to describe the adsorption process.

The adsorption data were analyzed using monolayer and double-layer models to elucidate surface interactions and determine whether adsorption occurs as a single layer or involves multilayer coverage. Two new physical models were used: single-layer and double-layer adsorption models [45].

The first model is a monolayer model, which was applied by assuming that dye removal occurred through a monolayer process, with an associated energy describing the interactions between ARS molecules and the active sites on the adsorbent surfaces. In addition, it was assumed that a secondary dye layer could be involved in the adsorption process for both materials. Consequently, a second energy term can be introduced to characterize the interactions between dye molecules, making a double-layer model a suitable option for studying this adsorption system. The mathematical expressions of the two models are given by the following equations:

Monolayer model:

$$q_e = \frac{n \times D_m}{1 + \frac{C_e^{\frac{1}{2}}}{C_1}} \quad (\text{Eq. 12})$$

D_m : the density of functional groups on the adsorbents; N : the number of dye molecules bound to the functional groups of the adsorbents; $C_1^{1/2}$: the half-saturation concentration of the layer formed by dye molecules.

Double Layer Model:

$$q_e = \frac{(n \times D_m) \times \left(\left(\frac{C_e}{C_1} \right)^n + \left(2 \times \frac{C_e}{C_2} \right)^{2n} \right)}{1 + \left(\frac{C_e}{C_1} \right)^n + \left(\frac{C_e}{C_2} \right)^{2n}} \quad (\text{Eq. 13})$$

C_1 and C_2 are the half-saturation concentrations of the dye.

The application of these two models can be used to confirm the validity of the appropriate model of adsorption isotherms, “Langmuir-Freundlich”. Experimental data on ARS adsorption from both models are shown in Table 8. After examination, it was found that the R^2 regression coefficients of the monolayer and double-layer adsorption models are 0.971 to 0.999, respectively. So, the double-layer model is more appropriate than the single-layer model, given that the regression coefficients are closer to 1 than in the single-layer model. This means that physical interactions are involved in the process of adsorption and that the phenomenon has taken place in two layers [46]. In this model, n is a very important parameter because it indicates the orientation of ARS molecules on the adsorbent surface (horizontally or vertically) during adsorption [46].

- If ($n < 1$): This is probably due to the adsorption incorporation of the eliminated ARS molecules being horizontal or vertical;
- If ($n < 0.5$): This condition indicates that the ARS Molecule can interact with at least two adsorbent sites;
- If $n \in$ to (0.5, 1): This indicates that the ARS dye can be adsorbed on the surface of the adsorbents by both types of orientation (i.e., parallel and non-parallel);
- If ($n > 1$): ARS can be adsorbed on HFA via a total non-parallel orientation [38].

Table 8 Parameter of the two physical models for the adsorption of ARS by the two adsorbents.

N	Mono-layer Model					Double-layer Model				
	Dm mg·g ⁻¹	C ^{1/2} mg·L ⁻¹	RMSE	R ²	n	Dm mg·g ⁻¹	C ₁ mg·L ⁻¹	C ₂ mg·L ⁻¹	RMSE	R ²
0.96	34.84	52.65	3.67	0.980	1.02	61.19	734.66	11.07	0.28	0.999

The value of $n = 1.02$, the orientation of the ARS molecule is non-parallel, and the storage of this molecule on the surface of HFA is a multi-storage.

