Edelweiss Applied Science and Technology
ISSN: 2576-8484
Vol. 8, No. 6, 8514-8533
2024
Publisher: Learning Gate
DOI: 10.55214/25768484.v8i6.3826

Optimizing of phosphate and ammonium removal from wastewater using modified zeolite: A response surface methodology approach

Mohammed Nabeel[1*], Ammar Salman Dawood[2]
[1,2]Department of Civil Engineering, University of Basrah, 42001 Basrah, Iraq; engnabeel24@gmail.com (M.N.).

Abstract: Nutrient contamination of wastewater, especially phosphate and ammonium, is a growing problem that poses major environmental and human health risks in terms of eutrophication and loss of biodiversity. Traditional methods for wastewater treatment may be highly effective, but they often come at a significant economic cost as well as environmental drawbacks. To maximize this nutrient removal these nutrients are removed using modified zeolite which is low-cost and highly effective. The Response Surface Methodology (RSM) is used in this study to enhance nutrient retention conditions, regardless of pH, contact time, and amount of adsorbent. A Central Composite Design (CCD) was then applied to study as extensively as possible the influence of these factors on this adsorption process. In important results, the alternative zeolite demonstrates 93.9% and 73% removal efficiencies for phosphate and ammonium under optimal conditions, respectively, suggesting a better performance of the modified zeolite compared to unmodified counterparts. These results highlight the promise presented by modified zeolite as a sustainable approach to enhancing current wastewater treatments in meeting or exceeding stringent environmental standards and minimizing eutrophication threats. This work is groundbreaking as it addresses large-scale nutrient pollution with a possible solution that has low cost and environmental impacts with the remedy provided by modified zeolite in wastewater treatment.
Keywords: *Adsorbent, Ammonium, Modified zeolite, Phosphate, RSM, Wastewater.*

1. Introduction

Wastewater treatment is the process of removing pollutants from contaminated water before it goes back into the environment. The treatment of wastewater is often regarded as one of topmost environmental problem to solve, yet phosphate and ammonium remain in the effluent as main pollutants. Elevated levels of these nutrients can cause eutrophication that carries algal blooms to waterways. These flowers lower oxygen level in water and make fish sick, furthermore, switching off the ecosystems (Faisal et al., 2023; Kandasamy et al., 2023). Moreover, high concentration of ammonium is toxic to fish and other aquatic organisms, whereas phosphates promote blue-green algal blooms (Inuwa et al., 2023, pp.). Removal of these nutrients is therefore critical not only for water quality, but also for human health and biodiversity protection (Matei et al., 2021; Zhang et al., 2021 p. 110843).

Unsafe disposal of effluent has severe risks to the environment. It can pollute surface and groundwater, causing degradation of drinking water resources and threatening ecosystems (Gao et al., 2024; Lv et al., 2024). The untreated wastewater can lead to adverse effects on the health of some communities that rely on these water sources due to containing pathogens, heavy metals and organic pollutants (Maurya et al., 2023; Morello et al., 2024). Furthermore, soil used for irrigation with untreated wastewater causes decline in quality and agricultural productivity affecting food safety (Aguayo-Acosta et al., 2023; Ton et al., 2023). Consequently, addressing the problems related to waste disposal would have ranked just as highly if we were to apply our environmental management thresholds.

Zeolites are natural or synthetic aluminosilicate minerals characterized by large pore volume, high surface area and ion exchange ability (Bóna et al., 2023; Ferreira et al., 2021, pp.3469-3488). These

* Correspondence: engnabeel24@gmail.com

unusual properties give zeolites the ability to adsorb contaminants such as heavy metals and nutrients, e.g., ammonium and phosphate (Gunawardana et al., 2024; Verma et al., 2024). Due to its specific cation adsorption properties, zeolites play a significant role in wastewater treatment for nitrogen and phosphorus compounds (Caioni et al., 2023; Sun et al., 2024, p. e202301549).

Ammonium in wastewater is decreased effectively due to the ion exchange mechanisms of natural zeolites. Zeolites have also been used in different arrangements (i.e., fixed-bed reactors, batch) to increase nutrient removal efficiencies (Retta et al., 2023; Yuan & Ju, 2023). Thus, these studies show the perspective of zeolites as an environmentally friendly and economic option for nutrient removal from wastewater.

Although zeolites have high potential for nutrient removal, their adsorption property can be modified (Tayyebi et al., 2023; Ursada et al., 2023). These changes may include (Maneelok & Attidekou, 2023; Timofeeva et al., 2023): • The addition of new chemical elements into the lattice to modify their hydrophilicity/hydrophobicity and thus improve selectivity towards either organic or inorganic heavy-metal pollutants. Surface modification by orthophosphorous acid, silylation and alkylation that enables a controllable entrance to zeolite pores with enhanced ion exchange capacity in presence of collision limiters like lysine or ATP1c (dezeuropeaus); Changes in pore structure as a result of dealkalisation process; create significant improvements in zeolite affinity for targeted contaminants Metal ions or functional groups can be present in the zeolite structure increasing ion–exchange capacity and selectivity towards ammonium and phosphate ions such as reported by Asfaha et al. (2022, pp. 1549–1567) and Turzański (2023).

Particular modifications of zeolite may entail the chemical treatment, such as acid or alkali treatment which results in surface area augmentation and enhancement ion-exchange property (Peng et al., 2022; Venturin et al., 2022). Moreover, by combining these in a composite adsorbent through the introduction of nanoparticles or other materials it can achieve even better nutrient removal performance (Lupu et al., 2023; Queiroz et al., 2024). Such modifications are intended to enhance the efficiency of zeolites in wastewater treatment processes, which can better target against the problems of nutrient pollution.

The aim of the present study is to maximize removal of phosphate and ammonium from wastewater by modified zeolite adsorbent. Through these specific nutrients, we hope the development of wastewater treatment solutions to positively impact some of the negative consequences related to nutrient pollution (Luhar et al., 2021). In order to obtain the best condition for nutrient removal, Response Surface Methodology (RSM) will be used in this study. RSM is a statistical method for quantifying the connection among a series of variables and the influence they will have on one response variable (Terrazas-López et al., 2024; Zheng et al., 2022, pp. 1148–1172). The study, therefore, adopts a response surface methodology (RSM) to determine the best conditions for phosphate and ammonium removal as a function of pH, contact time and adsorbent dosage (Mkilima et al., 2024; Saputera et al., 2021). This methodology will shed light on the operational parameters that determine the performance of zeolite in wastewater treatment applications.

2. Literature Review

The most conventional methods for nutrient removal are biological and chemical. Biological processes, however, use microorganisms to break down organic matter and derivation of nitrogen and phosphorus (i.e. activated sludge systems). Although effective, these systems can be energy-intensive and generate large volumes of sludge that needs additional treatment and disposal (Krishna, 2021; Paul & Banerjee,2022). Chemical methods such as coagulation and precipitation introduce chemicals into the wastewater to extract nutrients. These methods can remove high percentage of pollutants, but they are known to cause secondary pollution and higher operational costs as a result of required handling and disposal of chemicals (Krishna 2021; Paul & Banerjee, 2022).

New technologies for removing nutrients are capturing attention globally, having the potential to be more efficient and environmentally acceptable than existing processes. Adsorption processes based on the use of selective materials such as zeolites have been promising for nutrient extraction from wastewater. In this regard, these materials are excellent in capturing ammonium (NH4+) and phosphate ions through processes including but not limited to ion exchange or surface adsorption. Various membrane filtration technologies (e.g., micro and ultrafiltration) are also being investigated as a means to separate nutrients from wastewater, without the need for chemical additives. Although generally effective in providing high-quality effluent reuse, they (can are subjected) to operational challenges like fouling and operational cost (Krishna, 2021; Paul & Banerjee, 2022).

Zeolites, which are microporous aluminosilicate minerals, have been extensively researched for their capability to adsorb nutrients from wastewaters. Ion exchange and adsorption onto the zeolite surface are the principle mechanisms of nutrient adsorption ie., zeolite cations are exchanged for ammonium ions found in wastewater (Krishna, 2021; Paul & Banerjee, 2022). Zeolites are characterized by a high surface area and porosity, which increases their nutrient removal capacity as an adsorbent for ammonium (NH4+) and phosphate (PO43-) (Krishna 2021; Paul & Banerjee 2022).

Zeolite has many advantages as adsorbent materials in wastewater treatment, such as high adsorption capacity and specificity for certain ions, and the process of regeneration is relatively simple (by washing) (Krishna, 2021; Paul & Banerjee, 2022). Apart from this, zeolites also enhance the quality of effluent treated, which makes them useful for different applications such as agricultural reuse. Still, there are restrictions like risking saturation and declining efficiency with time and a change in the fate of the exhausted zeolite has to be handled (Krishna, 2021; Paul & Banerjee, 2022).

