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Optimization of synthesis conditions of amine-functionalized activated rice husk ash for simultaneous removal of methyl orange, nitrate, and phosphate in water

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ABSTRACT

The capacity of adsorbent materials to simultaneously treat multiple pollutants plays a crucial role in determining the efficiency of practical water and wastewater treatment. Triamine-functionalized activated rice husk ash (TRI-ARHA) was successfully synthesized and exhibited considerable potential as a simultaneous adsorbent for organic compounds, nitrate, and phosphate. This study investigated the effects of the HF concentration in the process of activating rice husk ash as a support, the ratio of triamine silane to activated rice husk ash, and the type of amine functional group used in the grafting process on the synthesis of the TRI-ARHA material; these synthesis conditions were optimized using an experimental design approach. The results showed that the maximum adsorption capacities of TRI-ARHA material for MO, nitrate, and phosphate were approximately 15.8 mgMO/g, 34.3 mgNO₃⁻-N/g, and 13.4 mgPO₄³⁻-P/g, respectively, under the optimal synthesis conditions with an HF concentration of ~ 4.86% and triamine silane to an activated rice husk ash volume ratio of ~ 3.12 mL/g. Validation of the optimized TRI-ARHA material demonstrated practical adsorption performance, achieving approximately 93.1% of the model's predicted performance. Overall, a basic TRI-ARHA synthesis procedure has been established to support further research, development, and practical applications. This contributes to improved water and wastewater treatment efficiency, promoting the circular economy of rice husk ash waste.

1. Introduction

Among the most critical environmental problems of our time is the pervasive issue of water pollution.

It can cause severe consequences for biodiversity, human health, and ecosystems. Wastewater typically comprises a diverse array of pollutants, encompassing organic materials and nutrients

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such as nitrate and phosphate [1]. The simultaneous presence of these pollutants in water sources not only causes pollution but also exacerbates phenomena such as eutrophication. This leads to excessive algal growth, which results in oxygen depletion and subsequent aquatic life mortality [1, 2]. Consequently, the simultaneous treatment of multiple pollutants in wastewater is essential for safeguarding the environment and securing clean water supplies for human activities, both industrial and domestic.

To treat multi-component wastewater, various methods have been researched and applied, including physical, chemical, and biological approaches. Every approach has its strengths and weaknesses. Among these, adsorption is considered one of the effective and versatile methods [3]. The adsorption method is based on the principle of using adsorbent materials capable of retaining pollutants on their surfaces. The pros of adsorption involve the capability to simultaneously remove multiple contaminants, simplicity, ease of operation, and applicability to various types of wastewater [4].

Various adsorbent materials have been investigated and utilized for wastewater treatment, including activated carbon [5, 6], zeolites [7], biosorbents [8], and synthetic materials [9]. Each material exhibits distinct adsorption properties, rendering them suitable for the removal of certain pollutants. Nevertheless, existing adsorbent materials are subject to several limitations, including: (1) suboptimal adsorption performance for certain contaminants, particularly large organic molecules and persistent organic pollutants (POPs); (2) elevated material production costs, contributing to increased wastewater treatment expenditures; and (3) restricted regeneration potential. Therefore, the development of a novel material that exhibits simultaneous multi-component adsorption with high efficiency, cost-effectiveness, and multiple regeneration cycles continues to pose a significant challenge for researchers.

In our recent study [10], a novel adsorbent material, designated TRI-ARHA, was successfully synthesized. This material was prepared by grafting triamine functional groups onto activated rice husk ash, a support derived from waste. Initial findings

indicate that TRI-ARHA exhibits excellent efficiency in the simultaneous adsorption of three major wastewater pollutants: organics, nitrate, and phosphate. This effect can be attributed to the remarkable properties of the support and the active triamine groups present on its surface. A key highlight of this work is the discovery of an entirely new conjugated adsorption mechanism, validated by theoretical computations along with experimental studies using prepared and real wastewater samples. Furthermore, this novel material exhibits superior adsorption performance compared to other commercial adsorbents, such as ion-exchange resins and activated carbon, in experiments examining the adsorption of single and multi-pollutants [10]. Although TRI-ARHA has shown great potential for wastewater treatment applications, the factors influencing material synthesis and the TRI-ARHA production process have not yet been optimized to achieve the best possible adsorption performance.

This study focuses on investigating the key factors influencing the synthesis of the TRI-ARHA material, including the concentration of hydrofluoric acid (HF) used in the activation of rice husk ash, the volume ratio of the amine precursor to the mass of the activated rice husk ash support, and the specific type of amine functional group employed for surface grafting. The primary objective is to optimize the synthesis conditions to maximize the simultaneous adsorption capacity of the resulting material for three target pollutants: nitrate, phosphate, and organic substances (i.e., methyl orange, MO). The findings of this research will contribute to a broader research program focused on the valorization of rice husk ash waste into novel adsorbents for the treatment of multi-component pollutants in aqueous environments. This optimized material is expected to provide an efficient and cost-effective method for wastewater remediation.

2. Materials and methods

2.1. Raw rice husk ash and chemicals

The rice husk ash was obtained from brick kilns in the Cho Moi district, An Giang province, Vietnam, and used as the raw material for adsorbent synthesis. The main chemicals of hydrofluoric acid

(HF) for rice husk ash activation, 3-(triethoxysilyl)propan-1-amine, N'-(3-trimethoxysilylpropyl)ethane-1,2-diamine, and 2-N-(2-aminoethyl)-5-trimethoxysilylpentane-1,2-diamine, along with toluene and pentane solvents, were employed for amine grafting onto activated rice husk ash. HCl was used for material activation prior to adsorption, and methyl orange (powder form), KNO_3 , and KH_2PO_4 were used to prepare synthetic wastewater solutions for adsorption experiments. Additionally, other auxiliary chemicals such as H_2SO_4 , NaOH, and deionized (DI) water were used for pH adjustment and adsorption experiments. All chemicals used in this study were primarily sourced from reputable international suppliers, such as Merck, Aldrich Sigma, and Xilong, and reputable chemical suppliers in Vietnam.