3.7 Regeneration Study

The most important aspect of the adsorption process is the adsorbent's reusability; therefore, it is crucial to investigate the regeneration of dye-loaded adsorbents [45]. A regeneration study was conducted to evaluate the potential for the adsorbent's repeated use without significant loss of performance. Following regeneration, 0.1 M NaOH was used to desorb the HFA-adsorbent-saturated ARS dye molecules with a contact time optimized to 20 minutes to avoid the partial dissolution of HFA. The interactions between the ARS dye molecules and the adsorbent surface will be hindered by the alkalinity of the NaOH molecule. The adsorbed molecule then begins to desorb from the adsorbent surface. After the desorption step, the adsorbent was cleaned and oven-dried for three hours at 100°C. As illustrated in Figure 16, the adsorption capacity declined gradually yet remained limited across multiple cycles. Specifically, the capacity decreased from 40.75 to 36.91 mg·g⁻¹, given during five consecutive cycles. Likewise, similar results were obtained after the adsorbent's calcinations at 500°C at each end of the cycle. This study, however, did not consider this later process because it was assumed to be an energy-intensive procedure. This minimal loss in performance demonstrates the robust reusability of the material and aligns with previous studies on HAP-based adsorbents for organic dye removal [18]. Investigating dye-loaded adsorbents for regeneration is essential, as adsorbent reusability is the most significant component of the adsorption process [45, 47]. To determine if the adsorbent could be used repeatedly without experiencing a noticeable decline in performance, regeneration research was carried out. Over several cycles, the adsorption capacity decreased slightly but remained controlled, as shown in Figure 16. Investigating dye-loaded adsorbents for regeneration is essential since the reusability of the adsorbent is the most significant component of the adsorption process [45].

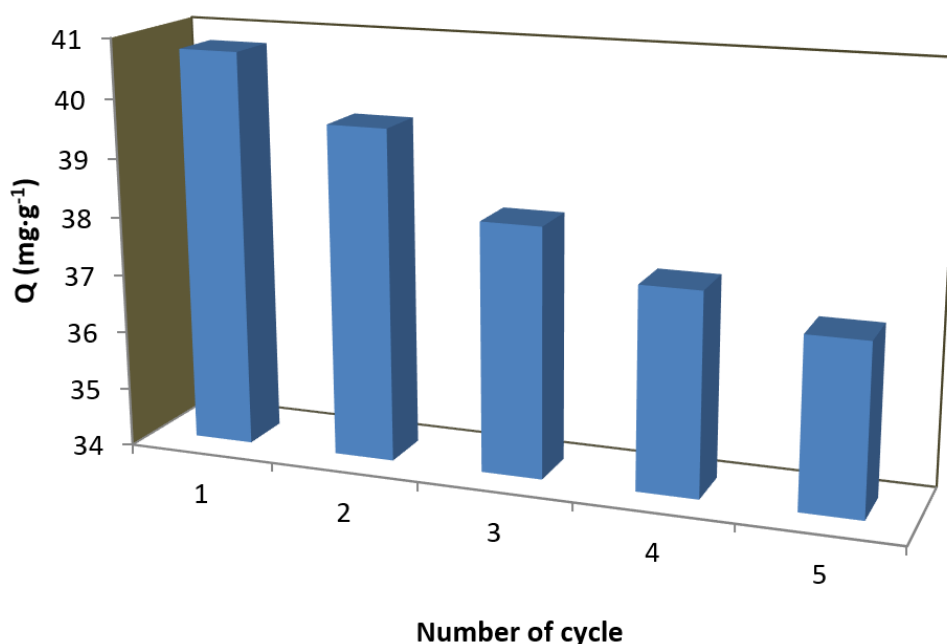


Figure 16 Reuse of HFA for different adsorption/regeneration cycles.

3.8 Comparative Study

A comparative study was conducted to assess the efficiency of HFA synthesized in this work with other adsorbents in the literature for the removal of ARS and other dyes. Results are summarized respectively in Table 9 and Table 10. Compared with numerous traditional adsorbents documented in the literature, the synthesized HFA showed good adsorption efficiency. The strong affinity of HA-based materials for both organic and inorganic contaminants is well recognized, owing to their surface hydroxyl and calcium active sites, which facilitate ion exchange, surface complexation, and electrostatic interactions. Furthermore, HA and modified apatite materials have demonstrated competitive adsorption capacities for a variety of dyes, such as Methylene blue, Rhodamine B, methyle orange and Congo Red. These findings demonstrate the adaptability and strong adsorption capacity of apatite-based materials, the affinity of HFA for ARS removal, and the adsorption of other studied dyes. Thus, the produced HFA can be regarded as a promising and effective biosourced adsorbent.