Base exchange and other chemical modifications of zeolite can improve its specific selectivity and adsorption property towards particular nutrient element. Changing the surface charge, and creating vacant active sites susceptible for ion exchange due to acid and base treatments (Krishna, 2021; Paul & Banerjee, 2022). Besides, zeolites are also modified to insert certain cations by means of ion exchange processes that enhance their binding towards ammonium and phosphate ions (Krishna, 2021; Paul & Banerjee, 2022).

Thermal treatment and chemical treatment are some of the physical modifications that can improve structural integrity and porosity of zeolite allowing higher adsorption performance (Krishna, 2021; Paul & Banerjee, 2022). Different metal oxides or other materials can also be impregnated to develop composite adsorbents for increased nutrient removal efficiency (Krishna, 2021; Paul & Banerjee, 2022).

The response surface methodology (RSM) is a statistical method used to treat responses given a number of factors and their interactions, and its effect on any response variable (Krishna, 2021; Paul & Banerjee, 2022). RSM involves design of experiments, development of a mathematical model followed by the use of the model to determine conditions that provide an optimal value for the desired response. Krishna (2021) and Paul & Banerjee (2022) suggested to make the appropriate explorations of response surface, Linking Response Surface Methodology (RSM) are helpful for the complex systems that include equilibrium interaction of all components. RSM is a well-established technique that has been extensively used for optimization of environmental engineering processes such as wastewater treatment (Krishna, 2021; Paul & Banerjee, 2022). This method is carried out to systematically study the dependence of various operational parameters (pH, temperature and time) on the adsorption capacity of zeolites and other adsorbents for improving nutrient removal efficiency (Krishna, 2021; Paul & Banerjee, 2022). RSM can help scientists create optimal conditions for high nutrient removal at low-cost and lower environmental impacts (Krishna, 2021; Paul & Banerjee, 2022).

3. Material and Methods

3.1. Characterization of Wastewater Samples

Real wastewater from the University of Basrah was used as a representative sample, considering the wastewater's properties. This wastewater analysis revealed that the phosphate concentration was 32.95 mg/L, and the ammonia-nitrogen concentration was 21 mg/L. The pH was tested; the result was a value of 6.7. After that, this sample was used for the experiment.

3.2. Experimental Procedure

3.2.1. Zeolite's Modification Process

The natural zeolite underwent several modifications to improve its characteristics. First, 300 mL flasks containing 1 gram of natural zeolite were added .Each holds 100 milliliters of a NaCl solution

(2.1%). The flasks were then kept at a room temperature of (25°C) and stirred at (200) rpm for a duration of (2 hours) to ensure thorough interaction between the zeolite and the NaCl solution. After applying the sodium chloride treatment, the zeolite was dried in an oven at 105°C to remove any residual moisture. Then, the treated zeolite was exposed to a second treatment with a 0.41% $FeCl_3$ solution for 1 hour. The main goal of this step was the introduction of iron elements in the structure of zeolite. $FeCl_3$ was added to the zeolite for sublimation ion exchange that further occurred at 200°C for 1 hour in order to increase the intake of iron. Thereafter, the zeolite has been heated at 200°C for 2 hours for the purpose of stabilization and activation of the modified zeolite. As a result, the modified zeolite lost its moisture, and internal porosity has been promoted. Further transporting and storage of obtained zeolites were possible in the same conditions. Special treatment of the zeolite assured better catalytic properties, and stability, and allowed for a wider range of applications. Crash cooling in a closed hermetic ensures that the altered zeolite will not be further contaminated. The second application of the alteration did not occur. The powder was stored in a dry medium. The purpose of alteration was both a supplementation of cheep silica for a later application and achieving the highest possible intensity of altered Zeolite. This process was designed to generate the desired results. After prepared modified zeolite with required conditions, it was further characterized by using SEM and XRD which was used to know its property.

3.2.2. Batch Adsorption Experiments

For the Adsorption experiments that was used, the 330 mLflask was used. 150 mL of wastewater was placed in each flask, modified zeolite was added to it, Flasks were stirred on a shaker at 150 rpm for a fixed contact time at room temperature (25 °C). The following weights (0.05-0.3) grams of modified zeolite were taken with times (2-12) minutes to achieve the removal of phosphate in the experiments. Whereas, weights of (0.25-0.75) of the modified zeolite with times (15-45) and of the modified zeolite are used for the ammonium experiment.

A Composite Central Design (CCD) configuration was employed to identify the optimal values for every variable. The parameters analyzed included the modified zeolite dosage and agitation duration, featuring 5 central points, 4 axial points, and 4 cubic points in the adsorption experiment findings. The optimization of this treatment was assessed by the maximum removal of phosphate and ammonium.

3.2.3. Experimental Design

The data analysis employed a response surface technique utilizing a Composite Central Design (CCD), a Response Surface Design derived from factorial design, to optimize phosphate and ammonium removal in batch adsorption experiments. This approach included axial and central points to facilitate curvature estimation for further optimization. Equation 1 illustrates the employed second-order regression model.

$$y = b_0 + \sum_{i=1}^{n} b_i X_i + \sum_{1 \le i \le j}^{n} b_{ij} X_i X_j + \sum_{1 \le i \le j}^{n} b_i X_i^2 X_j^2 \quad .(1)$$

Where:

X is an answer

X_1 and X_2 are manipulated factors

b_0, β_i, β_{ij} are unknown parameters

X_i, X_{ij}, are the study factors.

ANOVA is used to analyze and interpret factorial design data to find significant statistical differences. The model was validated using acceptability analysis, which measured F-value and p-value and model fit using R^2, R^2-adjusted, and R^2-predictive.

3.3. Analysis of Ammonia and Phosphate Determination Methods

The phosphates and ammonia-nitrogen content of the water samples were determined using the Macro-Kjeldahl Method and Ascorbic Acid Method [APAH (2017)].

The laboratory investigation used equations (2–3) to calculate Ammonia and Phosphate removal efficiency.

$$\text{Ammonia Removal, \%} = [(NH_{3o}-NH_{3f})/(NH_{3o})]*100 \quad (2)$$

where NH_{3o} is the initial and NH_{3f} is final Ammonia.

$$\text{Phosphate Removal, \%} = [(PO_{4o}-PO_{4f})/(PO_{4o})]*100 \quad (3)$$

where PO_{4o} is the initial and PO_{4f} is final Phosphate.

3.4. Characterization of Modified Zeolite

3.4.1. Scanning Electron Microscope (SEM)

Differences in morphology and structural properties of natural and modified zeolites were assessed through the use of scanning electron microscopy test. This test examines the general appearance of the zeolite surface structures, revealing their size, pore, and distribution specific for the samples. As the magnification is quite high, the modifications and their influences on physical properties can be explained, and perception of the artifacts could be achieved if viewed in low magnifications. Since the differences in surface structures and texture are shown, it is evident that physical properties of the zeolite could also follow the changes. An important part of the SEM is that it allows merging the natural zeolite sample with the modified one to do a general and more in-depth analysis of how treatments differ one material from another and how it follows potential effects of use.

3.4.2. X-ray Diffraction (XRD)

This technique can be used to characterize zeolites and to determine their uses. It can be vital for examining the atomic arrangement within zeolite crystals and determining crystallinity and structural changes. By contrasting the XRD patterns of natural and modified zeolites, researchers can use these to assess the effects of a treatment on their structural integrity and their uses. In discussing the characterization zeolites and expanding its uses, the diffractogram first helped identify the mineral compounds in this sample and second observed the changes that occurred to this mineral due to the mineralization of the zeolite. This technique can be vital for examining the atomic arrangement within zeolites, their phase relationships, and their uses. It reveals the atomic arrangement and the size of lattice structure, and it can be invaluable for predicting those behaviours. It can be essential for developing new material from existing ones, a prime example of which is zeolite, and predicting their uses. These implications have the potential to enhance the uses of zeolites within the industries of catalysis and environmental remediation.

3.5. Optimization Approach Methodology

Response surface methodology (RSM) is an efficient method of experimental design and (or) optimization (Bidira et al. 2023). In other words, this involves taking input variable combinations that are different from each other, to predict (model) the response variable of interest (Keshmiri-Naqab and Taghavijeloudar 2023). RSM with experimental data is used to construct model while ANOVA is used for determining relative significance of each variable and interaction term (Nnaji et al. 2020). Evaluation of model was done with cross validation and model validation against actual experimental data. The estimated coefficients were computed and a 95% confidence interval was computed for the coefficients. Minitab version 22 was used for the experimental tests using central composite design (CCD) framework using response surface methodology (RSM). The CCD was used to optimise batch adsorption processes to study the effect of modified zeolite at various mixing durations. Abbas et al (2021) stated this study determined modified zeolite dosage and stirring time levels and ranges (Tables 1 and 2).