2.2. Preparation of the TRI-ARHA material

To enhance surface properties, the original rice husk ash (RHA) was activated by a pore-forming method using hydrofluoric acid (HF) [10, 11]. The activation process can be described as follows: 20 grams of dry rice husk ash were introduced into 800 mL of hydrofluoric acid (HF) solution. The HF concentration varied from 0 to 9 volume percent, according to the experimental design. The mixture was moderately stirred at room temperature for 30 minutes. Subsequently, the solid residue (the portion of RHA insoluble in HF) was collected by filtration and rinsed repeatedly with deionized water until neutrality was reached. This recovered material was then desiccated at 110 °C for 12 hours (overnight) and allowed to cool, resulting in the activated rice husk ash (ARHA) product.

ARHA support was functionalized with amine groups via a simple and efficient surface grafting method, which has been widely applied to mesoporous silica materials [12]. The basic procedure was as follows. One gram of ARHA was placed in a two-necked round-bottom flask containing 150 milliliters of toluene. The resulting mixture was stirred until it became a uniform suspension. Then, 0.3 mL of deionized water was introduced, and stirring continued for an additional 30 minutes. The flask was then submerged in a silicone oil bath, heated, and stirred magnetically, with the temperature regulated at 85 °C. A specific

volume (0 to 5 mL, depending on the experiment) of triamine silane solution was then added, and the reaction proceeded under stirring for 16 hours. The resulting solid was isolated by filtration and rinsed with a sufficient volume of toluene and then pentane. The final product was dried at 100 °C for one hour and designated TRI-ARHA. Before each adsorption experiment, TRI-ARHA materials were activated by soaking in 0.1 M HCl (1 g/L) for 3 hours, then filtered and air-dried overnight [10, 11].

2.3. Adsorption experiments

Batch adsorption experiments were performed under laboratory conditions, with each experiment conducted in triplicate. The basic adsorption procedure was as follows: 30 milligrams of the material were precisely measured and added to 100-mL Erlenmeyer flasks, each containing 50 mL of solution. These solutions consisted of MO (10 mg/L initial concentration), nitrate (50 mg NO_3^- -N/L), and phosphate (10 mg PO_4^{3-} -P/L); their pH was adjusted to the desired value for each experiment using 0.1 M NaOH and 0.1 M HCl, with the working pH maintained at approximately 6. The mixtures were then agitated at 120 rpm. All experiments were conducted at ambient temperature (approximately 30 °C) and standard atmospheric pressure (around 1 atm). Following a pre-set adsorption period of roughly 30 minutes, the material was isolated from the solution by centrifugation at 10,000 rpm for 10 minutes. The residual MO concentration in the solution after adsorption was determined using UV-Vis spectrophotometry with a SPECORD 210 instrument (Analytik Jena, Germany) at 464 nm. Nitrate concentration was measured at 410 nm in accordance with the Vietnamese standard TCVN 4562:1988 (Wastewater – Method for determining nitrate content). Phosphate concentration was analyzed at 880 nm following TCVN 6202:2008 (Water quality – Determination of phosphorus – Spectrometric method employing ammonium molybdate). Adsorption capacity (mg/g) is evaluated through Formula (1):

$$Q_e = \frac{C_0 - C_e}{m} \times V \quad (1)$$

In this equation, C_0 denotes the initial adsorbate concentration in the solution (mg/L); C_e represents

the equilibrium adsorbate concentration in the solution (mg/L); V signifies the solution volume (mL); and m stands for the mass of adsorbent used (mg).

2.4. Optimization of material synthesis conditions by experimental design

Mathematical optimization methods employing pre-defined design models are necessary to minimize experimental time and cost. Response surface methodology (RSM) is a modern statistical approach used to establish experimental conditions and evaluate experimental results. In RSM, first- or second-order polynomial functions are employed to describe the studied system and investigate experimental conditions to identify optimal values. The Central Composite Design (CCD) and Box-Behnken Design (BBD) are experimental design models widely applied within RSM [13].

To establish the optimal synthesis conditions for novel materials from rice husk ash, the CCD model was applied. The CCD model offers the advantage of satisfying orthogonality, where the column vectors of the coded factor matrix are pairwise orthogonal (the removal of a coefficient in the equation does not significantly affect the remaining coefficients) and rotatability (the variance is the same in all directions in the coded factor space). This model is widely used in experimental optimization to reduce the number of experiments while still predicting optimal results with high accuracy [13].

The experiments were structured using Design-Expert software to examine the significant variables affecting the material synthesis, along with three response variables: MO, nitrate, and phosphate adsorption capacities. The experimental design domain for each factor was selected as the region likely to achieve extreme values, following an initial phase of experimentation investigating the influencing factors. The optimization results were determined using Design-Expert software.

3. Results and discussion

Previous studies have demonstrated that raw rice husk ash (RHA) after activation with HF exhibits excellent adsorption capacity for organic compounds and significantly improved surface

characteristics, making it highly suitable as a support material for the fabrication of adsorbents [14]. The preliminary results shown in Figure 1 clearly illustrate the influence of HF solution concentration on the specific surface area and the adsorption performance of ARHA. Specifically, with a 5% HF concentration, the specific surface area of ARHA reached 415 m²/g compared to 16 m²/g for the raw RHA. This substantial increase significantly enhanced the material's adsorption capacity for organic compounds such as MO. However, the results from this preliminary investigation also revealed that ARHA exhibited negligible adsorption capacity for anions such as nitrate and phosphate. This phenomenon may be explained by the fact that ARHA mainly adsorbs through physical interactions, which leads to effective adsorption of organic compounds like MO but limited efficiency for anions such as nitrate and phosphate (similar to activated carbon). Review studies have demonstrated that amine-grafted materials on silica-based supports exhibit excellent adsorption efficiency for anions such as nitrate and phosphate [15-17].