Table 9 Comparative study of HA-Based Adsorbents for Dye Removal.

Dye	Hydroxyapatite-Based Adsorbent	Adsorption Capacity ($q_{\max}$, mg/g)	References
Methylene Blue	Hydroxyapatite (synthetic HAp)	~49 mg/g	[48]
Methylene Blue	Nano-hydroxyapatite	~71 mg/g	[49]
Congo Red	Hydroxyapatite powder	~34 mg/g	[50]
Congo Red	Modified hydroxyapatite	~85 mg/g	[51]
Rhodamine B	Hydroxyapatite nanoparticles	~23 mg/g	[52]
Methyl Orange	Hydroxyapatite-based composite	~40 mg/g	[53]
Reactive Blue dye	Hydroxyapatite derived from biowaste	~60 mg/g	[54]
Alizarin Red S	Hydroxyfluorapatite	40.75 mg/g	This study

Table 10 Comparative study of adsorbents for Alizarin Red S Removal.

Dye	Adsorbents	Adsorption Capacity ($q_{\max}$, mg/g)	References
Alizarin Red S	Fe-clay (activated clay with Fe)	32.7	[55]
Alizarin Red S	Zeolite L	95.24	[56]
Alizarin Red S	SSZ-13 zeolite	210.75	[57]
Alizarin Red S	Fe ₂ O ₃ @BC-KC composite	174.9	[58]
Alizarin Red S	Activated carbon/ γ -Fe ₂ O ₃	108.69	[59]
Alizarin Red S	Hydroxyfluorapatite	40.75	This study

4. Conclusion

This work demonstrates that HFA can serve as an efficient adsorbent for removing Alizarin Red S (ARS) from aqueous solutions. Contact time, adsorbent dose, pH, and temperature all affected the adsorption process; the best removal was obtained at 60 minutes, 0.35 g of adsorbent, natural pH (~6), and 20°C. Thermodynamic results indicate that the process is exothermic and primarily driven by physical interactions. At the same time, kinetic and isotherm analyses show that the adsorption is well described by pseudo-second-order kinetics and the Langmuir isotherm. Additionally, the adsorbent showed remarkable reusability with no capacity loss. To examine the impact of various parameters on the adsorption capacity of HFA, a quadratic polynomial model based on a Box-Behnken Design (BBD) was created using Response Surface Methodology (RSM). Examining the residuals and model precision revealed an excellent fit to the normal distribution, and analysis of variance (ANOVA) validated the model's high significance. Additionally, main-effect plots showed that low adsorbent dose, high ARS concentration, and medium pH were the conditions that produced the best ARS adsorption capacity onto HFA. The adsorption phenomena followed the Langmuir-Freundlich isotherm model. Thermodynamic analysis revealed that the adsorption process is exothermic and non-spontaneous. The adsorption kinetics were well-described by the pseudo-second-order model, suggesting that chemical interactions are a key mechanism in ARS adsorption. Mass transfer during the adsorption process is controlled by internal and external diffusion limitations. Finally, an adsorption-regeneration study demonstrated the potential reusability of HFA over three successive cycles. These findings underscore the efficacy of green-synthesized adsorbent material for dye removal and its potential for sustainable applications.

Author Contributions

The study conception and design were a collaborative effort of all authors. Takwa Tabbassi: Conceptualization, Methodology, Formal analysis, Investigation, Data curation, Writing – Original draft. Zohra Sghaier: Methodology, Formal analysis, Investigation, Data curation, Writing – Original draft. Asma Abdedayem: Methodology, Formal analysis, Investigation, Data curation, Writing – Original draft, Supervision. Mustapha Hidouri: Conceptualization, Methodology, Investigation, Writing – Review & Editing, Supervision, Visualisation. Amor Hafane: Review & Editing the original draft, Supervision. All authors provided feedback on earlier versions of the manuscript. The final manuscript was read and approved by all authors.

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Competing Interests

The authors have no competing interests to declare.