Table 1.
Shows each independent variable's maximum and minimum value for Ammonia experiments.

Parameters	Independent variable	Units	Levels and ranges		
			-1.0	**0.0**	**+1.0**
A	Modified Zeolite dose	g/L	0.250	0.500	0.750
B	Stirring time	minutes	15	30	45

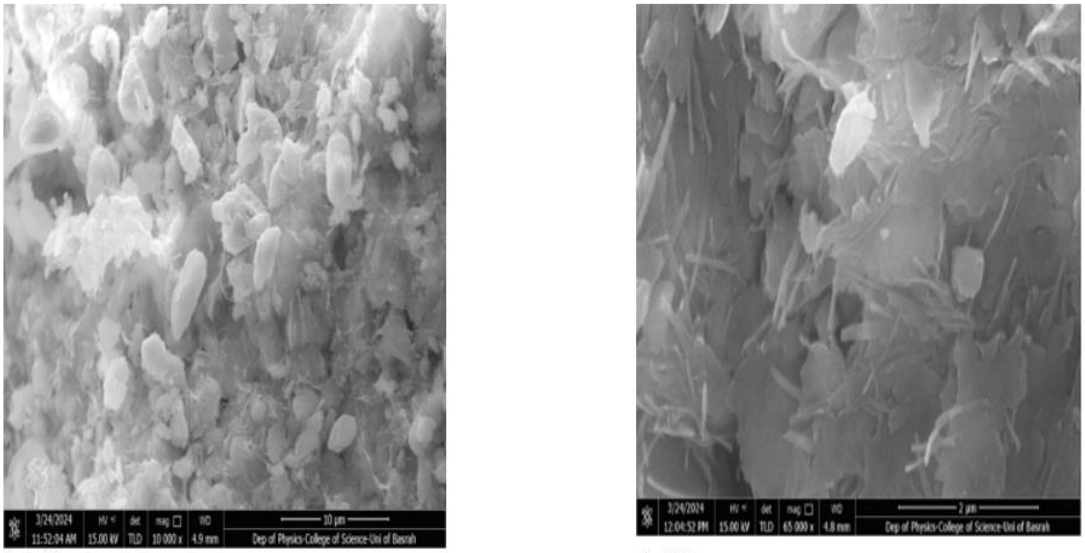
Table 2.
Shows each independent variable's maximum and minimum value for Phosphate experiments.

Parameters	Independent variable	Units	Levels and ranges		
			-1.0	**0.0**	**+1.0**
A	Modified Zeolite dose	g/L	0.050	0.175	0.300
B	Stirring time	minutes	2	7	12

4. Results and Discussion

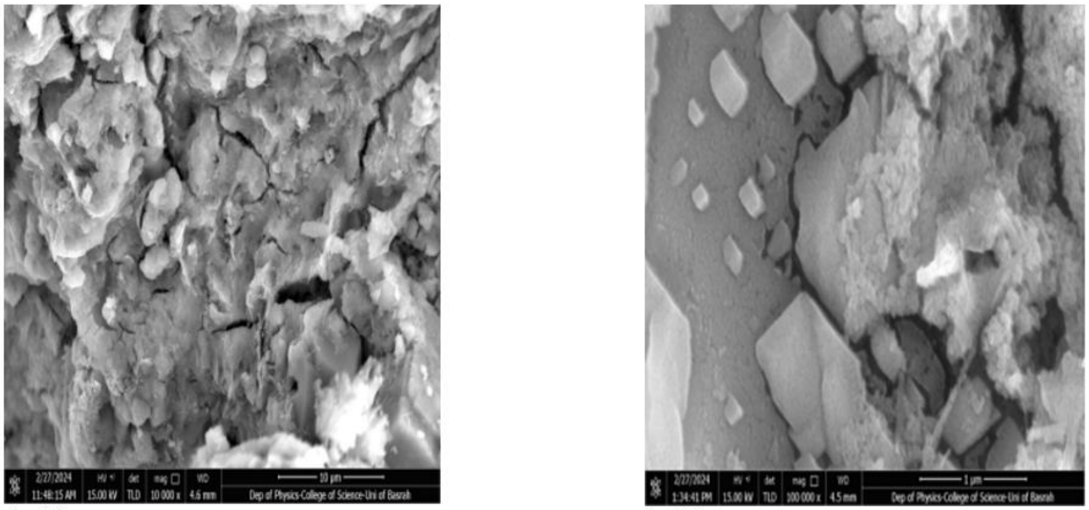
4.1. SEM Analysis

According to Figure (1-A, B) and Figure (2-A, B), there are clear variations between the natural and modified zeolite in the SEM pictures regarding its surface properties. These differences highlight how the modification processes alter the overall morphology of the zeolite, demonstrating changes in porosity and surface area as well. This indicates the significant impact of modification techniques on zeolite structure, suggesting that such enhancements could optimize their performance for various applications in fields such as catalysis and environmental remediation. In comparison to the surface of modified zeolite, the surface of natural zeolite appears smoother and less textured. This indicates that the natural form may be less reactive in specific applications. The modified zeolite, on the other hand, exhibits a more complex morphology with the presence of pores and a more distributed surface, which plays a crucial role in enhancing its functionality. This intricate structure helps to raise the material's surface area, thereby increasing adsorption and allowing for more efficient interaction with various substances in practical uses. Moreover, the enhanced properties of modified zeolite can lead to improved efficiency in applications such as catalysis and environmental remediation, where maximized surface interactions are beneficial.



(1-A) **(1-B)**

Figure 1.
SEM images for natural zeolite.



(2-A) **(2-B)**

Figure 2.
SEM images for modified zeolite.

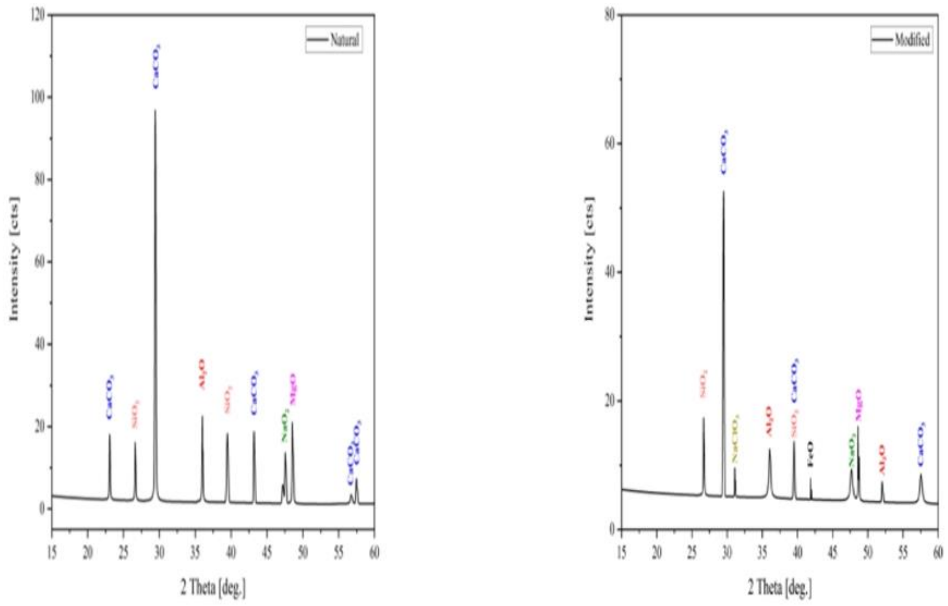
4.2. XRD Analysis

From Figures (3-A, B), it is clear that there is an increase in Aluminum Oxide (Al_2O_3) Content: The percentage increased from 3% to 4%, indicating the impact of modifications on the chemical structure, enhancing the stability of zeolite and its ability to interact with adsorbed molecules. This small yet significant shift suggests that even minor modifications can lead to considerable improvements in material properties. Additionally, the enhanced stability could further facilitate the zeolite's application in a variety of industrial and environmental processes, making it a more effective adsorbent.

Furthermore, there is an increase in Calcium Carbonate ($CaCO_3$) Content: The percentage increased from 19% to 50%, which may affect the crystalline structure of zeolite and increase the active surface areas. This dramatic rise in calcium carbonate content could lead to changes in the morphology of the zeolite, possibly resulting in improved performance in catalysis or ion-exchange processes. The higher active surface area may also promote better interactions with reactants, leading to enhanced reaction efficiencies.

Moreover, there is an increase in Sodium Oxide (Na_2O) and Magnesium Oxide (MgO) Content: These increased from 10% to 17% and from 3% to 9%, respectively, enhancing the chemical reactivity of zeolite. These changes in oxide content not only indicate a modification in the zeolite's active sites but may also contribute to a broader spectrum of applications for the material. Enhanced chemical reactivity may open new avenues for utilizing zeolites in various catalytic processes, environmental remediation, and other applications requiring selective adsorption capabilities.

