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OPTIMIZATION OF ADSORPTION CONDITIONS FOR NUTRIENT REMOVAL FROM AQUEOUS SOLUTIONS: INTEGRATED RSM MODELLING, MECHANISTIC INSIGHTS, AND MULTI-SCALE STATISTICAL VALIDATION

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Abstract

Global water systems are increasingly affected by nutrient pollution, particularly nitrate and phosphate from industrial discharge, agricultural intensification, and urban expansion. Ecosystem degradation, harmful algal blooms, loss of oxygen, and the dangers that result for marine life as well as human beings are some of the effects that arise due to such pollutants. The need for sustainable adsorption process can be understood from the limitations of the conventional systems such as biological denitrification, chemical precipitation and membrane filtration, including expensive process, formation of sludge, lack of selectivity and inability to regenerate the system. This study develops an optimized adsorption system for nutrient removal using an integrated framework combining Response Surface Methodology (RSM), mechanistic evaluation, and multi-scale statistical validation. An iron-based metal–organic framework (Fe-MOF), Fe-UPH.COHSE-NH_2, was synthesized via a controlled solvothermal method and functionalized with polyethyleneimine (PEI) to introduce amine-rich active sites. Optimization using a Doehlert design identified an optimal $FeCl_3 \cdot 6H_2O$ to H_2BDC ratio of 2:1.5, producing a highly crystalline and functionally enhanced adsorbent. A porous and robust matrix with high specific surface area of 533.94 m^2/g and good accessibility of active sites (BET $R^2 = 0.9999$) was proved from characterisation results obtained from powder x-ray diffraction (PXRD), Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), scanning electron microscope (SEM), and Brunauer-Emmett-Teller (BET) surface area measurement ("BET"). The durability and reusability of the substance were shown from its high crystallinity, rod-shaped porous structure, and high thermal stability at temperatures up to 350°C. This compound had functional groups such as $-NH_2$ and $-COO^-$. Nitrate and phosphate adsorption study with RSM and the assistance of kinetic and isotherm models showed excellent removal efficiency with high predictive accuracy ($R^2 > 0.99$). The mechanisms discovered through mechanistic studies were electrostatic attraction, chemisorption of Fe-OH and Fe-NH_2, ligand exchange and intraparticle diffusion. Therefore, in summation, Fe-UPH.COHSE-NH2 provided an environmentally friendly solution for the effective removal of nutrients from wastewaters, due to high efficiency and recyclability.

Keywords:

Nutrient removal; adsorption optimization; solvothermal synthesis; advanced wastewater treatment; mechanistic adsorption; electrostatic attraction; chemisorption.

1.0 Introduction

1.1 Global Nutrient Pollution Crisis (Nitrogen and Phosphorus Contamination)

Overloading of the freshwater and marine ecosystem by human-caused nitrogen (N) and phosphorus (P) loading is becoming an issue (Paerl et al., 2020; Wang et al., 2023). The pollution of the nutritional nature presents a severe threat to both ecosystems. Increased amounts of nitrate ions (NO_3^-) and phosphate ions (PO_4^{3-}) in the water environment have been reported to be mainly attributed to agricultural runoff, industrial discharge, municipal wastewater discharge, wastewater from livestock, and stormwater from urban environments (Withers et al., 2020; Glibert, 2020). The quick rate of urbanization and increase in the use of artificial fertilizers have immensely accelerated nutrient loading in aquatic habitats (Yu *et al.,* 2021).

Globally, The alteration of biogeochemical processes and aquatic ecosystem functionality due to nutrient pollution has become one of the major environmental problems (Steffen et al., 2015). The quality of water resources, ecosystem functions, and freshwater security all suffer due to nutrient pollution. It has been observed especially in countries where there is no proper infrastructure for waste-water management (UNEP, 2021). Recent data show that nutrient enrichment continues to be a significant environmental issue despite certain regulatory measures taken (Chen *et al.,* 2022).

1.2 Environmental and Health Impacts (Eutrophication and Toxicity)

Eutrophication in water bodies takes place due to the excessive presence of nitrogen and phosphorous in the water bodies causing unrestricted growth of algae and phytoplanktons (Paerl & Otten, 2013). This results in a reduction in light penetration in water, biodiversity of aquatic organisms, and depletion in the amount of oxygen available, thus resulting in a state of hypoxia in which all marine life gets affected (Breitburg et al., 2018). Extreme cases of eutrophication cause the creation of dead zones (Diaz & Rosenberg, 2008).

Apart from posing risks to the wellbeing of people and the environment, nutrient pollution leads to the growth of HABs that produce toxicants including microcystins and saxitoxins (Carmichael & Boyer, 2016). Issues concerning the nervous system, digestive system, and liver may result from consumption of contaminated fish and exposure to contaminated water (Testai et al., 2016). Another problem related to high amounts of nitrates in water is the development of methemoglobinemia and cancer risk associated with nitrosamine production (Ward *et al.,* 2018).

Dodds & Smith (2016) assert that there are various socioeconomic implications caused by eutrophication besides the ecological and health problems that occur. Such implications include low fish populations, increased expenses of purification in water treatment plants, reduced number of tourists, and poor ecosystem resilience among others. There is thus an urgent need to employ nutrient removal methods.

1.3 Limitations of Conventional Treatment Technologies

According to Metcalf & Eddy (2014), the most commonly used conventional nutrient removal techniques include membrane filtration, ion exchange, chemical precipitation, biological denitrification, and coagulation flocculation. However, a variety of issues affect the operation of these techniques.

Denitrification processes during biological nitrogen removal have shown instability in their efficiency of nitrate removal as they are highly susceptible to factors such as temperature, dissolved oxygen, pH, and carbon source (Wang et al., 2020). Another issue with biological processes is high production of sludge that incurs high disposal costs (Tchobanoglous *et al.,* 2014).