Meanwhile, silica, a major chemical component of rice husk ash (accounting for over 80% according to Bondioli et al. [18]), is almost entirely discarded into the environment.

Therefore, utilizing the silica source within the rice husk ash structure for grafting amine groups onto the activated rice husk ash surface is a novel and promising approach to create a material capable of adsorbing both organic compounds and nitrate and phosphate ions. Preliminary results of the synthesis of amine-grafted materials on the activated rice husk ash support are highly effective in adsorbing MO, nitrate, and phosphate. The HF concentration employed during support preparation is a critical determinant of the material's adsorptive capabilities. Furthermore, research screening reported procedures for amine grafting onto silica substrates [19-22] indicates that influencing factors such as the type of amine grafted (mono-, di-, tri-amine) and the ratio of amine precursor to support are also crucial considerations in the material synthesis procedure.

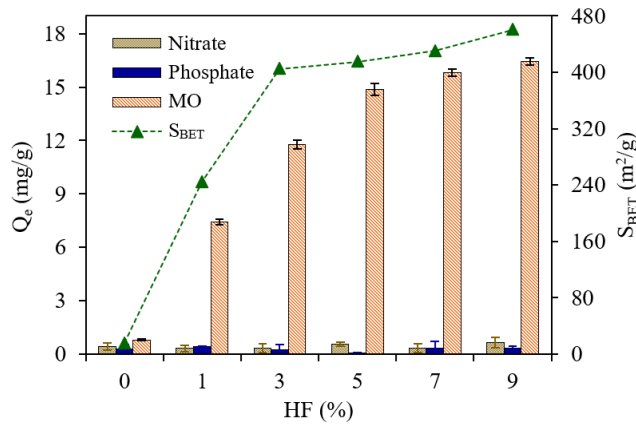


Fig. 1. Effect of HF concentration on the specific surface area and adsorption capacity of activated rice husk ash. (Experimental conditions: ARHA (0-9% HF) 0.6 g/L, C_{MO} 10 mg/L, $C_{nitrate}$ 50 mgNO₃⁻-N/L, $C_{phosphate}$ 10 mgPO₄³⁻-P/L, $t \sim 30$ min)

3.1. Factors affecting the material synthesis process

3.1.1 Effect of HF acid concentration on rice husk ash activation

The experimental results in Figure 2 demonstrate the adsorption efficiency of triamine-grafted materials on rice husk ash supports activated with HF at various concentrations. As expected, the amine-grafted ARHA showed a marked increase in nitrate and phosphate removal. Specifically, increasing the HF concentration from 0 to 5 vol% for support activation led to an increase in the TRI-ARHA material's ability to adsorb MO, nitrate, and phosphate, reaching maximum capacities of 16.4 mgMO/g, 33.5 mgNO₃⁻-N/g, and 12.9 mgPO₄³⁻-P/g, respectively, at 5% HF. Further increasing the HF concentration beyond 5% resulted in a significant decrease in the nitrate and phosphate adsorption capacities of TRI-ARHA. These preliminary findings underscore the significant role of HF concentration in support activation, which directly affects the material's adsorption capacity. To explain the improved performance, the reaction between HF and SiO₂ in the rice husk ash composition is a key factor. The HF activation process not only removes impurities but also extracts a certain amount of SiO₂ (depending on the HF concentration) from the rice husk ash structure, creating pores and defects. This consequently increases the rice husk ash's specific surface area (illustrated in Figure 1). This facilitates the grafting of amine groups onto the

support surface via the reaction between triamine silane and SiO₂ [23]. By functionalizing the ARHA support with amine groups, the material's capacity to adsorb nitrate and phosphate ions was significantly boosted, as illustrated in Figure 2. For materials prepared with HF concentrations > 5%, the adsorption capacity began to decrease. This could be attributed to the excessive dissolution of SiO₂ from the rice husk ash structure at higher HF concentrations. Although ARHA exhibited a higher specific surface area, the remaining SiO₂ content on the rice husk ash surface might have become significantly low, reducing the efficiency of the amine grafting process. The surface chemical composition analysis using the Fourier-transform infrared (FTIR) spectroscopy of ARHA with different HF concentrations (Figure 3) strongly supports this observation.

In other words, the number of grafted amine sites on these materials might still be present, but potentially fewer compared to the material activated at 5% HF.

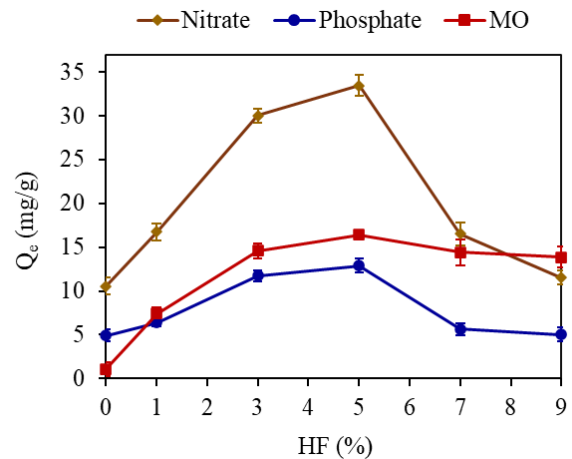


Fig. 2. Effect of HF concentration used for activating rice husk ash on the adsorption capacity of TRI-ARHA material. (Experimental conditions: TRI-ARHA (0-9% HF, 3 mL triamine silane/g ARHA) 0.6 g/L, C_{MO} 10 mg/L, $C_{nitrate}$ 50 mgNO₃⁻-N/L, $C_{phosphate}$ 10 mgPO₄³⁻-P/L, $t \sim 30$ min)

The FTIR spectra of the rice husk ash samples activated with HF concentrations from 0% to 5% (curves (1) to (4) in Figure 3) clearly showed the characteristic peaks of silicon bonds in the rice husk ash structure, such as observed vibration peaks at 1088 cm⁻¹, 796 cm⁻¹, and 620 cm⁻¹, corresponding to Si-O-Si and Si-H bonds,

respectively [14]. Concurrently, there is a readily apparent increase in the intensity of these characteristic peaks with increasing HF concentration from 0% to 5%. This indicates a growing presence of silicon atoms on the surface of rice husk ash. In other words, the chemical etching with HF in this concentration range gradually exposes silicon atoms on the rice husk ash surface. However, a significant change occurred in the FTIR spectra of ARHA when activated with HF solutions at concentrations >5% (curves (5) and (6) in Figure 3), where the characteristic peaks of silicon bonds were almost no longer clearly visible (as FTIR cannot accurately detect when the elemental content is < 3%). The reason for this result is probably that at higher HF concentrations, the silicon components on the rice husk ash surface reacted and dissolved significantly into the HF solution. In the solid phase at this point, the silicon content is still present but very low, mainly consisting of a highly porous carbon structure. This is reflected in the specific surface area measurements of ARHA (Figure 1).