Data Availability Statement

Data will be made available upon request.

AI-Assisted Technologies Statement

Artificial intelligence (AI) tools were used solely for basic grammar correction and language refinement in the preparation of this manuscript. Specifically, you.com was employed to improve the readability and linguistic clarity of the English text. All scientific content, data interpretation, and conclusions were developed independently by the authors. The authors have thoroughly reviewed and edited the AI-assisted text to ensure its accuracy and accept full responsibility for the content of the manuscript.

References

1. Salehi M. Global water shortage and potable water safety; Today's concern and tomorrow's crisis. *Environ Int.* 2022; 158: 106936.
2. Zaoui F, Choumane FZ, Hakem A. Malachite green dye and its removal from aqueous solution by clay-chitosane modified. *Mater Today Proc.* 2022; 49: 1105-1111.
3. Sharma P, Iqbal HM, Chandra R. Evaluation of pollution parameters and toxic elements in wastewater of pulp and paper industries in India: A case study. *Case Stud Chem Environ Eng.* 2022; 5: 100163.
4. Aguiar JB, Martins AM, Almeida C, Ribeiro HM, Marto J. Water sustainability: A waterless life cycle for cosmetic products. *Sustain Prod Consum.* 2022; 32: 35-51.
5. Alharbi HA, Hameed BH, Alotaibi KD, Al-Oud SS, Al-Modaihsh AS. Recent methods in the production of activated carbon from date palm residues for the adsorption of textile dyes: A review. *Front Environ Sci.* 2022; 10: 996953.
6. Nure JF, Mengistu A, Abewaa M, Angassa K, Moyo W, Phiri Z, et al. Adsorption of Black MNN reactive dye from tannery wastewater using activated carbon of *Rumex Abysinicus*. *J Taiwan Inst Chem Eng.* 2023; 151: 105138.
7. Sewu DD, Boakye P, Woo SH. Highly efficient adsorption of cationic dye by biochar produced with Korean cabbage waste. *Bioresour Technol.* 2017; 224: 206-213.
8. Al-Tohamy R, Ali SS, Li F, Okasha KM, Mahmoud YA, Elsamahy T, et al. A critical review on the treatment of dye-containing wastewater: Ecotoxicological and health concerns of textile dyes and possible remediation approaches for environmental safety. *Ecotoxicol Environ Saf.* 2022; 231: 113160.