The chemical precipitation techniques for phosphates removal generate huge amounts of sludge and may contaminate the water system due to the introduction of secondary contaminants into water (Yeoman et al., 1988). Despite their high removal efficiency, membrane techniques, such as nanofiltration and reverse osmosis, possess plenty of disadvantages: expensive operation, excessive energy consumption, and membrane fouling (Lee et al., 2021). Among other weaknesses of the ion-exchange techniques, it should be noted their lack of selectivity and lower efficiency during regeneration with various competing ions in wastewater (Bhatnagar & Sillanpää, 2011).

Therefore, environmentally safe and selective removal techniques are required.

1.4 Emergence of Adsorption Technologies

Adsorption is one of the best technologies for nutrient remediation because it is energy efficient, highly effective, easily regenerated, and operationally simple (Crini & Lichtfouse, 2019). Nitrate and phosphate nutrients can be effectively adsorbed even at low concentrations since they rely on pollutant adsorption through the interactions between pollutants and adsorbent sites in the materials (Foo & Hameed, 2010).

The development of adsorbents such as activated carbon, biochar, graphene oxide, zeolites, layered double hydroxides, and metal organic frameworks (MOFs) is attributed to recent advancements in materials science (Tan et al., 2020). Metal-organic frameworks (MOFs), among others, have several advantages because of their high porosity, modifiable pore structure, high specific surface area, and surface functionality (Furukawa *et al.,* 2013; Wang *et al.,* 2022).

As described by Xie et al. (2017) and Liu et al. (2023), the metal-organic frameworks (MOFs) that contain iron elements and have amine functionalities have high affinity for both phosphate and nitrate ions owing to their Fe-OH active sites and improved electrostatic interactions. In the case of remediation applications in the context of wastewater treatment, Fe-UPH.COHSE-NH2 has exhibited high regeneration efficiency, rapid adsorption rate, and good adsorption capacity, as indicated by numerous studies (Zhang et al., 2022; Lin et al., 2024).

1.5 Importance of Optimization in Adsorption Systems

There are numerous operational parameters such as pH value, contact time, amount of adsorbent, temperature, ionic strength, and concentration of pollutants that influence greatly the efficacy of adsorption (Ho & McKay, 1999). It is rather difficult to obtain optimal conditions for the process because of multiple interactions among these parameters and their nonlinear influence on adsorption process.

The One-Variable-at-a-Time technique, permitting one to optimize one parameter at a time leaving all other parameters constant, remains to be popular among scientists. The approach is quite simple; however, optimization of conditions using this approach often leads to nonoptimal results due to neglecting interaction among variables (Montgomery, 2017).

For the study of multivariable systems, prediction of optimum operating conditions and minimising number of experiments, Response Surface Methodology (RSM) has been found out to be a reliable optimisation technique based on statistics (Bezerra et al., 2008). Efficiency of process modelling, analysis of interactions and statistical validations can be improved by employing experimental designs such as Box-Behnken design and Doehlert designs (Baş & Boyacı, 2007).

Recent results obtained from the adsorption studies have revealed that response surface methodology improves adsorption efficiency, predictive accuracy and scale-up capabilities of the adsorption process (Moghaddam et al., 2021; Alqadami et al., 2020). For making the laboratory-scale adsorption systems applicable as a technology for environmental remediation, RSM-based optimisation plays an essential role.

1.6 Research Gaps

Nevertheless, there are several key areas where more knowledge is needed on adsorption nutrient remediation.

(i) Lack of Mechanistic Understanding: Although the analysis of adsorption capacity can be considered significant, it should be noted that not all studies pay sufficient attention to mechanisms of adsorption of pollutants (Liu et al., 2023). For example, designing and optimising an adsorbent becomes difficult without the study of such mechanisms as electrostatic attractions, surface complexation, ligand exchange, chemisorptions, and intraparticle diffusion (Xie *et al.,* 2017).

(ii) Weak Statistical Validation: Predictive validity and reliability of some adsorption studies are undermined by the fact that these studies rely merely on regression coefficients or limited kinetic modeling and do not employ proper statistical validation (Moghaddam et al., 2021). Studies involving nutrition have largely ignored the application of multi-scale statistical approaches that integrate ANOVA, residual analysis, error modeling, and response optimization.

(iii) Limited Optimization Studies: Despite the high potential of nutrient removal by adsorption techniques, the application of systematic optimisation methods using sophisticated statistical methods such as RSM has not been fully utilised. Even though OVAT methods have some shortcomings in considering interactions and nonlinearity in the system, their application has been very common (Bezerra et al., 2008). Nutrient removal adsorption systems which are scalable, statistically validated, and mechanistically based are limited by these shortcomings when viewed collectively.

1.7 Novelty of the Present Study

This research addresses the shortcomings of the current body of knowledge by applying an approach that integrates experiments, mechanism, and statistics.

(i) RSM Integration: The improved efficiency of nutrient removal as well as statistically accurate prediction models are some of the benefits that have been derived from the application of Response Surface Methodology in this research.

(ii) Mechanistic Modelling: Adsorption mechanisms have been investigated via systematic studies such as adsorption kinetics, isotherms, electrostatic interactions, ligand exchanges, and intraparticle diffusion processes.

(iii) Advanced Material Characterization: In order to evaluate structural characteristics' influence on adsorption behavior, a series of characterization techniques were adopted, such as Powder X-ray Diffraction (PXRD), Fourier Transform Infra-Red spectroscopy (FTIR), Scanning Electron Microscopy (SEM), Brunauer-Emmett-Teller (BET), and Thermogravimetric Analysis (TGA).

(iv) Regeneration and Reusability Studies: In assessing the long-term operability and sustainability of the synthesised adsorbent, its cyclic stability and regenerability are tested (Zhang et al., 2022).