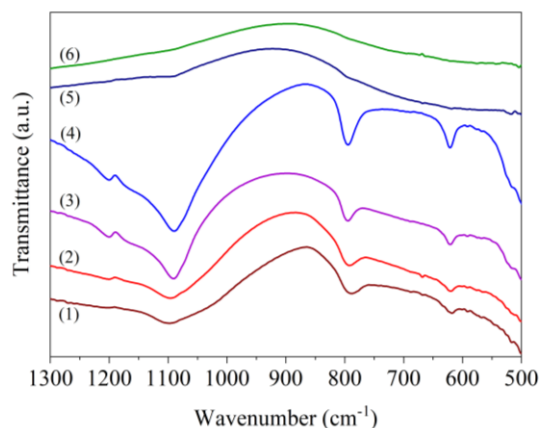


Fig. 3. FTIR spectra of activated rice husk ash (ARHA) at different HF concentrations: 0% (1), 1% (2), 3% (3), 5% (4), 7% (5), and 9% (6). (Note: These spectra correspond to the HF activation step only, before amine grafting; therefore, NH_2 -related bands are not present at this stage)

XRD data presented in Figure 4 also recorded similar findings regarding the diffraction intensity of the characteristic silicon peaks in the ARHA samples with 0%, 5%, and 9% HF concentrations. Specifically, the ARHA sample with 5% HF showed that it had been purified of impurities while retaining the typical silica crystalline structure,

whereas the ARHA sample with 9% HF completely lost its original crystalline structure.

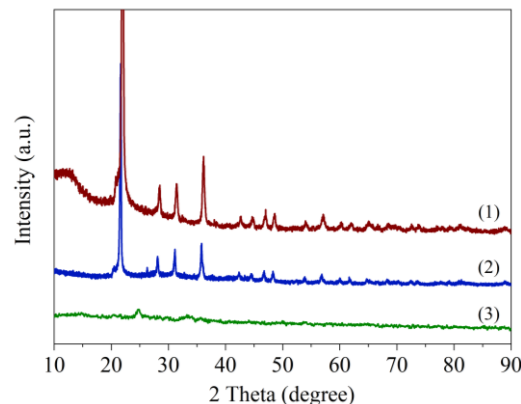


Fig. 4. XRD patterns of ARHA with HF concentrations of 0% (1), 5% (2), and 9% (3).

3.1.2 Effect of the ratio of triamine silane volume to ARHA support mass

In the TRI-ARHA material synthesis process, the volume ratio of triamine silane to ARHA support is one of the crucial factors influencing the amount of amine successfully grafted onto the material surface. In this experiment, the ARHA sample with 5% HF treatment was used as the support for the amine grafting reaction, where triamine silane/ARHA ratios were varied from 0 to 5 mL/g. The results shown in Figure 5 indicate that increasing the volume of triamine silane used for material synthesis per unit of ARHA support enhances the material's adsorption capacity, especially for nitrate ($\sim 34.4 \text{ mgNO}_3^- \text{-N/g}$) and phosphate ($\sim 13.6 \text{ mgPO}_4^{3-} \text{-P/g}$). Regarding MO, the adsorption capacity of ARHA after amine grafting also showed an increasing trend, but was not significant ($\sim 16.6 \text{ mgMO/g}$). This initially suggests that the porous structure and high specific surface area of the ARHA support are the key determinants of TRI-ARHA's adsorption capacity for organic pollutants like MO. Meanwhile, amine grafting is the principal factor responsible for the improved adsorption of nitrate and phosphate ions.

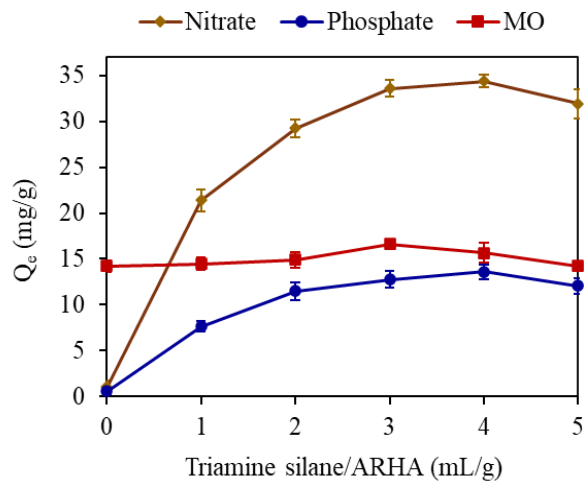


Fig. 5. Effect of triamine silane/ARHA ratio on the adsorption capacity of TRI-ARHA material. (Experimental conditions: TRI-ARHA (5% HF, 0-5 mL triamine silane/g ARHA) 0.6 g/L, C_{MO} 10 mg/L, $C_{nitrate}$ 50 mgNO₃⁻-N/L, $C_{phosphate}$ 10 mgPO₄³⁻-P/L, $t \sim 30$ min. Note: At 0 mL/g, the material corresponds to activated rice husk ash (ARHA) without amine grafting)

The adsorption capacity of TRI-ARHA for nitrate and phosphate increased rapidly when the triamine silane ratio increased from 0 mL/g to 3 mL/g, gradually slowed down when the ratio was > 3 mL/g, and started to decrease slightly at ratios > 4 mL/g. This phenomenon could be attributed to the fact that with triamine silane ratios > 4 mL/g, the large number of amine molecules might have obscured the pores on the ARHA surface, leading to a decrease in the material's specific surface area and reduced contact with the adsorbates.