9. Ahmed MA, Mohamed AA. A systematic review of layered double hydroxide-based materials for environmental remediation of heavy metals and dye pollutants. *Inorg Chem Commun.* 2023; 148: 110325.
10. Foroutan R, Peighambardoust SJ, Esvandi Z, Khatooni H, Ramavandi B. Evaluation of two cationic dyes removal from aqueous environments using CNT/MgO/CuFe₂O₄ magnetic composite powder: A comparative study. *J Environ Chem Eng.* 2021; 9: 104752.
11. Chenna M, Kebaili M, Lardjane N, Drouiche N, Lounici H. Modeling and optimization by rsm for the removal of the dye “*Palanil Blue R*” by coagulation-flocculation process. *Int J Environ Res.* 2022; 16: 35.
12. Khan MI, Elboughdiri N, Shanableh A, Lashari MH, Shahida S. Application of the commercial anion exchange membrane for adsorptive removal of Eriochrome Black-T from aqueous solution. *Desalin Water Treat.* 2022; 252: 437-448.
13. Liu S, Wang Z, Feng X, Pyo SH. Refractory azo dye wastewater treatment by combined process of microbial electrolytic reactor and plant-microbial fuel cell. *Environ Res.* 2023; 216: 114625.
14. Moradihamedani PJ. Recent advances in dye removal from wastewater by membrane technology: A review. *Polym Bull.* 2022; 79: 2603-2631.
15. Afzal S, Akhtar MN, Gurbanova L, El-Sheikh MA, Ahmad A, Choi CH, Karim MR, Shah SS, et al. Synergistic effect SnO₂/g-C₃N₄ heterojunction cocatalyst for photodegradation of methyl orange. *ChemistrySelect.* 2025; 10: e02037.
16. Maqsood K, Ali R, Ahmad K, El-Sheikh MA, Iqbal R, Karim MR, et al. Synthesis and photocatalytic degradation efficiency of MgFe₂O₄@CuO nanocomposite for Bromophenol blue dye removal. *J Chin Chem Soc.* 2025; 72: 390-400.
17. Ba M, Ezzeddine A, Dorozhkin SV, Hidouri M. Application of the Doehlert design for the defluoridation of industrial wastewater by adsorption onto natural clay. *Desalin Water Treat.* 2022; 264: 141-150.
18. Boussaha N, Slimen JB, BA M, Hidouri M. Hydroxyapatite biomaterial for adsorption based toxic indigo carmine dye removal: Optimization and modeling. *Chem Afr.* 2025; 8: 3643-3661.
19. Kheradmand A, Negarestani M, Kazemi S, Shayesteh H, Javanshir S, Ghiasinejad H. Adsorption behavior of rhamnolipid modified magnetic Co/Al layered double hydroxide for the removal of cationic and anionic dyes. *Sci Rep.* 2022; 12: 14623.
20. Alali AF, Almojil SF, Almohana AI, Anqi AE, Rajhi AA, Alamri S, et al. Hydroxyapatite@Mn-Fe composite as a reusable sorbent for removal of Nile blue dye and Cr(VI) from polluted water. *Environ Sci Pollut Res.* 2023; 30: 18419-18437.
21. Sulistiyo CD, Cheng KC, Su'andi HJ, Yuliana M, Hsieh CW, Ismadji S, et al. Removal of hexavalent chromium using durian in the form of rind, cellulose, and activated carbon: Comparison on adsorption performance and economic evaluation. *J Clean Prod.* 2022; 380: 135010.
22. El-Zahhar AA, Awwad NS. Removal of malachite green dye from aqueous solutions using organically modified hydroxyapatite. *J Environ Chem Eng.* 2016; 4: 633-638.
23. Bankole AA, Poulouse V, Ramachandran T, Hamed F, Thiemann T. Comparative study of the selective sorption of organic dyes on inorganic materials—A cost-effective method for waste treatment in educational and small research laboratories. *Separations.* 2022; 9: 144.
24. Ofudje EA, Sodiya EF, Olanrele OS, Akinwunmi F. Adsorption of Cd²⁺ onto apatite surface: Equilibrium, kinetics and thermodynamic studies. *Heliyon.* 2023; 9: e12971.