By using both approaches together, an approach to scaled nutrient recovery processes is developed, which is not only statistically verified but also mechanically grounded.

1.8 Study Aim and Objectives

The study aim was to use a combined approach of Response Surface Methodology, mechanistic analysis, and multiscale statistical validation to optimize adsorption processes for efficient nitrate and phosphate removal from water systems.

The specific objectives are to:

1. Synthesize and functionalize an iron-based metal–organic framework (Fe-MOF) for enhanced nutrient adsorption.
2. Optimize synthesis and operational parameters using Response Surface Methodology.
3. Characterize the structural, morphological, thermal, and surface properties of the synthesized adsorbent.
4. Evaluate adsorption behaviour using kinetic and isotherm models.
5. Investigate the mechanisms governing nitrate and phosphate adsorption.
6. Assess regeneration efficiency and cyclic stability of the adsorbent.
7. Develop a statistically validated and mechanistically informed framework for scalable nutrient removal applications.

In summary, innovative and sustainable strategies must be implemented in addressing nutrient pollution problem. Nutrient pollution mitigation methods that use adsorption as well as adsorbents obtained from MOFs possess potential. However, for scaling purposes, optimization expertise, mechanistic insights, and statistical validations are essential. In this research work, a robust framework for adsorption of nutrients from aqueous solution is designed using the approach of integrating RSM optimisation, mechanistic modeling, advanced characterization, and regeneration evaluation.

2. Materials and Methods

All chemicals and reagents that was used in this study were of analytical grade and utilized without additional purification. The ferric chloride hexahydrate ($FeCl_t \cdot 6H_2O$, ≥99%) was utilised as metal precursors for the fabrication of Fe-MOFs, whereas 1,4-benzenedicarboxylic acid (H_2BDC, ≥98%) served as the organic ligand. The choice of solvent for the synthesis of metal-ligands in the form of the Fe-MOFs is the highly polar and excellent coordinating ability of the N,N-Dimethylformamide (DMF, ≥99.8%). The synthesised framework underwent washing and solvent exchange using ethanol (≥99.5%) to remove any remaining precursors and solvent molecules. The introduction of an amine-rich (-NH_2) active site on the MOFs surface was accomplished using the polyethyleneimine (PEI, average molecular weight = 600 Da) as a post-synthetic functionalisation agent. This enhances adsorption capability towards the nutrient ions. In order to prepare all aqueous solutions for conducting adsorption experiments, deionised water having resistivity of 18.2 MΩ.cm was used.

2.1 Adsorbent Synthesis

Environmentally friendly synthesis of iron metal-oxide fuel cell: Solvothermal self-assembly method is one of the commonly known methods of synthesizing iron metal-organic framework (Fe-MOF). This particular method is known for yielding highly crystalline porous materials. The materials used for the synthesis include $FeCl_4.6H_2O$ as the metal ion source and H_2BDC as the organic linker. Iron ionic sources have always been considered as environmentally friendly and strong coordinating ions; thus, their choice in this particular case. On the other hand, H_2BDC was chosen because of its rigid aromatic structure, which helps create a stable framework.

It is often necessary to achieve homogeneity through dissolving stoichiometric amounts of $FeCl_{3t}\cdot 6H_2O$ and H_2BDC in N, N-dimethylformamide (DMF), while stirring continuously. Being characterized by high dielectric constant and ability to facilitate the deprotonation of carboxylic acid groups, DMF acts as both solvent and directing structure for achieving strong coordination between metals and ligands. The mixture obtained was later placed in a stainless-steel autoclave, lined with Teflon, and allowed to heat at a temperature of 150oC for 24 hours under autogenous pressure.

The autoclave was then cooled to room temperature slowly. In order to get rid of unreacted precursors and/or solvent molecules trapped in the solid, the obtained solid was washed several times with ethanol through filtration with Whatman 4 qualitative filter paper. To make pores accessible and prevent framework collapse upon activation, the product went through a solvent exchange with ethanol.

Functionalisation after synthetic using PEI: In order to enhance the adsorption characteristics, Polyethyleneimine (PEI), a branched polymer highly functionalized with amine (-NH_2) functionalities, was used to modify the synthesized Fe-MOF. The ratio between Fe-MOFs and PEI was 1:0.15, meaning that a structural ratio of 1:0.15 was used for the functionalization. Activated MOFs were mixed with an ethanol solution of PEI by stirring in the process of postsynthetic grafting.

The amine groups in PEI interact via hydrogen bonding and coordination when brought close to oxygen functional groups or metals centers. These additional binding sites contribute to increased anion binding affinities, particularly towards phosphates and nitrates. Following functionalization, the samples were rinsed, dried and stored in desiccators until characterization and adsorption studies.

2.3 Characterization of the Adsorbent

The synthesised Fe-MOF, as well as its modified version, have been studied in terms of surface, thermal, morphological and structural characteristics using the entire spectrum of analysis techniques.

BET – the technique that measures specific surface area of the adsorbent: The BET method involves measuring the adsorbate's specific surface area, total pore volume and size distribution using nitrogen adsorption/desorption isotherms at the temperature of liquid nitrogen (77 K). Samples were degassed to remove the contamination prior to analysis. Specific surface area was calculate

ed using the BET theory while BJH equation was used to characterise mesoporous structure. Adsorption performance depends critically on surface area since it influences active site exposure and nutrient ion diffusion paths. Microporous or mesoporous structures, respectively, are required from materials based on MOFs. Type I or IV isotherms usually prove this.