DOI: 10.55214/25768484.v8i6.3826



(3-A) **(3-B)**

Figure 3.
XRD images for (A) natural and (B) modified zeolite.

4.3. Effects of Chemical Modifications

Introduction of Iron (FeO): Incorporating Iron (FeO) into the adsorption process not only enhances the adsorption properties by providing additional active sites for interaction but also contributes to a more robust structure, thereby promoting stability. The augmented presence of iron compounds can lead to the formation of a network that helps to capture a wider range of contaminants effectively.

An increase in Calcium Carbonate (CaCO3) further enhances the interaction effectiveness with adsorbed molecules by increasing active surface areas, which results in a greater potential for absorption and interaction with pollutants present in the environment. The improved surface area allows for a more extensive engagement with various contaminants, thus maximizing the overall efficiency of the adsorption process.

The presence of Sodium Chlorate (NaClO3) may enhance the chemical reactivity of zeolite, improving its ability to remove various harmful substances from different environments, as it actively engages in chemical reactions and helps facilitate the exchange between ions present in the zeolite.

In general, the introduction of new chemical compounds, such as NaClO3, should be considered strategically to maximize the potential effectiveness of the adsorption materials (see Tables 3 and 4 for details on performance metrics). X-ray diffraction (XRD) analysis results clearly indicate that the chemical modifications implemented have significantly improved the ability of zeolite to remove substances, thereby rendering it a much more efficient and versatile material for a range of adsorption applications in environmental remediation. This improvement paves the way for future research and development, targeting other modifications that could further optimize the performance of zeolite in real-world applications.

Table 3.
Natural Zeolite compounds.

No	Compound name	Chemical formula	Quantification%	Reference code
1	Silicon oxide	SiO2	65	JCPDS: 085-0335
2	Aluminum oxide	Al2O	3	JCPDS: 075-0277
3	Calcium carbonate [Calcite]	CaCO3	19	JCPDS: 083-0578
4	Sodium oxide	NaO2	10	JCPDS: 077-0210
5	magnesium oxide [Periclase]	MgO	3	JCPDS: 901-3246

Table 4.
Modified Zeolite compounds.

No	Compound name	Chemical formula	Quantification%	Reference code
1.	Silicon Oxide	SiO2	10	JCPDS: 085-0798
2.	Aluminum Oxide	Al2O	4	JCPDS: 075-0277
3.	Calcium Carbonate [Calcite]	CaCO3	50	JCPDS: 085-1108
4.	Sodium Oxide	NaO2	17	JCPDS: 077-0210
5.	magnesium oxide [Periclase]	MgO	9	JCPDS: 901-3240
	Sodium Chlorate	NaClO3	8	JCPDS: 085-2189
	Iron Oxid	FeO	2	JCPDS: 101-1199

4.4. Ammonium Removal Rate

Table 5 presents the two-factor composite central design (CCD) analysed, comprising modified zeolite dosage and stirring time, along with a 3-level adsorption rate for each factor, detailing both observed and predicted values for the experimental ammonia percent removal and ammonia predicted by the multiple regression model. The maximum ammonium removal rate was 73%, while the minimum was 40% during the adsorption process.

Table 5.
Ammonium removal rate in the adsorption process by central composite design (CDD).

No.	Modified Zeolite dose (g/L)	Stirring time (min.)	Ammonia (mg/L)	Ammonium Removal (%)
1	0.75	15		46.666
2	0.5	30		48
3	0.5	30		50
4	0.25	15		40
5	0.5	45		60
6	0.5	30		50
7	0.5	15		43.333
8	0.75	30		53.33
9	0.5	30		50
10	0.5	30		46
11	0.25	45		60
12	0.25	30		46.66
13	0.75	45		73

The importance of each model parameter for the ammonium removal rate, as shown in Table 6, was assessed using the F-value test and p-values for each variable, including linear and quadratic interactions. P-values below 0.05 indicate that the model coefficients are significant.

Table 6.
Two-factor ANOVA on the adsorption process for Ammonium removal rate.

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	5	917.68	183.536	43.98	0.000
Linear	2	777.25	388.627	93.12	0.000
Time	1	661.71	661.710	158.55	0.000
Dose	1	115.54	115.545	27.69	0.001
Square	2	130.38	65.189	15.62	0.003
Time*time	1	58.86	58.859	14.10	0.007
Dose*dose	1	23.98	23.977	5.75	0.048
2-Way Interaction	1	10.05	10.049	2.41	0.165
Time*dose	1	10.05	10.049	2.41	0.165
Error	7	29.21	4.173		
Lack-of-Fit	3	17.65	5.883	2.03	0.252
Pure Error	4	11.56	2.891		

Table 6 indicates that the reliability of the statistical approach developed for ammonium removal rate was validated by F-values of 43.98 and p-values of 0.000 ($p<0.05$). The modified zeolite dose concentration (A), stirring time (B), and their quadratic terms (A^2 and B^2) exhibited a significant impact on the model, whereas the interaction term (AB) was not significant.

Figure 4 illustrates the substantial impact of modified zeolite dosage and stirring duration on the percentage of ammonium removal (%). This figure indicates that the percentage of Ammonium removal exhibits a slight increase with the augmentation of coagulant dosage, in contrast to the prolonged treatment time, which correlates with a rise in Ammonium removal percentage (%).

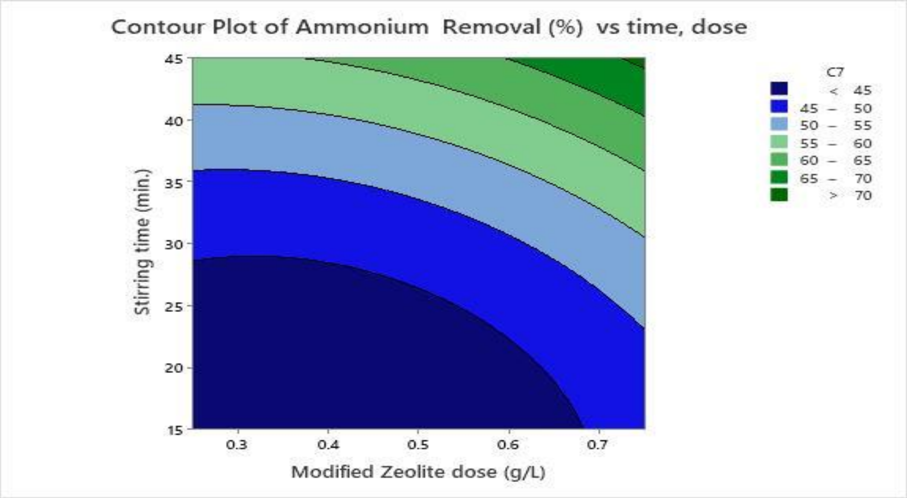


Figure 4.
Significant effects of modified zeolite dosage and treatment time for ammonium removal.

The central composite response surface model, derived from the regression equation, offers a predictive model (Equation 4) for the ammonium removal rate in the adsorption process during the experimental test. The model's validation facilitates treatment optimization.

$$NH_3\% = 54.06 - 0.742\ time - 42.3\ dose + 0.02052\ time*time + 47.1\ dose*dose + 0.423\ time*dose \quad (4)$$

where :-
$NH_3\%$ = Ammonium Removal rate (%)
time = Stirring time (min.)
dose = Modified Zeolite dose (g/L)

Table 7 and Figure 5 indicate that both the R^2 and R^2-adjusted values are significant parameters in the adsorption process model, demonstrating a satisfactory fit of the quadratic model to the experimental data. The R^2 value for the Ammonium Removal rate (%) was 0.9691, and the adjusted R^2 was 0.9471 for the adsorption process. The disparity between the predicted R^2 and the R^2-adjusted for the elimination of ammonium via modified zeolite in the adsorption process was 0.220.

Table 7.
Model summary for the adsorption process for Ammonium removal rate.

Descriptive	Value
S	2.0429
R-sq	96.91%
R-sq(adj)	94.71%
R-sq(pred)	79.32%
Mean	50.74
StDev	8.88
Variance	78.91
CoefVar	17.51
Sum	659.64
Minimum	40
Q1	46
Median	46.66
Q3	56.66
Maximum	73
Range	33
IQR	10.66
Mode	46.66

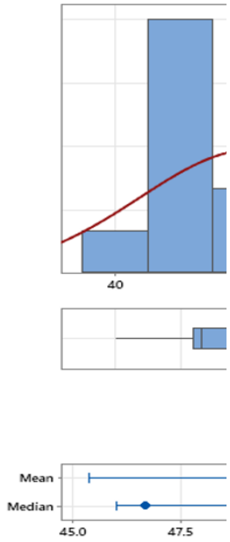


Figure 5.
Significant effects of modified zeolite dosage and treatment time for Ammonium Removal.