25. Billah RE, Kaya S, Şimşek S, Halim EM, Agunaou M, Soufiane A. Removal and regeneration of As(V) in aqueous solutions by adsorption on calcined fluorapatite. *Int J Environ Sci Technol.* 2023; 20: 5197-5206.
26. Vinayagam R, Kandati S, Murugesan G, Goveas LC, Baliga A, Pai S, et al. Bioinspiration synthesis of hydroxyapatite nanoparticles using eggshells as a calcium source: Evaluation of Congo red dye adsorption potential. *J Mater Res Technol.* 2023; 22: 169-180.
27. Nikčević I, Jokanović V, Mitrić M, Nedić Z, Makovec D, Uskoković D. Mechanochemical synthesis of nanostructured fluorapatite/fluorhydroxyapatite and carbonated fluorapatite/fluorhydroxyapatite. *J Solid State Chem.* 2004; 177: 2565-2574.
28. Slimen JB, Mehnaoui M, Jebahi S, Boughzala K, Hidouri M. Thermal and structural properties of sodium, potassium and carbonate doped strontium hydroxyfluorapatite. *J Indian Chem Soc.* 2022; 99: 100475.
29. Ali RH, Sghaier Z, Ageorges H, Salem EB, Hidouri M. Magnesium-substituted zinc-calcium hydroxyfluorapatite bioceramics for bone tissue engineering. *J Mech Behav Biomed Mater.* 2025; 166: 106933.
30. Chen Y, Miao X. Thermal and chemical stability of fluorohydroxyapatite ceramics with different fluorine contents. *Biomaterials.* 2005; 26: 1205-1210.
31. Azami M, Jalilifiroozinezhad S, Mozafari M, Rabiee M. Synthesis and solubility of calcium fluoride/hydroxy-fluorapatite nanocrystals for dental applications. *Ceram Int.* 2011; 37: 2007-2014.
32. Bbumba S, Karume I, Kayiwa R, Talibawo J, Musoke P, Aturagaba G, et al. Activated carbon from banana peels for alizarin removal: Understanding the adsorption process through isotherms, kinetics, and predictive modeling. *BMC Chem.* 2025; 19: 301.
33. Abidi SS, Murtaza Q. Synthesis and characterization of nano-hydroxyapatite powder using wet chemical precipitation reaction. *J Mater Sci Technol.* 2014; 30: 307-310.
34. Wang Q, Song H, Li W, Wang S, Liu L, Li T, et al. Facile synthesis of polypyrrole/graphene composite aerogel with Alizarin Red S as reactive dopant for high-performance flexible supercapacitor. *J Power Sources.* 2022; 517: 230737.
35. Lemlikchi W, Sharrock P, Fiallo M, Nzihou A, Mecherri MO. Hydroxyapatite and Alizarin sulfonate ARS modeling interactions for textile dyes removal from wastewaters. *Procedia Eng.* 2014; 83: 378-385.
36. El Naeem GA, Abd-Elhamid AI, Farahat OO, El-Bardan AA, Soliman HM, Nayl AA. Adsorption of crystal violet and methylene blue dyes using a cellulose-based adsorbent from sugarcane bagasse: Characterization, kinetic and isotherm studies. *J Mater Res Technol.* 2022; 19: 3241-3254.
37. Chemingui H, Rezma S, Lafi R, Alhalili Z, Missaoui T, Harbi I, et al. Investigation of methylene blue adsorption from aqueous solution onto ZnO nanoparticles: Equilibrium and Box-Behnken optimisation design. *Int J Environ Anal Chem.* 2023; 103: 2716-2741.
38. Plazinski W, Dziuba J, Rudzinski W. Modeling of sorption kinetics: The pseudo-second order equation and the sorbate intraparticle diffusivity. *Adsorption.* 2013; 19: 1055-1064.
39. Nodehi R, Shayesteh H, Rahbar-Kelishami A. Enhanced adsorption of Congo red using cationic surfactant functionalized zeolite particles. *Microchem J.* 2020; 153: 104281.