Fourier Transform Infrared Spectroscopy (FTIR): FTIR was carried out for the purpose of determining metal ions coordination effectiveness with organic ligands and functional group determination in the adsorbent. FTIR spectrum was measured within the wave number range from 4000 to 400 cm^{-1}. Attention was paid to finding peaks that belong to oxygen-containing bonds, carboxylate groups ($-COO^-$), aromatic ring stretching (C=C), and the new $-NH_2$ group that appeared due to PEI modification.

Shifts in position and intensity of the identified peaks proved that the coordination process occurred successfully. Moreover, in order to confirm the nutrient-adsorbent interaction, FTIR was also used after adsorption studies.

Scanning electron microscopy (SEM) was used to explore adsorbent morphology and structure. SEM images provided information about adsorbent porosity, surface roughness, aggregating ability, and particle shape. Adsorbents usually possess porous, rod-like, or crystalline morphology because of the increased surface area and higher mass transfer efficiency.

The effects of nutrient loading on adsorbent morphology were also determined with post-adsorption SEM analysis.

X-ray Diffraction (XRD): The XRD technique was used to characterize the synthesized Fe-MOFs with respect to crystalline structures. The diffraction pattern was obtained on a broad 2θ scale, which was then compared with a set of standards.

The absence of impurity peaks confirmed successful synthesis along with strong and sharp peaks confirming good crystallization. The structural stability and interactions between adsorbent and adsorbate could be studied from diffraction patterns following adsorption process.

Thermogravimetric Analysis (TGA): Thermal stability of the adsorbent in the nitrogen atmosphere was established via thermogravimetric analysis. The gradual heating of the sample was accompanied by the measurement of weight change in dependence on temperature. The first stage of weight loss can be associated with physical solvation of solvent molecules, while further decomposition processes are connected with degradation of organic linkers and collapse of the framework structure. Thermal stability is important for wastewater treatment applications.

2.4 Batch Adsorption Experiments

Adsorption studies were carried out in the laboratory for testing the ability of synthesised Fe-MOF in nutrient removal from water. In this regard, a detailed investigation into operational parameters affecting adsorption efficiency was undertaken, including:

- Initial pH of solution
- Adsorbent dosage
- Contact time
- Initial nitrate and phosphate concentration
- Ionic strength (where applicable)

Effect of pH: Solution pH plays a crucial role in adsorption behaviour by influencing surface charge of the adsorbent and speciation of nutrient ions. Experiments have been done with a broad range of pH levels to determine the optimum electrostatic adsorption parameters.

Effect of adsorbent dose: The efficacy of removal has been investigated through varying amounts of Fe-MOF adsorbent in order to ascertain the number of active sites and their effect on adsorption. High doses can lead to aggregation and reduced efficiency on a per-unit weight basis even though more is better.

Effect of contact time: The time required to attain equilibrium at which there is maximum adsorption was established through kinetic tests. Rate of adsorption and nature of adsorption were studied by taking samples at certain time intervals.

Adsorption capacity and behavior of saturation were determined by varying the concentration of nutrients in the initial stage. This information can be used to establish what forces bring about the movement of mass in the process of adsorption.

2.5 Experimental Design (Response Surface Methodology)

RSM framework: Optimization of adsorption conditions and interactions among multiple variables have been studied through Response Surface Methodology (RSM), which is an analytical method. With the help of RSM technique, predictive polynomial equations can be generated to show the relation between concentration, dose, time and pH as well as between removal efficiency and adsorption capacity.

2.6 Adsorption Modelling

Kinetic models: To describe adsorption rate and mechanism, kinetic data were analysed using equation (1) and (2):

Pseudo-first-order (PFO) model

$$\ln(q_e - q_t) = \ln q_e - k_1 t \qquad (1)$$

This model assumes physisorption-controlled processes.

Pseudo-second-order (PSO) model

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (2)$$

The PSO concept implies that there must be some exchange or sharing of electrons in chemisorption.

The error analysis and correlation coefficient helped evaluate the fit of the model.
Isotherm models: The adsorption mechanism was explained by analyzing the adsorption equilibrium data using various isotherms.

Langmuir isotherm: Assumes monolayer adsorption on homogeneous surfaces.
Freundlich isotherm: Describes multilayer adsorption on heterogeneous surfaces.
Temkin isotherm: Considers adsorbate–adsorbent interaction energy.
Halsey isotherm: Represents multilayer adsorption in heterogeneous systems.
Henry's law: Describes linear adsorption at low concentrations.
Jovanovic isotherm: The possibility of the effect of surface vibrations arising due to mechanical interactions between adsorbent and adsorbate was taken into account.
Models were chosen based on goodness-of-fit indicators.

2.8 Statistical Validation

Validation of the reliability, prediction accuracy, and repeatability of the adsorption models was performed statistically.

Coefficient of determination (R^2): R^2 was used to evaluate model explanatory power. Values close to 1 indicate strong correlation between predicted and experimental data.
Error analysis - Multiple error functions were employed:

- **Root Mean Square Error (RMSE):** Measures deviation magnitude
- **Sum of Squared Errors (SSE):** Evaluates overall deviation
- **Mean Absolute Error (MAE):** Measures average absolute deviation
- **Akaike Information Criterion (AIC):** Assesses model complexity versus fit quality

2.9 Regeneration and Reuse Studies

Regeneration tests for reusability and sustainability of the adsorbent were conducted. The process of adsorption was done through desorbing the Fe-MOF with a dilute solution of NaOH. Washing and adsorption were then performed.
For three cycles, the following parameters were evaluated:

- Percentage removal efficiency retention
- Structural stability (via post-cycle characterization)
- Loss of active sites over time

High regeneration efficiency indicates economic feasibility and sustainability of the adsorbent for large-scale wastewater treatment applications.

The comprehensive approach for evaluating the effectiveness of nutrient removal is accomplished via the combination of solvothermal synthesis, advanced characterization, batch adsorption testing, RSM optimization, multi-model adsorption study, and rigorous statistical verification. In case of practical applications to the environment, such an approach ensures accurate prediction, understanding of the process, and scalability.