3.1.3 Effect of amine functional group variety on surface grafting

The influence of the amine group/type used in the synthesis process is also considered an important factor [21]. In this experiment, different amine groups, including monoamine, diamine, and triamine, were grafted onto the ARHA support under the same experimental conditions and synthesis procedure. The adsorption capacities of the materials for MO, nitrate, and phosphate are presented in Figure 6.

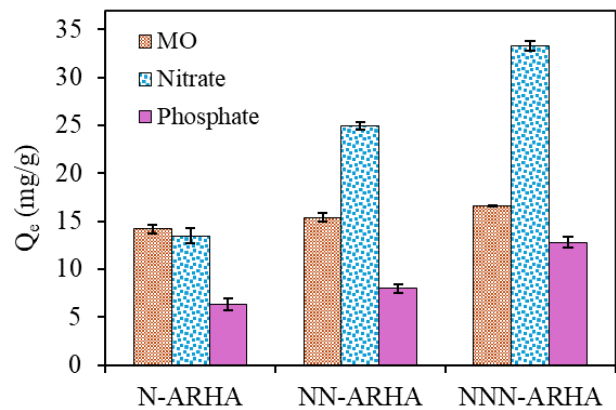


Fig. 6. Effect of grafted amine type on the adsorption capacity of the material. (Experimental conditions: N-(monoamine), NN-(diamine), NNN-(triamine)ARHA (5% HF, 3 mL amine solution/g ARHA) 0.6 g/L, C_{MO} 10 mg/L, $C_{nitrate}$ 50 mgNO₃⁻-N/L, $C_{phosphate}$ 10 mgPO₄³⁻-P/L, $t \sim 30$ min)

The results clearly show that the triamine material (TRI-ARHA) exhibited better adsorption performance than the monoamine and diamine materials for all three targets, including MO, especially nitrate and phosphate. This is attributed to the fact that the number of amine sites, calculated as N, in the triamine group within a grafted organic silane molecule is 3 and 1.5 times higher than that of the monoamine and diamine groups, respectively. This result is consistent with the research by Safia et al. [21] on the influence of amine groups grafted onto the SBA-15 support for the removal of nitrate and phosphate ions. Therefore, the material synthesis procedure utilized the triamine group for the surface grafting reaction to enhance the nitrate and phosphate adsorption capacity of ARHA.

In summary, the key factors significantly influencing the adsorption efficiency of TRI-ARHA for MO, nitrate, and phosphate have been clearly demonstrated. Among these, triamine was the chosen functional group for the surface grafting reaction in material fabrication [21, 24]. The two remaining influencing factors, including the HF concentration for the rice husk ash activation and the triamine silane/ARHA ratio, will be further optimized using experimental design to determine the optimal conditions for the material synthesis process.

3.2. Optimizing the synthesis parameters of TRI-ARHA material

Optimization of the material synthesis conditions was performed using Design-Expert software, employing a quadratic optimization model and Central Composite Design [25]. The experimental plan was established with two influencing factors: A – HF concentration (%), B – triamine silane/ARHA ratio (mL/g), and three responses: R1 – MO adsorption capacity (mg/g), R2 – nitrate adsorption capacity (mg/g), and R3 – phosphate adsorption capacity (mg/g). The experimental

design range for each factor was selected as the region likely to achieve extreme values according to the outcomes of the preliminary investigations into influencing variables. Specifically, the HF concentration was chosen from 3% to 7%, and the triamine silane/ARHA ratio from 1 mL/g to 4 mL/g. The design methodology dictated the boundaries and the discrete levels of the influencing factors, which are detailed in Table 1. Table 2 displays the experimental design matrix alongside the corresponding results obtained from each experiment.

Table 1. The limits and variation levels of the influencing factors.

No.	Factors	Coding variables	Unit	Research range				
				-1.414 (- α)	-1	0	+1	+1.414 (+ α)
1	HF concentration	X ₁	%	2.172	3	5	7	7.828
2	Triamine silane /ARHA ratio	X ₂	mL/g	0.379	1	2.5	4	4.621

Table 2. Experimental design matrix and corresponding experimental results.

Std	Run	Factor 1	Factor 2	Response 1	Response 2	Response 3
		A:HF %	B:Triamine silane/ARHA mL/g	MO mg/g	Nitrate mg/g	Phosphate mg/g
1	12	3	1	14.2	18.9	3.65
2	9	7	1	16.4	9.89	2.15
3	2	3	4	14.5	29.3	10.9
4	4	7	4	15.6	16.1	5.14
5	13	2.172	2.5	10.4	23.4	8.24
6	11	7.828	2.5	16.6	13.8	5.02
7	1	5	0.379	15.2	10.2	2.53
8	7	5	4.621	14.6	31.5	12.0
9	3	5	2.5	16.2	32.7	12.6
10	8	5	2.5	16.0	32.2	12.2
11	10	5	2.5	15.9	32.5	12.8
12	5	5	2.5	16.1	32.8	12.6
13	6	5	2.5	16.1	32.7	12.7

The coded second-order polynomial model representing how the adsorption capacities of TRI-ARHA for MO, nitrate, and phosphate are affected by the influencing factors, HF concentration (%) and triamine silane/ARHA ratio (mL/g), has the following form: $Y = a_0 + a_1X_1 + a_2X_2 + a_{12}X_1X_2 + a_{11}X_1^2 + a_{22}X_2^2$. Table 3 shows the calculated coefficient values for the models pertaining to the three responses under investigation.