40. Ewis D, Ba-Abbad MM, Benamor A, Mahmud N, Nasser M, El-Naas M, et al. Adsorption of 4-nitrophenol onto iron oxide bentonite nanocomposite: Process optimization, kinetics, isotherms and mechanism. *Int J Environ Res*. 2022; 16: 23.
41. Matouq M, Jildeh N, Qtaishat M, Hindiye M, Al Syouf MQ. The adsorption kinetics and modeling for heavy metals removal from wastewater by Moringa pods. *J Environ Chem Eng*. 2015; 3: 775-784.
42. Jeppu GP, Clement TP. A modified Langmuir-Freundlich isotherm model for simulating pH-dependent adsorption effects. *J Contam Hydrol*. 2012; 129: 46-53.
43. Al-Ghouti MA, Da'ana DA. Guidelines for the use and interpretation of adsorption isotherm models: A review. *J Hazard Mater*. 2020; 393: 122383.
44. Abdedayem A, Chemingui H, Nouri H, Hafiane A, Ben Amor T. Green iron oxide nanoparticles from *Opuntia ficus-indica* (L.) extract for efficient dye removal: Optimization and mechanism investigation. *Biomass Convers Biorefinery*. 2025; 15: 20817-20838.
45. Somashekara D, Mulky L. Sequestration of contaminants from wastewater: A review of adsorption processes. *ChemBioEng Rev*. 2023; 10: 491-509.
46. Altalhi T, Jethave G, Fegade U, Mersal GA, Ibrahim MM, Mahmoud MH, et al. Adsorption of magenta dye on PbO doped MgZnO: Interpretation of statistical physics parameters using double-layer models. *Int J Environ Res Public Health*. 2022; 19: 12199.
47. Zhang J, Zhang J, Yang M, Han R. Efficient sequestration of Alizarin red from solution using a novel adsorbent based on zirconium and diethylenetriamine functionalized wheat straw. *Desalin Water Treat*. 2021; 235: 283-299.
48. Hossain MS, Hossain MS, Ahmed S, Mobarak MB. Characterization and adsorption performance of nano-hydroxyapatite synthesized from *Conus litteratus* waste seashells for Congo red dye removal. *RSC Adv*. 2024; 14: 38560-38577.
49. Hou H, Zhou R, Wu P, Wu L. Removal of Congo red dye from aqueous solution with hydroxyapatite/chitosan composite. *Chem Eng J*. 2012; 211: 336-342.
50. Mobarak MB, Pinky NS, Chowdhury F, Hossain MS, Mahmud M, Quddus MS, et al. Environmental remediation by hydroxyapatite: Solid state synthesis utilizing waste chicken eggshell and adsorption experiment with Congo red dye. *J Saudi Chem Soc*. 2023; 27: 101690.
51. Srilakshmi C, Saraf R. Ag-doped hydroxyapatite as efficient adsorbent for removal of Congo red dye from aqueous solution: Synthesis, kinetic and equilibrium adsorption isotherm analysis. *Microporous Mesoporous Mater*. 2016; 219: 134-144.
52. Pompeu LD, Druzian DM, Oviedo LR, Viana AR, Mortari SR, Pavoski G, et al. Adsorption of Rhodamine b dye onto novel Biochar: Isotherm, Kinetic, thermodynamic study and antibiofilm activity. *Inorg Chem Commun*. 2023; 158: 111509.
53. Herradi S, Zerrouk M, Bouayad A, Bouhazma S, Ouarsal R, Khaldi M, et al. Removal of methylene blue with a highly effective hydroxyapatite-silica nanocomposite. *Mor J Chem*. 2024; 12: 267-285.
54. Ghanavati Nasab S, Semnani A, Teimouri A, Kahkesh H, Momeni Isfahani T, Habibollahi S. Removal of Congo red from aqueous solution by hydroxyapatite nanoparticles loaded on zein as an efficient and green adsorbent: Response surface methodology and artificial neural network-genetic algorithm. *J Polym Environ*. 2018; 26: 3677-3697.
55. Fu F, Gao Z, Gao L, Li D. Effective adsorption of anionic dye, alizarin red S, from aqueous solutions on activated clay modified by iron oxide. *Ind Eng Chem Res*. 2011; 50: 9712-9717.

56. Insuwan W, Srihongthong S, Permngam N, Tongkasee P. Effectiveness of adsorption of alizarin red s and alizarin yellow 2G from aqueous solutions using zeolite L. *Agric Nat Resour*. 2023; 57: 163-172.
57. Gollakota AR, Munagapati VS, Volli V, Gautam S, Wen JC, Shu CM. Coal bottom ash derived zeolite (SSZ-13) for the sorption of synthetic anion Alizarin Red S (ARS) dye. *J Hazard Mater*. 2021; 416: 125925.
58. Ohale PE, Chukwudi K, Ndive JN, Michael ME, Abonyi MN, Chukwu MM, et al. Optimization of Fe₂O₃@BC-KC composite preparation for adsorption of Alizarin red S dye: Characterization, kinetics, equilibrium, and thermodynamic studies. *Results Surf Interfaces*. 2023; 13: 100157.
59. Fayazi M, Ghanei-Motlagh M, Taher MA. The adsorption of basic dye (Alizarin red S) from aqueous solution onto activated carbon/ γ -Fe₂O₃ nano-composite: Kinetic and equilibrium studies. *Mater Sci Semicond Process*. 2015; 40: 35-43.