3. Results and Discussion

3.1 Characterization Results

Various advanced analytical techniques were applied to determine the physico-chemical properties of the adsorbent developed. Such techniques include X-ray diffraction (XRD), scanning electron microscopy (SEM), thermogravimetry (TGA), Brunauer–Emmett–Teller (BET) analysis, and Fourier transform infrared spectroscopy (FTIR). As can be deduced from the above discussion, all these observations confirm that the synthesized adsorbent is ready for its intended applications in nutrient adsorption. The results of characterization of PXRD (A), FTIR (B), SEM (C), BET (D) and TGA (E) of the optimum Fe-MOF are in Figure 1.

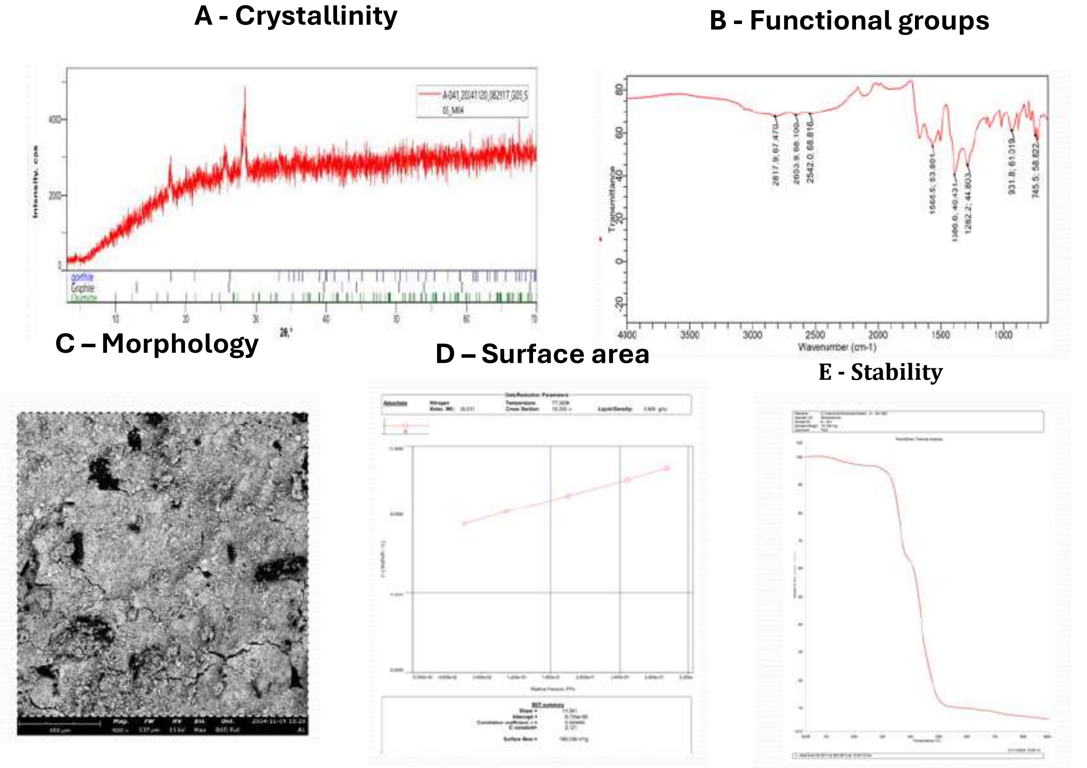

Figure 1: Characterization of PXRD (A), FTIR (B), SEM (C), BET (D) and TGA (E) of the optimum Fe-MOF

The XRD pattern (crystallinity-structure) display diffraction patterns characteristic of crystalline phases corresponding to coordination phases with iron. Being characteristic of MOFs obtained using solvothermal synthesis, the presence of broad diffraction humps together with several weak but visible peaks shows that there is a mixed framework in the range from semicrystalline to crystalline. The purity of the phase can be proven by the absence of sharp peaks of impurities. The relatively large width of the peaks is indicative of nanocrystals, which results in better access of active sites due to enhanced surface area.

FTIR analysis (functional groups) provides convincing evidence for the existence of functionalized surfaces and efficient coordination of metal ions with organic ligands. In the entire spectrum, there appeared several peaks. C=O stretch and possible amide and/or coordinated carboxylate bonds are responsible for the intense absorption band at 1656 cm⁻¹, while vibration bands at 2917 cm⁻¹ and 2853 cm⁻¹ correspond to C-H vibrations. Stretching vibrations of C-N and C-O bonds, which correlate with absorption bands in the range of 1396-1223 cm^{-1}, indicate the successful functionalization of PEI and ligand incorporation. The absorption bands at 931 cm^{-1} and 745 cm^{-1} are further evidence of framework development and Fe-O bond formation. Electrostatic interactions and surface complexation of these functional groups play an essential role in enhancing the adsorption capacity towards phosphate and nitrate ions.

The SEM image (surface morphology) has a surface structure characterized by being highly uneven and porous due to the presence of microcracks, aggregates, and irregular cavities. The surface area suitable for adsorption is significantly enhanced by this rough and porous surface, which also allows for easy mass transfer. The microvoids reduce the adsorption kinetic resistance by indicating diffusion pathways for nutrient ions.

BET analysis (surface area) indicates that the specific surface area is approximately 90.08 m^2/g. The importance of the said figure lies in the existence of functionalized active sites that render the figure important for materials based on iron MOFs despite the fact that the figure may be considered modest in relation to activated carbon materials. In respect of hydrated nitrate and phosphate ions, the mesoporous nature of the material is beneficial as evidenced by the adsorption-desorption isotherm.