As evidenced by the modeling outcomes presented in Table 3, both HF concentration and the triamine silane/ARHA ratio play a role in determining the

TRI-ARHA material's adsorption capacities for MO, nitrate, and phosphate. Specifically, the coefficients a_1 and a_{11} in all three models have p -values < 0.05. This suggests that HF concentration plays a crucial role in determining the material's capacity to adsorb MO, nitrate, and phosphate. Meanwhile, the coefficients a_2 and a_{22} have p -values < 0.05 in the nitrate and phosphate models but have p -values > 0.05 in the MO model. This result implies that the triamine silane/ARHA ratio is a major influencing factor on nitrate and phosphate adsorption capacities, but does not

significantly influence the MO adsorption capacity. The coefficient α_{12} has *p-values* > 0.05 in all cases, demonstrating that the interaction between the two factors within the investigated range is small and does not create a significant influence on the three responses.

Figure 7 illustrates the desirability plots and contour plots for the analyzed responses. The simulation outcomes suggest that the experimental design range for finding extreme values for the responses is appropriate. The highest adsorption capacities for MO, nitrate, and phosphate by the TRI-ARHA material can be achieved within the investigated range.

The overlay plot between the investigated regions and the optimal point determined by Design-Expert software is shown in Figure 8. The results

determined the maximum adsorption capacities of the TRI-ARHA material for MO, nitrate, and phosphate to be ~ 15.8 mgMO/g, ~ 34.3 mgNO₃⁻-N/g, and ~ 13.4 mgPO₄³⁻-P/g, respectively, with material synthesis conditions at an HF concentration of ~ 4.86% and a triamine silane/ARHA ratio of ~ 3.12 mL/g.

To verify the calculated results from the model, a practical experiment with the optimal material synthesis conditions was conducted, yielding the results shown in Table 4. The adsorption capacities of the TRI-ARHA material for MO, nitrate, and phosphate were found to be ~ 15.7 mgMO/g, ~ 34.0 mgNO₃⁻-N/g, and ~ 13.1 mgPO₄³⁻-P/g, respectively. The verification demonstrated that experimental findings align with the model's calculated outcomes.

Table 3. Coefficients of the second-order polynomial model for the responses

Coefficients of the model		α_0	α_1	α_2	α_{12}	α_{11}	α_{22}
	MO	16.06	1.5085	-0.1686	-0.2750	-1.0363	-0.3363
p-values	0.0146		0.0021	0.6138	0.5616	0.0192	0.3587
	Nitrate	32.58	-4.4733	5.8416	-1.0475	-7.2844	-6.1594
p-values	< 0.0001		0.0008	0.0002	0.3809	< 0.0001	0.0002
	Phosphate	12.58	-1.4767	2.9541	-1.065	-3.3469	-3.0294
p-values	< 0.0001		0.0038	< 0.0001	0.0674	< 0.0001	< 0.0001

Note: Coefficients exhibiting *p-values* greater than 0.05 indicate a lack of statistical significance at the conventional 95% confidence threshold.

Table 4. Comparison of experimental and predicted results under optimal synthesis conditions.

HF (%)	Triamine silane/ARHA (mL/g)		MO (mg/g)	Nitrate (mg/g)	Phosphate (mg/g)	Desirability
4.86	3.12	Predict	15.8	34.3	13.4	0.931
		Experiment	15.7	34.0	13.1	

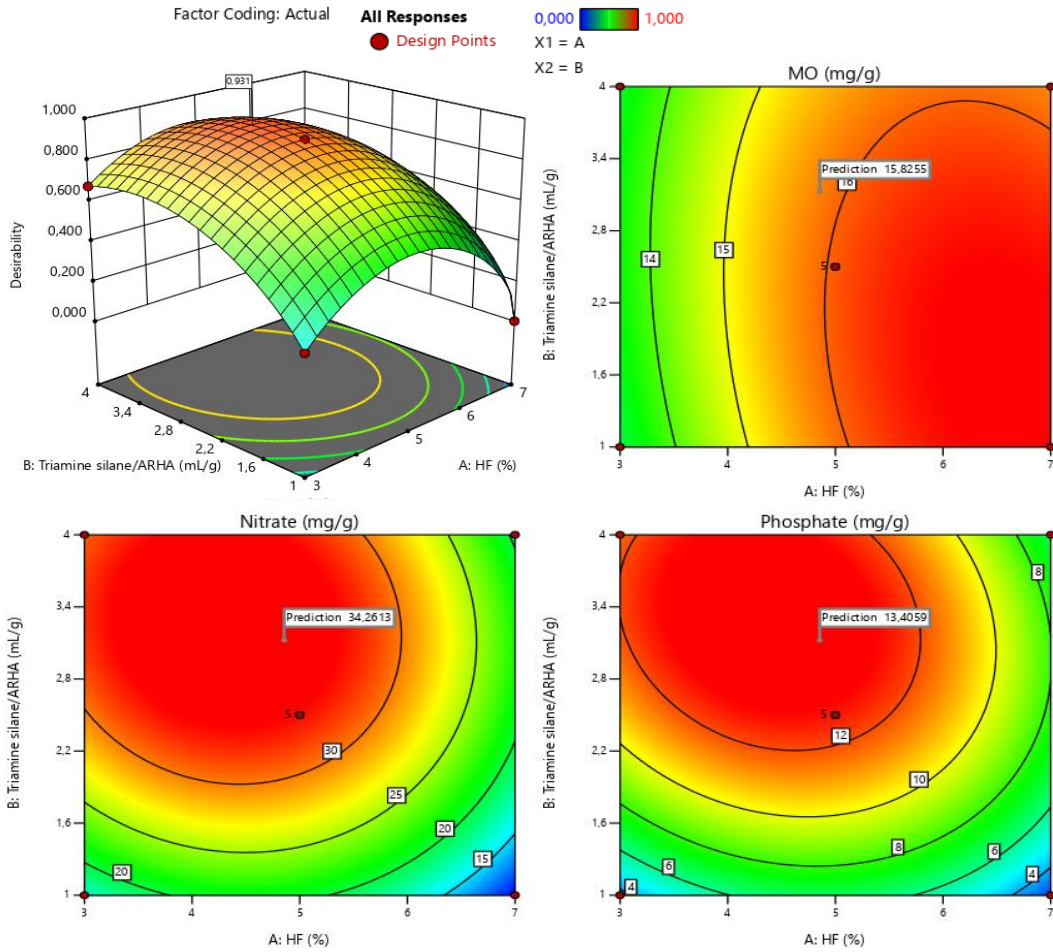


Fig. 7. Desirability plots and contour plots of the responses.