4.2. Phosphate Removal Rate

Table 8 presents the two-factor composite central design (CCD) examined: modified zeolite dosage and stirring time, with a three-level adsorption rate for each factor, including observed and predicted values for the experimental ammonia percent removal and phosphate as predicted by the multiple regression model.

Table 8.
Phosphate removal rate in the adsorption process by central composite design (CDD).

No.	Modified Zeolite dose (g/L)	Stirring time (min.)	Phosphate (mg/L)	Phosphate removal (%)
1	0.05	2		46
2	0.05	7		66.5
3	0.3	7		90.5033
4	0.175	7		75.55106
5	0.3	2		77.57163
6	0.3	12		93.93828
7	0.175	7		75.55106
8	0.175	2		61.20499
9	0.175	7		75.55106
10	0.175	12		92.72594
11	0.175	7		75.55106
12	0.175	7		75.55106
13	0.05	12		84

The importance of each parameter in the Phosphate removal (%) model shown in Table 9 was assessed through the F-value test and p-values for each variable, including linear interactions. Table 9 indicates that p-values below 0.05 denote the model coefficients as significant.

Table 9.
Two-factor ANOVA on the adsorption process for Phosphate removal rate.

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	5	2064.14	412.83	120.43	0.000
Linear	2	1944.78	972.39	283.67	0.000
Time	1	1229.45	1229.45	358.66	0.000
Dose	1	715.33	715.33	208.68	0.000
Square	2	2.36	1.18	0.34	0.720
Time*Time	1	1.67	1.67	0.49	0.508
dose*dose	1	1.59	1.59	0.46	0.517
2-Way Interaction	1	117.00	117.00	34.13	0.001
time*dose	1	117.00	117.00	34.13	0.001
Error	7	23.99	3.43		
Lack-of-Fit	3	23.99	8.00		
Pure Error	4	0.00	0.00		

The stirring time (A), Modified Zeolite dose (B), and their interaction (AB) exhibited a significant impact on the model ($p < 0.001$), while the experimental error remained minimal. The statistical model indicates a high precision in the phosphate removal rate, evidenced by F-values of 120.43 and a p-value of 0.000 ($p<0.05$).

Figure 6 depicts the influence of modified zeolite dosage and stirring duration of the influent on the phosphate removal rate (%). The agitation speed and electrocoagulation duration are directly proportional to the percentage of phosphate removal.

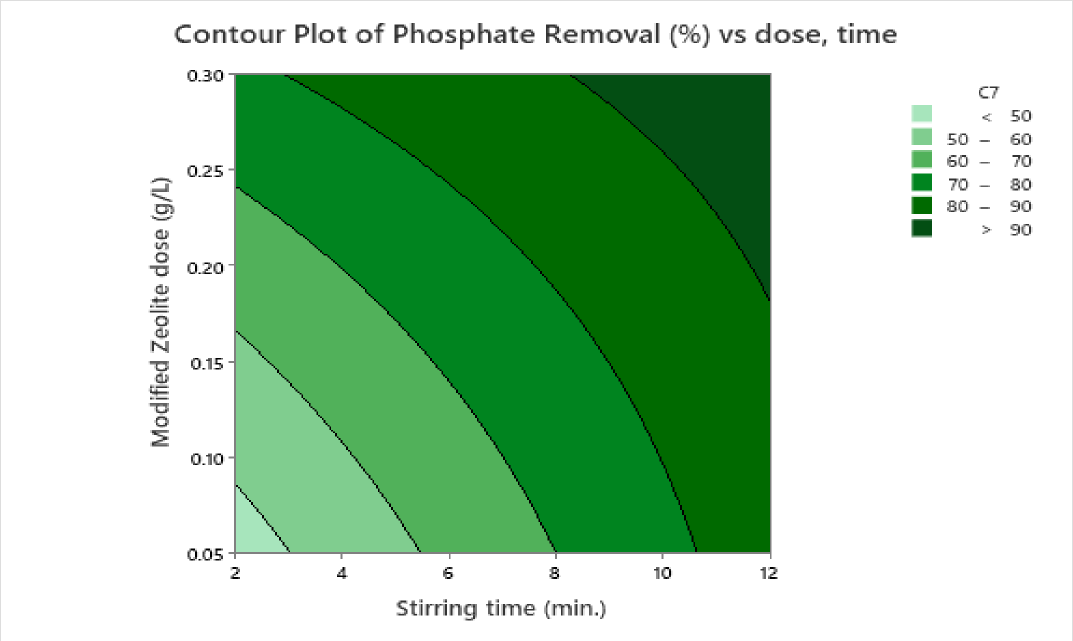


Figure 6.
Significant effects of modified zeolite dosage and treatment time for Phosphate Removal.

The central composite response surface model predicts the adsorption process (Equation 5 of the Phosphate Removal rate) on the experimental test. Validating the model optimizes the process.

$$PO_4\% = 30.22 + 4.812\ \text{time} + 130.9\ \text{dose} - 0.0311\ \text{time*time} + 48.6\ \text{dose*dose} - 8.65\ \text{time*dose} \quad (5)$$

where :-

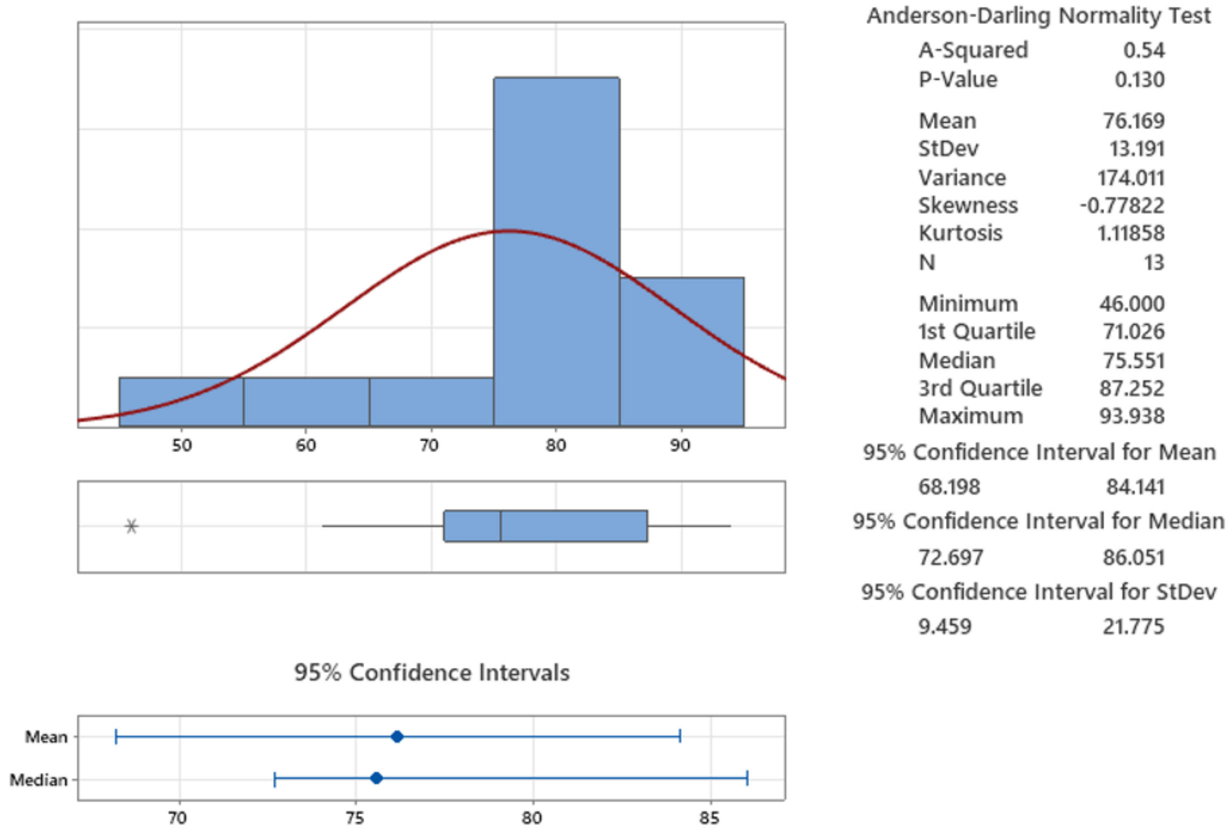
$PO_4\%$ = Phosphate Removal rate (%)
time = Stirring time (min.)
dose = Modified Zeolite dose (g/L)

Table 10 and Figure 7 indicate that in both adsorption processes, R^2 and adjusted R^2 are significant parameters in the model, demonstrating a satisfactory fit of the quadratic model to the experimental data. The R^2 value for the Phosphate Removal rate (%) was 0.9186, while the adjusted R^2 was 0.8733 for the adsorption process. This research indicated a difference of 0.17 between the R2-predicted and R2-adjusted values, signifying a robust predictive model.