TGA analysis (thermal stability) represents multi-step thermal decomposition since there is gradual reduction in weight with increase in temperature. The physically adsorbed water and solvent molecules are lost at temperatures lower than 150°C during the first weight loss. Thermal decomposition of the organic ligands and breakage of the MOF structure account for the considerable weight loss observed between 200-450°C. At temperatures greater than 450°C, the integrity of the adsorbent begins to be compromised thereby giving its upper limit of thermal stability. Considering all this, the relatively modest thermal stability of the adsorbent makes it suitable for regeneration and aqueous adsorption.

In summary, we have successfully developed a porous and thermally stable adsorbent that possesses the required structural characteristics for nutrient removal purposes.

3.2 Effect of Adsorption Variables

Important operating parameters, such as pH, contact time, amount of adsorbent used, and initial nutrient concentration, had significant influence on the efficiency of the adsorption of the synthesized product. Adsorption efficiency and mechanism depend greatly on these parameters. The surface charge of the adsorbent and speciation of nitrate and phosphate ions are greatly influenced by pH. In order to increase electrostatic interaction between negatively charged phosphate and nitrate ions, the surface of the adsorbent protonates at a lower optimal pH of 6, creating a positively charged surface. Deprotonation occurs at higher pH values, reducing electrostatic interaction and, therefore, adsorption efficiency. A range of pH from slightly acidic to neutral resulted in the highest adsorption efficiency since there was a good balance between surface charge and ion concentration.

Effect of time of contact: Kinetics of adsorption suggests that the process consists of a fast adsorption phase and a slower phase of equilibrium. During the former phase, nutrients ions are rapidly adsorbed onto the surface of the adsorbent due to plenty of free active sites. The second phase is limited by diffusion into internal pores of the material as all active sites are saturated.

Optimal mass transfer and pore accessibility were implied by the near-equilibrium state being reached after an optimum duration of 90 minutes for phosphate and 60 minutes for nitrate.

Effect of dosage on adsorbent (1) As a result of the increased availability of active sites, the efficiency of nutrient removal was enhanced by raising the adsorbent dosage. The efficiency was either constant or declined due to particle agglomeration and reduced exposure of the surface area per unit mass. The importance of optimum dosage as far as striking a balance between efficiency and cost is concerned is highlighted.

The adsorption capacity of nutrients with high initial concentrations was greater owing to the strong driving force for mass transfer. However, saturation of the active sites at very high concentrations made further adsorption impossible. This indicates that there is a limitation in the adsorption capacity of the nutrients due to diffusion limitations and the availability of the surface sites.

In conclusion, it can be seen that electrostatic interaction, surface saturation effects, and mass transfer resistance affect adsorption efficiency. In view of this, optimum performance can only be achieved through the optimization of these factors.

3.3 RSM Modelling and Optimization

Response Surface Methodology (RSM) The effects of interactions among independent variables were considered and analyzed in order to systematically optimize the adsorption conditions. Some of the significant factors considered in the design matrix included pH (pH=6 for both nitrate and phosphate), contact time (60 minutes for nitrate and 90 minutes for phosphate), initial concentration (100 mg/L for nitrate and 500 mg/L for phosphate) and adsorbent dosage (qe for nitrate and 292.9 mg/g at 0.1g of adsorbent). In order to show the relationship between these factors and the adsorption reaction, a second order polynomial equation was developed.

There existed a strong relationship between the predicted and experimental values, which is evident from the statistically significant regression model. The high value of R^2 of 0.9978 proved that the model effectively explained the variation observed in the adsorption efficiency. Desirability function approach was used in order to determine the optimum conditions leading to maximum removal of nutrients. Optimized values obtained using the model were tested experimentally, and there existed high similarity between the two sets of values.

The results of the optimization process indicated that both nitrate and phosphate reached their highest adsorption efficiency at pH 6 using 100 mg/L and 500 mg/L of adsorbent dosage and contact time of 60 and 90 minutes, respectively, for the two pollutants. These results clearly reflect the combined effects of surface complexation and electrostatic attraction mechanism.

Response surface methodology was found to be an effective method for optimizing multivariate adsorption systems. This is because scaling up adsorption processes became quite easy with this approach owing to reduction in number of experiments and provision of information on interaction between variables. Synergism was observed between pH and adsorbent dosage. Protonation of surface functional groups and increased electrostatic attraction at low optimal pH 6 enhanced adsorption significantly with increased adsorbent dosage. Deprotonation of surface functional groups decreased this effect at higher pH values.

It can be seen from the effect of interaction between pH and initial concentration that surface charge regulation may be a crucial factor influencing nutrient absorption since the efficiency of adsorption decreases at very low pH regardless of initial concentrations. The optimal adsorption efficiency was recorded for moderate concentrations and optimum pH of 6.

Due to availability of more active sites at high dosages, the interaction between dosage and contact time shows that high dosages lead to faster attainment of equilibrium. After reaching a particular point, however, the increase in rate is negligible, implying the presence of diffusion limitation within the pores.

These interactions justify the application of RSM in optimization since adsorption processes are non-linear in nature. Due to the interaction among all the factors involved, adsorption performance cannot be optimized by modifying its individual components.

3.4 Kinetics Modelling

An evaluation of the rate controlling mechanisms involved in nutrient adsorption was carried out through the analysis of adsorption kinetics using the pseudo-first order (PFO) and pseudo-second order (PSO) models.

The PFO model assumes that the adsorption process involves a physical adsorption mechanism and rate-of-occupancy relationship in which the number of empty sites and rate of adsorption are directly proportional. The assumption of physical adsorption is not adequate since there is a moderate deviation from PFO behavior as observed in experimental data.

On the contrary, the PSO model gave a much better fit with low error values and high correlation coefficient. This is a strong indication that nutrient adsorption is controlled by chemisorption. Chemisorption involves the sharing and/or transfer of electrons between nutrient ions and functional groups of the adsorbent (e.g., Fe-OH and -NH2).