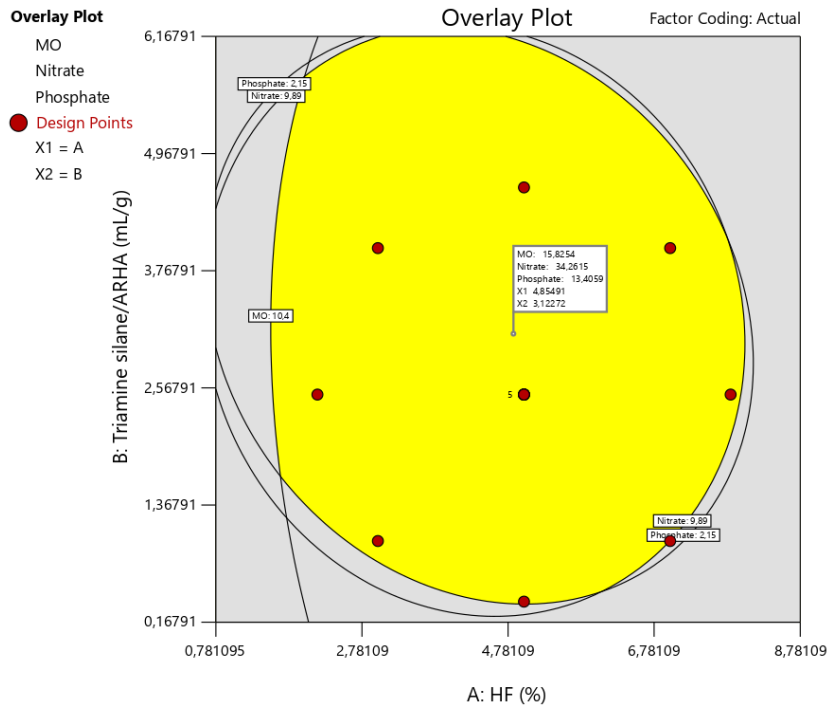


Fig. 8. Overlay plot of the experimental design space and the location of the optimal point.

4. Conclusion

This study demonstrated that the HF acid concentration used for activating rice husk ash to create the ARHA support and the triamine silane/ARHA ratio are two major factors influencing the adsorption efficiency of the material.

Optimization using response surface methodology determined the optimal HF concentration to be approximately 4.86% and the optimal triamine silane/ARHA ratio to be approximately 3.12 mL/g.

The research results showed that the TRI-ARHA material synthesized under optimal conditions exhibited adsorption capacities for MO, nitrate, and phosphate of approximately 15.7 mgMO/g, 34.0 mgNO₃⁻-N/g, and 13.1 mgPO₄³⁻-P/g, achieving 93.1% of the expected level predicted by the model. The optimization results of the TRI-ARHA material synthesis conditions from this study provide a basis for further research on a pilot model and propose a feasible material production process for practical applications towards commercializing this promising adsorbent material.

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Author's contribution

Phuoc Toan Phan: Investigation, Lab experiments, Data curation, Writing of original draft, Project administration. Quynh Anh Nguyen Thi: Visualization, Formal analysis, Review and editing. Tri Thich Le: Lab experiments, Data curation, Review and editing. Nhat Huy Nguyen: Methodology, Supervision and Editing the final draft. Trung Thanh Nguyen: Conceptualization, Validation, Advisor.

Conflict of interest

No potential conflict of interest was reported by the authors.

Data availability

The datasets generated and/or analyzed during the current study are available from the corresponding author on reasonable request.

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References

- [1] Manasa, R. L., & Mehta, A. (2020). Wastewater: Sources of pollutants and its remediation. In K. Gothandam, S. Ranjan, N. Dasgupta, & E. Lichtfouse (Eds.), *Environmental biotechnology Vol. 2 (Environmental Chemistry for a Sustainable World, Vol. 45)*. Springer International Publishing. (pp. 197-219)
https://doi.org/10.1007/978-3-030-38196-7_9
- [2] Akinawo, S.O. (2023). Eutrophication: Causes, consequences, physical, chemical and biological techniques for mitigation strategies. *Environmental Challenges*, 12, 100733.
<https://doi.org/10.1016/j.envc.2023.100733>
- [3] Yadav, A., Bagotia, N., Sharma, A. K. & Kumar, S. (2021). Simultaneous adsorptive removal of conventional and emerging contaminants in multi-component systems for wastewater remediation: A critical review. *Science of The Total Environment*, 799, 149500.
<https://doi.org/10.1016/j.scitotenv.2021.149500>
- [4] Crini, G., Lichtfouse, E. (2019). Advantages and disadvantages of techniques used for wastewater treatment. *Environmental Chemistry Letters*, 17(1), 145-155.
<https://doi.org/10.1007/s10311-018-0785-9>
- [5] Rattanapan, S., Srikram, J. & Kongsune, P. (2017). Adsorption of methyl orange on coffee grounds activated carbon. *Energy Procedia*, 138, 949-954.
<https://doi.org/10.1016/j.egypro.2017.10.064>
- [6] Zhang, Y., Song, X.L., Huang, S.T., Geng, B.Y., Chang, C.H. & Sung, I.Y. (2014). Adsorption of nitrate ions onto activated carbon prepared from rice husk by NaOH activation. *Desalination and Water Treatment*, 52(25-27), 4935-4941.
<https://doi.org/10.1080/19443994.2013.809984>
- [7] Sundari, C.D.D. et al. (2018). Synthesis of zeolite L using rice husk ash silica for adsorption of methylene blue: kinetic and