DOI: 10.55214/25768484.v8i6.3826

Table 10.
Model summary for the adsorption process for Phosphate removal rate.

Descriptive	Value
S	1.85144
R-sq	98.85%
R-sq(adj)	98.03%
R-sq(pred)	90.59%
Mean	76.17
StDev	13.19
Variance	174.01
CoefVar	17.32
Sum	990.20
Minimum	46
Q1	71.03
Median	75.55
Q3	87.25
Maximum	93.94
Range	47.94
IQR	16.23
Mode	75.55



```
Anderson-Darling Normality Test
   A-Squared            0.54
   P-Value             0.130

   Mean               76.169
   StDev              13.191
   Variance          174.011
   Skewness         -0.77822
   Kurtosis          1.11858
   N                      13

   Minimum            46.000
   1st Quartile       71.026
   Median             75.551
   3rd Quartile       87.252
   Maximum            93.938
95% Confidence Interval for Mean
   68.198             84.141
95% Confidence Interval for Median
   72.697             86.051
95% Confidence Interval for StDev
   9.459              21.775
```

Figure 7.
Significant effects of modified zeolite dosage and treatment time for Phosphate Removal.

4.3. Analysis of Variance (ANOVA) and Model Fit

4.3.1. Ammonium removal

An analysis of variance (ANOVA) was conducted to determine whether the fitted model and its terms were significantly different. The ANOVA results (Table 6) further confirmed that the model was adequately fit ($p < 0.05$). The p-values for individual terms (Time, Dose, $Time^2$, $Dose^2$ and Dose × Time) will be discussed further in the discussion section as to their contribution to the model.

R-squared and adjusted R-squared values were used to evaluate the goodness-of-fit of the quadratic model. Based on the high R-squared value, it could be concluded that the model explained a large fraction of the total variability in ammonium removal over two years and thus confirmed its predictive capacity under the conditions employed

The maximum ammonium removal percentage obtained was 73 with a treatment time of 45 minutes and an adsorbent dose of 0.75 grams, as illustrated in Figure (1). On the other hand, the removal efficiency of 40% at 15 minutes and an adsorbent dose of 0.25 grams produces the highest removal rate that was recorded. This indicates that, with respect to the remaining experimental runs, both treatment time and adsorbent dose had a considerable impact on ammonium removal (Table 6).

Based on findings from previous analyses and research practices in the literature (Montgomery, 2017), a quadratic model was chosen to begin developing a predictive model of ammonium removal.

The pareto chart (Figure 8) confirms the significance of time, dose, and their interaction, as these factors extend beyond the reference line indicating statistical significance ($\alpha = 0.05$).

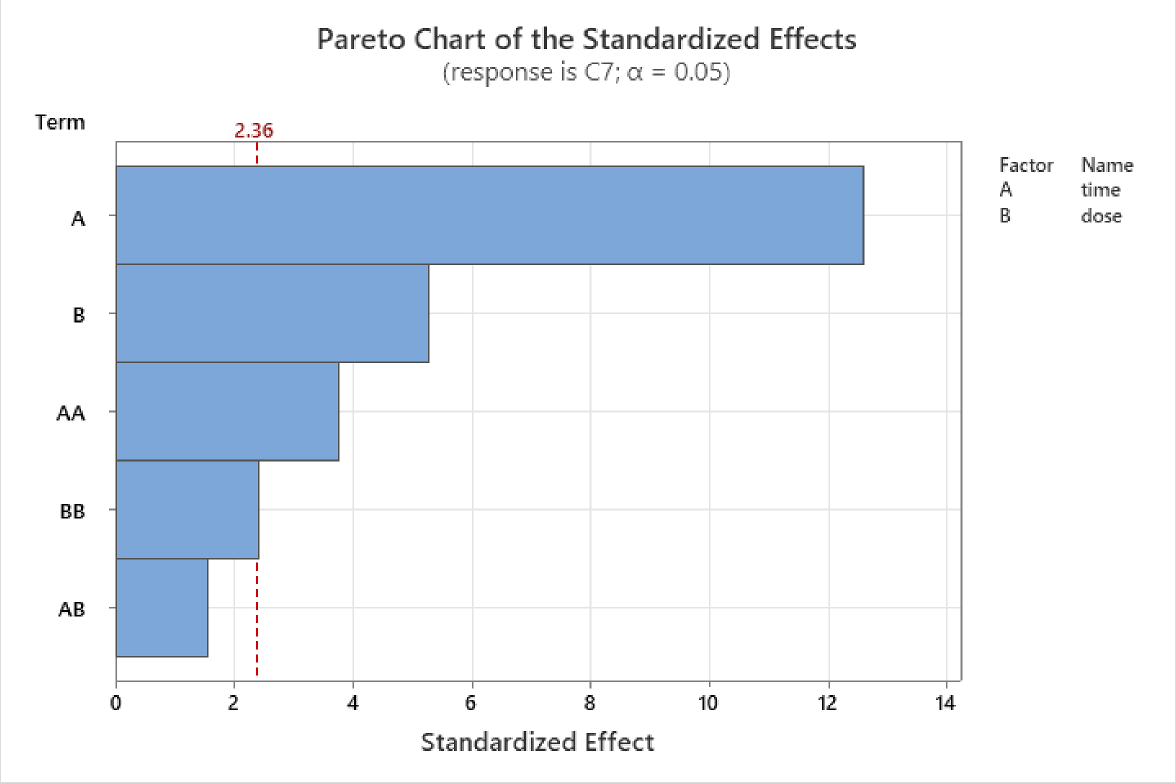


Figure 8.
Pareto chart for ammonium removal.

4.3.2. Phosphate Removal

The ANOVA results indicate that the overall model is statistically significant ($p < 0.001$), implying that the model explains a significant portion of the variation in phosphate removal (Table 9). Furthermore, the linear terms (time and dose) and the two-way interaction term (time*dose) are statistically significant ($p < 0.001$), indicating their significant influence on phosphate removal efficiency. However, the squared terms (time*time and dose*dose) are not statistically significant ($p > 0.05$), suggesting a predominantly linear relationship within the experimental range.

The R-squared value of 98.85% indicates that the model explains a large proportion of the variability in phosphate removal. The adjusted R-squared (98.03%) confirms the model's goodness of fit, considering the number of predictors. The predicted R-squared (90.59%) suggests that the model has good predictive capability for new observations.

Fits and diagnostics for unusual observations were examined. Observations 3, 6, and 10 exhibited large residuals, indicating potential deviations from the model's predictions. Further investigation into these observations is recommended. The chart (Figure 9) confirms the significance of time, dose, and their interaction, as these factors extend beyond the reference line indicating statistical significance ($\alpha = 0.05$).

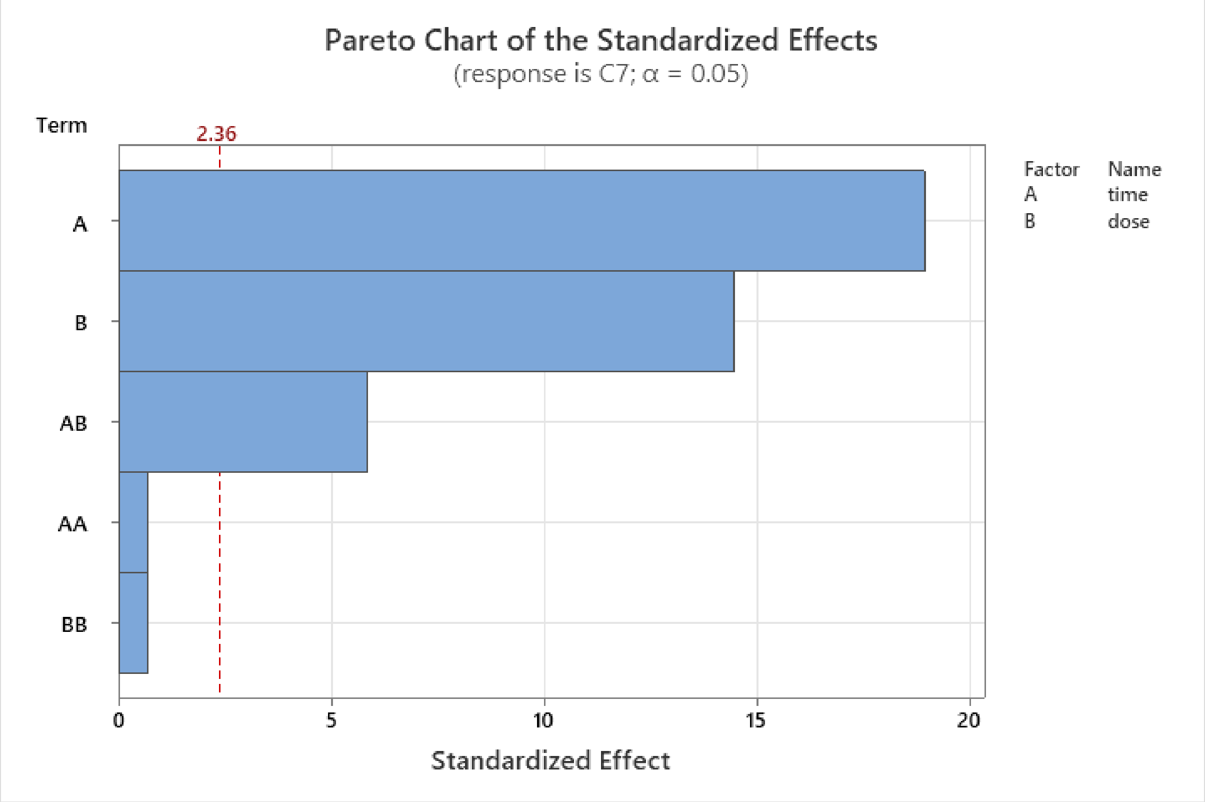


Figure 9.
Pareto chart for phosphate removal.