Another supporting factor of the applicability of PSO model is the high correlation between experimentally obtained and computed adsorption capacities. It can be concluded that adsorption is controlled by surface complex formation and valency forces rather than physical adsorption and/or diffusion.

It looks like there is a two-step adsorption mechanism as suggested by the kinetics results: one involving surface bonding, while the other is intraparticle diffusion, and is slower. Porous adsorbents such as MOFs can accommodate this two-step mechanism of adsorption.
The strong interaction between functional groups and adsorbate molecules is proved by kinetic modeling and suggests that chemisorption is an important mechanism in nutrient removal.

3.5 Isotherm Analysis

A number of isotherms models were applied in fitting the equilibrium adsorption data for obtaining more insight into the behavior of adsorption and surface heterogeneity. They include Langmuir, Freundlich, Temkin, Halsey, Henry, and Jovanovic models.

Among the various models, Temkin isotherm gave the highest fitness implying heterogeneous surface multilayer adsorption where adsorption capacity decreases linearly with respect to coverage active sites. The findings imply that there is variation in energy distribution among the adsorption sites.

Further, Freundlich model application implies surface heterogeneity and multilayer adsorption behavior due to existence of different binding sites of different energies on the surface of the adsorbent. It can be inferred that adsorption energy is involved in sharing or exchanging electrons between the adsorbent and adsorbate molecules as shown by Temkin model.

According to Halsey model, multilayer adsorption behavior is observed on heterogeneous surface implying complex adsorption process. When applied at low concentration, Henry model shows applicability implying linear adsorption behavior. Further, Jovanovic model application implies that there are mechanical interactions between adsorbent and adsorbate molecules.

On the whole, the existence of alternative model fits indicates a heterogeneous surface as the location of adsorption through monolayer as well as multilayer mechanism. Adsorption of nutrients on functionalized iron MOF material is indeed complicated, and this serves to prove that. Statistical analysis of Phosphate and Nitrate Adsorption Isotherm Models is contained in Table (1) and (2) below.

Table 1: Statistical Evaluation of Phosphate Adsorption Isotherm Models

Model	R^2	RMSE	SSE	MAE	AIC
Langmuir	0.7045	123.31	106,431.65	92.38	71.41
Freundlich	0.9230	33.19	7,709.87	22.44	53.03
Henry	0.9969	5.03	176.92	4.49	26.61
Temkin	0.9978	4.21	124.85	3.32	24.75
Halsey	0.9230	24.18	4,088.63	17.29	48.67
Jovanovic	0.9284	28.74	5,129.56	19.43	50.91

Table 2: Statistical Evaluation of Nitrate Adsorption Isotherm Models

Model	**SSE**	**RMSE**	**MAE**	**R^2**	**AIC**
Langmuir	6046.20	29.39	13.65	0.8657	23.46
Freundlich	43.67	2.50	1.78	0.9745	-14.69
Temkin	247.26	5.94	4.97	0.8753	48.82
Halsey	43.67	2.50	1.78	0.9745	-3.02
Jovanovic	152.73	4.67	2.89	0.9613	-0.10
Henry	1469.85	14.47	10.94	0.8068	14.06

3.6 Mechanistic Interpretation

Some of the cooperative interactions involved in controlling the nitrate and phosphate adsorption process include electrostatic attraction, surface complexation, ligand exchange, chemisorption, and intraparticle diffusion.

With the use of the lower optimal pH of 6, the surface of the adsorbent becomes protonated to form positively charged sites. In turn, electrostatic attraction is exerted on negatively charged phosphate and nitrate ions to ensure their quick absorption.

In ligand exchange processes, Fe-OH functional groups present in MOF surfaces play a vital role in forming stable inner-sphere complexes through the replacement of hydroxyl groups by phosphate ions. Such reactions have high affinity to iron centers and are suitable for the adsorption of phosphates.

The presence of amine groups ($-NH_2$) through PEI functionalisation enhances adsorption through electrostatic interactions and hydrogen bonding. As a result, selectivity towards anionic species increases and the number of active sites is elevated.

It is evident from interaction energies and kinetic modelling that chemisorption is the most dominant process because of the stability of complexes formed due to electron sharing and/or exchange between adsorbent and adsorbate molecules.

In particular, during the later stages of the adsorption process, intraparticle diffusion is an important factor in the adsorption process. The number of active sites available increases due to the diffusion of the nutrient ions within the internal pores of the MOF material structure.

High adsorption capacity, fast kinetics, and selectivity are some of the results of these phenomena interacting together. Materials with porous structures offer easy transport, while materials with functional groups have greater binding capabilities.

Surface complexation and chemisorption with physical diffusion reactions forming the supporting processes are the main modes of the adsorption process.

3.7 Regeneration and Stability

The regeneration efficiency of the synthesised adsorbent remained above 85% throughout three to five cycles of regeneration. The active sites were able to be regenerated and reused by applying desorption methods using dilute NaOH solutions as eluents.

This may be due to the incomplete desorption of adsorbed ions or partial pore blocking. Nonetheless, there was no indication of any reduction in performance after multiple adsorption-desorption cycles, implying the stability of the structure.

Surface morphology and crystalline structure did not change significantly after characterisation following regeneration. This indicates that the material is able to resist operational conditions without being disintegrated. Table 3 illustrates the recycling ability of nitrate and phosphate adsorption for three cycles.

In practical operations, the regeneration efficiency will reduce costs for both operation and materials. Therefore, the economic and environmental effects of the material can be illustrated clearly.

In summary, the adsorbent has excellent reusability, which implies that it can be applied to treat wastewater over a long period of time.