- adsorption isotherm. *MATEC Web of Conferences*, 197, 05002.
<https://doi.org/10.1051/mateconf/201819705002>
- [8] Fakhri, V. et al. (2024). Green solutions for blue waters: Using biomaterials to purify water from microplastics and nanoplastics. *Journal of Water Process Engineering*, 65, 105854.
<https://doi.org/10.1016/j.jwpe.2024.105854>
- [9] Tatarchuk, T., Bououdina, M., Al-Najar, B., & Bitra, R. B. (2019). Green and ecofriendly materials for the remediation of inorganic and organic pollutants in water. In M. Naushad (Ed.), *A new generation material graphene: Applications in water technology* (pp. 69-110). Springer International Publishing.
https://doi.org/10.1007/978-3-319-75484-0_4
- [10] Phan, P.T., Nguyen, T.T., Padungthon, S., Nguyen, T.T. & Nguyen, N.H. (2022). A novel conjugate mechanism for enhancing the adsorption capacity of amine-functionalized activated rice husk ash for simultaneous removal of organics and anions in wastewater: Experimental and theoretical explanations. *ACS Omega*, 7(33), 28866-28874.
<https://doi.org/10.1021/acsomega.2c01955>
- [11] Phan, P.T., Nguyen, T.T., Nguyen, N.H. & Padungthon, S. (2018). Triamine-bearing activated rice husk ash as an advanced functional material for nitrate removal from aqueous solution. *Water Science and Technology*, 79(5), 850-856.
<https://doi.org/10.2166/wst.2018.445>
- [12] Nguyen, T.T. (2016). Amine-bearing activated rice husk ash for CO₂ and H₂S gas removals from biogas. *KKU Engineering Journal*, 43(S3), 396-398.
<https://doi.org/10.14456/kkuenj.2016.139>
- [13] Oza, S., Kodgire, P. & Kachhwaha, S. S. (2022). Analysis of RSM based BBD and CCD techniques applied for biodiesel production from waste cotton-seed cooking oil via ultrasound method. *Analytical Chemistry Letters*, 12(1), 86-101.
<https://doi.org/10.1080/22297928.2021.2019611>
- [14] Phan, P.T., Nguyen, T.T. & Ngo, T.D.T. (2016). Characterizations and methyl orange adsorption capacity of activated rice husk ash. *Journal of Science, Can Tho University*, 42(A), 50-57.
<https://doi.org/10.22144/ctu.jvn.2016.039>
- [15] Bhatnagar, A., Sillanpää, M. (2011). A review of emerging adsorbents for nitrate removal from water. *Chemical Engineering Journal*, 168(2), 493-504.
<https://doi.org/10.1016/j.cej.2011.01.103>
- [16] Huang, W., Zhang, Y. & Li, D. (2017). Adsorptive removal of phosphate from water using mesoporous materials: A review. *Journal of environmental management*, 193, 470-482.
<https://doi.org/10.1016/j.jenvman.2017.02.030>
- [17] Loganathan, P., Vigneswaran, S. & Kandasamy, J. (2013). Enhanced removal of nitrate from water using surface modification of adsorbents—A review. *Journal of environmental management*, 131, 363-374.
<https://doi.org/10.1016/j.jenvman.2013.09.034>
- [18] Bondioli, F., Andreola, F., Barbieri, L., Manfredini, T. & Ferrari, A.M. (2007). Effect of rice husk ash (RHA) in the synthesis of (Pr, Zr)SiO₄ ceramic pigment. *Journal of the European Ceramic Society*, 27(12), 3483-3488.
<https://doi.org/10.1016/j.jeurceramsoc.2007.01.019>
- [19] Saad, R., Belkacemi, K. & Hamoudi, S. (2007). Adsorption of phosphate and nitrate anions on ammonium-functionalized MCM-48: Effects of experimental conditions. *Journal of Colloid and Interface Science*, 311(2), 375-381.
<https://doi.org/10.1016/j.jcis.2007.03.025>
- [20] Saad, R., Hamoudi, S. & Belkacemi, K. (2008). Adsorption of phosphate and nitrate anions on ammonium-functionalized mesoporous silicas. *Journal of Porous Materials*, 15(3), 315-323.
<https://doi.org/10.1007/s10934-006-9095-x>
- [21] Safia, H., Abir, E.N., Maissa, B. & Khaled, B. (2012). Adsorptive removal of nitrate and phosphate anions from aqueous solutions using functionalised SBA-15: Effects of the organic functional group. *The Canadian Journal of Chemical Engineering*, 90(1), 34-40.
<https://doi.org/doi:10.1002/cjce.20582>
- [22] Hamoudi, S., Saad, R. & Belkacemi, K. (2007). Adsorptive removal of phosphate and nitrate anions from aqueous solutions using ammonium-functionalized mesoporous silica. *Industrial & Engineering Chemistry Research*, 46(25), 8806-8812.
<https://doi.org/10.1021/ie070195k>
- [23] Hayichelaeh, C., Reuvekamp, L., Dierkes, W.K., Blume, A., Noordermeer, J.W.M. & Sahakaro, K. (2018). Enhancing the silanization reaction of the silica-silane system by different amines

in model and practical silica-filled natural rubber compounds. *Polymers*, 10(6), 584.

<https://doi.org/10.3390/polym10060584>

- [24] Ghorbani, M., Nowee, S.M. (2015). Kinetic studies of Pb and Ni adsorption onto MCM-41 amine-functionalized nano particle. *Advances in Environmental Technology*, 1(2), 101-104.

<https://doi.org/10.22104/aet.2015.269>

- [25] Nematzadeh, M., Samimi, A., Shokrollahzadeh, S. & Mohebbi-Kalhari, D. (2019). Bentazon removal from aqueous solution by reverse osmosis; optimization of effective parameters using response surface methodology. *Advances in Environmental Technology*, 5(4), 193-201.

<https://doi.org/10.22104/aet.2020.4228.1209>

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