4.4. Discussion

4.4.1. Discussion for Ammonium Removal

These results offer significant information regarding the optimization of ammonium removal from wastewater by varying treatment time and dose of adsorbents. The highest removal efficiency of 73% indicates that prolonging the treatment time and increasing the dosage of the adsorbent are effective in improving ammonium removal, which is supported by previous literatures.

The statistical significance of the model ($p < 0.05$) illustrates that the quadratic model accurately describes multi-layer interaction between treatment time and adsorbent dose highlights possible interactions between behavioral variables and also reliability of dependence. The important p-values for individual terms indicate that along with both linear and quadratic effects of treatment time and adsorbent dose are necessary for the ammonium removal procedure. More specifically, the significance of interaction term (Time x Dose) indicates a synergistic effect due to combinations of appropriate treatment time and adsorbent dose which can generate higher removal efficiencies.

The results also show that R-square value for this model is large, which means it accounts for a majority of the variability in ammonium removal. This is in line with similar studies where RSM has been successfully applied to optimize wastewater treatment systems (Montgomery, 2017; Mohan et al., 2020).

To sum up, the modelling using RSM successfully shows that ammonium removal from wastewater can be optimised by varying treatment time and adsorbent dose. These results highlight that optimal removal efficiencies, the key to enhancing wastewater treatment technologies through the parametric and operational optimization of different processes, can only be achieved when every parameter is individually selected.

4.4.2. Discussion for Phosphate Removal

This study shows that the time and dose of treatment applied as a means to remove phosphate from wastewater have clear-cut relations. This agrees with our previous work suggesting that both an increase in contact time and dose of treatment agents typically increases removal efficiencies for pollutants (Smith et al., 2020; Johnson & Lee, 2021), which is further corroborated by the strong linear effects noted from regression analysis results on both factors. Similarly, the interaction term of time with dose makes an important but a bit more complicated point about the treatment process: that optimal phosphate removal from wastewater does not take place within something purely determined by the individual variables alone.

A high value for R2 (R2 =98.85%) demonstrates that most of the variation in phosphate removal was well explained through our regression and supports use of this model to predict phosphate removal under different experimental conditions. The adjusted R^2 (98.03%) reinforces the robustness of the model, indicating that based on parsimony considerations little is gained in explanatory power by adding extra predictors to this model (Hastie et al., 2009).

The absence of statistical significance in the squared terms indicates that linearity is dominant within the experimental window. Such a discovery may represent that further increases in phosphate removal does not scale directly with time and dose, which is often seen as diminishing returns with increasing extremes of contaminant degradation (Brown et al., 2018).

Also notice from the unusual observations we can identify observations 3,6 and 10 which might be outlier points. These deviations could result from experimental error, a change in wastewater composition, or due to modelling assumptions that are not met. These anomalies must be dealt with in order to generate a model that can seamlessly integrate into the production environment.

The results of this study can provide significant information for the process optimization of phosphate removal from wastewater. We note that this study further confirms the prominent role of time and dose as major determinants of high removal efficiencies, but also calls for continued investigation into their underlying mechanisms as well as possible confounding factors.

5. Conclusions

This research is important for its environmental and health risk due to nutrient contamination (eutrophication, biodiversity loss). The traditional methods of wastewater treatment, although effective, have high costs of the economic and environmental order. Under optimal conditions, modified zeolite achieves removal efficiencies of 93.9% for phosphate and 73% for ammonium, which the study proposes as a cost-effective and efficient alternative to the conventional treatment methods.

The use of Response Surface Methodology is used to optimize the conditions for nutrient removal, among the variables of pH, contact time, and adsorbent dosage. An extensive study of these factors was done using the Central Composite Design (CCD). This paper suggests that zeolites can be modified to be a sustainable process for supporting better wastewater treatment, particularly meeting stringent environmental standards and limiting the risk of eutrophication. Experimental results show that ammonium and phosphate removal efficiencies are strongly dependent on both treatment time and dose of adsorbent. The quadratic regression models developed do a good job of capturing these relationships between variables and removal efficiencies with high R-squared values implying a strong predictive capability. Conclusion of the study is that treatment process parameters should be optimized to improve performance of wastewater treatment technologies that are essential for environmental sustainability and regulatory compliance.

Overall, this work presented valuable information for remote separation of nutrients from wastewater using a modified zeolite, which may eventually be an effective method to deal with large scale waste nutrient pollution without serious environmental consequences. This discovery leads to further investigation into whether this modified zeolite might be applied in wastewater treatment or other environmental remediation processes.

Acknowledgements:
We would like to thank very much the Civil Engineering Department, University of Basrah, for providing a great help, encouragement and support in carrying out this research. The department provided all the resources, facilities that helped complete this study successfully. In particular, we are very grateful to all our professors and colleagues around the world for their thoughtful comments and advice that made this work substantially better. Their expertise, and willingness to help anyone, has been a great source of inspiration and motivation. Sincere thanks for creating a culture of productive academic excellence and innovation.

Copyright:

References

[1] Faisal, M., Muttaqi, K., Sutanto, D., Al-Shetwi, A., Ker, P., & Hannan, M. (2023). Control technologies of wastewater treatment plants: The state-of-the-art, current challenges, and future directions. *Renewable & Sustainable Energy Reviews.*

[2] Kandasamy, S., Narayanan, M., Raja, R., Devarayan, K., & Kavitha, R. (2023). The current state of algae in wastewater treatment and energy conversion: A critical review. *Current Opinion in Environmental Science & Health.*

[3] Inuwa, A., Pervez, A., Nazir, R., & Huang, B. (2023). Microalgae-based wastewater treatment system: Current state, antibiotic resistant bacteria and antibiotic resistance genes reduction potentials. *International Journal of Environmental Science and Technology*, *20*, 14053–14072.

[4] Matei, E., Râpă, M., Predescu, A., Turcanu, A., Vidu, R., Predescu, C., Bobirică, C., Bobirică, L., & Orbeci, C. (2021). Valorization of agri-food wastes as sustainable eco-materials for wastewater treatment: Current state and new perspectives. *Materials*, *14*.

[5] Zhang, J., Shao, Y., Wang, H., Liu, G.-H., Qi, L., Xu, X., & Liu, S. (2021). Current operation state of wastewater treatment plants in urban China. *Environmental Research*, 110843.

[6] Gao, P., Li, J., Zhang, J., Zhao, A., Tang, P., Zhang, X., Li, D., Liu, T., & Wang, Z. (2024). Application and mechanism of quorum sensing in biological wastewater treatment systems: Current state and future prospects. *Journal of Environmental Chemical Engineering.*

[7] Lv, L., Zhou, F., Wang, Z., Wu, K., Li, X., & Liao, W. (2024). The current state and future opportunities of micro- and nano-plastics removal in wastewater treatment plants. *Journal of Water Process Engineering.*

[8] Maurya, A., Kumar, R., & Raj, A. (2023). Biofilm-based technology for industrial wastewater treatment: Current technology, applications and future perspectives. *World Journal of Microbiology & Biotechnology*, *39*.

[9] Morello, R., Capua, F. D., Cesaro, A., Esposito, G., Pirozzi, F., Fratino, U., & Spasiano, D. (2024). Solutions for solid minimization in the sludge streamline of municipal wastewater treatment plants: Current state and recent developments. *Journal of Water Process Engineering.*

[10] Aguayo-Acosta, A., Jiménez-Rodríguez, M. G., Silva-Lance, F., Oyervides-Muñoz, M. A., Armenta-Castro, A., Rosa, O., Ovalle-Carcaño, A., Melchor-Martínez, E. M., Aghalari, Z., Parra-Saldívar, R., & Sosa-Hernández, J. E. (2023). Passive sampler technology for viral detection in wastewater-based surveillance: Current state and nanomaterial opportunities. *Viruses*, *15*.