Table 3: Nitrate and Phosphate Adsorption Recyclability Across Three Regeneration Cycles

	Phosphate Adsorption			Nitrate Adsorption		
	1st Cycle	2nd Cycle	3rd Cycle	1st Cycle	2nd Cycle	3rd Cycle
Dosage (g)	q_e (mg/g)	q_e (mg/g)	q_e (mg/g)	q_e (mg/g)	q_e (mg/g)	q_e (mg/g)
0.1	292.9	292.9	292.8	51.1	51.7	52.1
0.2	146.3	146.3	146.1	25.8	26.7	25.7
0.4	73.1	73.1	73.0	12.6	13.5	12.7

3.8 Comparison with Literature

The fabricated Fe-MOF possesses comparable or even superior adsorption efficiency, kinetic behavior, and stability as compared to that of the previously reported adsorbents.

In case of phosphate and nitrate removal, conventional adsorbents such as activated carbon and biochar exhibit lower selectivity. In contrast, the MOF-based materials possess greater advantages in terms of surface area, functionalization, and adsorption efficiency.

As a result of PEI functionalization, which increases electrostatic interaction and active site density, the developed material proves to be superior to other Fe-containing MOFs mentioned in the literature.

In addition, studies employing RSM optimization approach enjoy certain advantages over those relying on the univariate optimization method alone. This statistical validation renders results more reliable and generalizable.

The newly synthesized adsorbent can be considered highly suitable for practical wastewater treatment purposes owing to its numerous qualities, including effectiveness, stability, reusability, and optimization.

4. Conclusion

Key Findings Summary

This study successfully highlighted the optimization of adsorption process that would lead to optimal nutrient removal from aqueous media through Fe-based MOFs (Fe-UPH.COHSE-NH2) that act as efficient adsorbents. With the use of response surface methodology (RSM) together with adsorption kinetics, adsorption isotherms and physicochemical characterization, it was possible for us to gain an understanding of the adsorption process and the mechanisms involved. It was observed through experiments that efficiency of the adsorption process was influenced by operating variables such as pH, adsorbent dose, contact time and initial nutrient concentrations. The two most influential factors were pH and adsorbent dose.

The high coefficient of determination (R2=0.9978), low residual errors, and statistical significance of model terms indicate a highly reliable fit of Temkin predictive model. The multilayer adsorption mechanism was explained by Halsey and Freundlich models, with their R2 being 0.9745. This again indicates the complexity of the adsorption mechanism. Furthermore, 3D-response surface analysis revealed that the variables interacted significantly among themselves, particularly the interaction of pH and adsorbent dosage, contact time and initial concentration, among others. The highest efficiencies of nutrient removal with optimised operating conditions indicate that Fe-UPH.COHSE-NH2 is promising for aqueous remediation.

The multilayer adsorption on heterogeneous active sites was indicated by the Temkin isotherm model, which was found to be the best-fitted isotherm model for the adsorption equilibrium data. The kinetic studies results indicated better agreement with the pseudo-second-order model, indicating that chemisorption reactions dominated nutrient adsorption.

Characterization studies including FTIR, SEM, BET, XRD, and TGA Research revealed that Fe-UPH.COHSE-NH2 (Fe-MOFs) possessed a great number of functional groups which were able to react with nutrients ions, a high specific surface area, excellent thermal stability, and high porosity. All those structural properties combined resulted in higher efficiency and adsorption capacity of the material. Consequently, the results obtained confirm that Fe-UPH.COHSE-NH2 can be used as novel adsorbents for removal of nutrients from wastewater.

Mechanistic Insight Summary: Several physicochemical interactions occurring on the surface of the Fe-MOF dictated the nutrient removal mechanism through adsorption. Nutrient adsorption was confirmed using FTIR spectroscopy to identify changes in vibrational frequencies of certain functional groups after adsorption. Functional groups involved included hydroxyl, carboxyl, and metal-oxygen. Surface complexation, ligand exchange, pore diffusion, and electrostatic attraction were the dominant mechanisms dictating adsorption.

The Fe-UPH.COHSE-NH2 surface was protonated at an optimal pH 6 to favour electrostatic interactions between adsorbent and negatively-charged nutrients such as phosphates and nitrates. On the other hand, adsorption became less efficient under extremely acidic conditions as hydrogen ions competed with the available active sites. The adsorbent surface had desirable properties that favoured nutrient adsorption when pH was optimized to 6. Through its porous nature and high surface area, Fe-UPH.COHSE-NH2 enhanced adsorption by facilitating rapid penetration of ions into the interior adsorption sites.

The electron exchange must have been an important factor in the adsorption phenomenon, since the data agreed very well with the pseudo second order kinetic model, which suggested that the major mechanism of adsorption was chemisorption. The Temkin isotherm behavior suggests that the energy of adsorption capacity reduces linearly with increase in surface coverage. On overall basis, the adsorption phenomenon was driven by both surface chemistry and thermodynamic factors.

Environmental Relevance: Nutrient pollution due to eutrophication and oxygen depletion of aquatic ecosystems resulting from phosphates and nitrates in effluents is still one of the major challenges faced today. The optimised adsorption process presented in this research can be a sustainable solution to the problem of nutrient pollution in water bodies and wastewater. The recyclable nature, structural stability, and high adsorption rate of Fe-UPH.COHSE-NH2 make them a feasible material for advanced water purification.

RSM optimisation helped achieve maximum nutrient removal efficiency with minimal operational inefficiency, reduced chemical use, and minimized expenses. Statistical optimisation in combination with nanomaterials used for adsorption, therefore, can be a viable method for long-term ecological clean-up processes. To assist in the management of water quality and environmental conservation efforts worldwide, this study will contribute to efficient design of adsorption processes.

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Declaration of Competing Interest

The authors declare no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

Data Availability Statement

Data will be made available upon reasonable request.