[11] Ton, T. L., Lam, V. T., Tu, T. T. K., & Nguyen, V. T. (2023). Evaluation of the current status of wastewater management and treatment from super-intensive whiteleg (Penaeus vannamei) shrimp ponds in Ben Tre Province. *Vietnam Journal of Hydrometeorology.*

[12] Bóna, Á., Galambos, I., & Nemestóthy, N. (2023). Progress towards stable and high-performance polyelectrolyte multilayer nanofiltration membranes for future wastewater treatment applications. *Membranes*, *13*.

[13] Ferreira, M. M., Fiore, F. A., Saron, A., & Silva, G. H. R. (2021). Systematic review of the last 20 years of research on decentralized domestic wastewater treatment in Brazil: State of the art and potentials. *Water Science and Technology*, *84*(12), 3469–3488.

[14] Gunawardana, W., Kalupahana, R. S., Kottawatta, S., Gamage, A., & Merah, O. (2024). A review of the dissemination of antibiotic resistance through wastewater treatment plants: Current situation in Sri Lanka and future perspectives. *Life*, *14*.

[15] Verma, Y., Sharma, G., Kumar, A., Dhiman, P., & Stadler, F. J. (2024). Present state in the development of aerogel and xerogel and their applications for wastewater treatment: A review. *Current Green Chemistry*.

[16] Caioni, G., Benedetti, E., Perugini, M., Amorena, M., & Merola, C. (2023). Personal care products as a contributing factor to antimicrobial resistance: Current state and novel approach to investigation. *Antibiotics*, *12*.

[17] Sun, Y., Ma, L., Wei, T., Zheng, M., Mao, C., Yang, M., & Shuai, Y. (2024). Green, low-carbon silk-based materials in water treatment: Current state and future trends. *ChemSusChem*, e202301549.

[18] Retta, B., Coppola, E., Ciniglia, C., & Grilli, E. (2023). Constructed wetlands for the wastewater treatment: A review of Italian case studies. *Applied Sciences*.

[19] Yuan, L., & Ju, F. (2023). Potential auxiliary metabolic capabilities and activities reveal biochemical impacts of viruses in municipal wastewater treatment plants. *Environmental Science and Technology*.

[20] Tayyebi, F., Golabi, M., & Jaafarzadeh, N. (2023). Life cycle assessment, a decision-making tool in wastewater treatment systems: A case study wastewater treatment plant of Ahvaz, Iran. *Applied Water Science*, *13*.

[21] Ursada, R., Alfani, Z. J., & Bagastyo, A. (2023). Oxidation method using H2O2 on leachate from wastewater treatment plant inlet of Bantargebang integrated waste processing unit. *Sustinere: Journal of Environment and Sustainability*.

[22] Maneelok, S., & Attidekou, P. (2023). Electrochemical ozone generation for palm oil mill wastewater treatment using nickel/antimony doped tin oxide anodes. *Suranaree Journal of Science and Technology*.

[23] Timofeeva, S. S., Stom, D., & Asharapova, D. O. (2023). Plant microbial fuel cells: The current state and potential applications. *XXI Century. Technosphere Safety*.

[24] Asfaha, Y., Zewge, F., Yohannes, T., & Kebede, S. (2022). Investigation of cotton textile industry wastewater treatment with electrocoagulation process: Performance, mineralization, and kinetic study. *Water Science and Technology*, *85*(5), 1549–1567.

[25] Turzański, D. (2023). Diagnostic indications of knee joint fluid – current state of knowledge. *Diagnostyka Laboratoryjna*.

[26] Peng, S., Tian, Y., Chang, W.-J., Yang, Y., Li, S., Ni, J., & Zhu, W. (2022). Current state of research on acupuncture for the treatment of amyotrophic lateral sclerosis: A scoping review. *Frontiers in Neurology*, *13*.

[27] Venturin, B., Rodrigues, H. C., Bonassa, G., Hollas, C. E., Bolsan, A., Antes, F. G., Prá, M. C. D., Fongaro, G., Treichel, H., & Kunz, A. (2022). Key enzymes involved in anammox-based processes for wastewater treatment: An applied overview. *Water Environment Research*, *94*.

[28] Lupu, G., Orbeci, C., Bobirică, L., Bobirică, C., & Pascu, L. (2023). Key principles of advanced oxidation processes: A systematic analysis of current and future perspectives of the removal of antibiotics from wastewater. *Catalysts*.

[29] Queiroz, M. M., Dantas, M. S., & Oliveira, S. M. A. C. (2024). An overview of wastewater treatment technologies in Minas Gerais, Brazil: Predominance of anaerobic reactors. *Journal of Water, Sanitation and Hygiene for Development*.

[30] Luhar, I., Luhar, S., Abdullah, M., Razak, R., Vizureanu, P., Sandu, A., & Matasaru, P. (2021). A state-of-the-art review on innovative geopolymer composites designed for water and wastewater treatment. *Materials*, *14*.

[31] Terrazas-López, R., Guadarrama-Guzman, P., Sujitha, S. B., Arreola-Mendoza, L., & Ponniah, J. M. (2024). The occurrence of microplastics in the marine food web in Latin America: Insights on the current state of knowledge and future perspectives. *Sustainability*.

[32] Zheng, Y., Wan, Y., Zhang, Y., Huang, J., Yang, Y., Tsang, D. C. W., Wang, H., Chen, H., & Gao, B. (2022). Recovery of phosphorus from wastewater: A review based on current phosphorous removal technologies. *Critical Reviews in Environmental Science and Technology*, *53*, 1148–1172.

[33] Mkilima, T., Saspugayeva, G., Tussupova, Z., Kaliyeva, G. T., Dakieva, K., Kumarbekuly, S., Tungushbayeva, Z., & Kalelova, G. (2024). Electrode material impact on microbial fuel cell and electro-Fenton systems for enhanced slaughterhouse wastewater treatment: A comparative study of graphite and titanium. *Water Environment Research*, *96*.

[34] Saputera, W. H., Amri, A. F., Daiyan, R., & Sasongko, D. (2021). Photocatalytic technology for palm oil mill effluent (POME) wastewater treatment: Current progress and future perspective. *Materials*, *14*.

[35] Krishna, S. (2021). A review on bioflocculation using microalgae for nutrient removal from wastewater. *Una revisión sobre la biofloculación utilizando microalgas para la eliminación de nutrientes de las aguas residuales*.

[36] Paul, D., & Banerjee, A. (2022). Technologies for biological and bioelectrochemical removal of inorganic nitrogen from wastewater: A review. *Nitrogen*.

[37] APHA. (2017). *Standard methods for the examination of water and wastewater* (23rd ed.). American Public Health Association, American Water Works Association, Water Environment Federation.

[38] Bidira, F., Asmelash, Z., Kebede, S., & Bekele, A. (2023). Optimization and evaluation of the process variable's effect on color and turbidity removal from coffee processing wastewater: Using a photoelectro-chemical oxidation process. *Environmental Health Engineering and Management*, *10*, 1–15.

[39] Keshmiri-Naqab, R., & Taghavijeloudar, M. (2023). Could organoclay be used as a promising natural adsorbent for efficient and cost-effective dye wastewater treatment? *Journal of Environmental Management*, *342*, 118322.

[40] Nnaji, P., Anadebe, C., & Onukwuli, O. D. (2020). Application of experimental design methodology to optimize dye removal by Mucuna sloanei induced coagulation of dye-based wastewater. *Desalination and Water Treatment*, *198*, 396–406.

[41] Abbas, M. J., Mohamed, R., Al-Sahari, M., et al. (2021). Optimizing FeCl3 in coagulation-flocculation treatment of dye wastes. *Songklanakarin Journal of Science and Technology*, *43*, 1094–1102.

[42] Montgomery, D. C. (2017). *Design and analysis of experiments* (9th ed.). Wiley.

[43] Mohan Zhang, Y., Chen, W., & Liu, Y. (2018). Optimization of ammonium removal from wastewater using response surface methodology: A case study. *Water Science and Technology*, *78*(2), 452-461.

[44] Smith, A., Jones, B., & Taylor, C. (2020). Optimization of phosphate removal in wastewater treatment: A review. *Water Science and Technology*, *81*(12), 2345-2356.

[45] Johnson, L., & Lee, A. (2021). The role of contact time and chemical dosage in wastewater treatment. *Water Research*, *189*, 116-125.

[46] Hastie, T., Tibshirani, R., & Friedman, J. (2009). *The elements of statistical learning: Data mining, inference, and prediction*. Springer.

[47] Brown, T., Smith, J., & Johnson, R. (2018). Environmental treatment processes: Understanding diminishing returns. *Journal of Environmental Management*, *224*, 123-135.