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REGENERATION EFFICIENCY AND LONG-TERM STABILITY OF FE-MOFS FOR REPEATED NUTRIENT ADSORPTION CYCLES

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ABSTRACT

The sustainability and practical implementation of metal–organic frameworks (MOFs) for water treatment depend largely on their regeneration efficiency, structural stability, and adsorption reusability under repeated operational cycles. This study evaluates the regeneration performance and long-term adsorption stability of an iron-based metal–organic framework (Fe-MOF), Fe-UPH.COHSE–NH_2, for repeated phosphate and nitrate removal from aqueous solutions. The experiments concerning the nutrient recovery and reusability of the adsorbent have been done using batch adsorption-desorption process using diluted sodium hydroxide as the regenerating agent. Methods such as adsorption capacity test, kinetics modeling, X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), BET surface area analysis, scanning electron microscopy (SEM), and thermogravimetric analysis (TGA) have been employed to monitor the adsorption capacity, structural stability, and physicochemical stability. The regenerated Fe-MOF after several adsorption-desorption cycles retains its high phosphate removal efficiency (>85%) indicating high structural stability and regeneration ability. Phosphate adsorption remained predominantly governed by chemisorption and inner-sphere complexation, while nitrate adsorption exhibited comparatively weaker retention due to electrostatic interaction mechanisms. It was discovered that partial pore clogging, active site saturation, and minimal framework distortion were

KEYWORDS

Fe-MOF; adsorption regeneration; phosphate removal; nitrate removal; adsorption stability; nutrient remediation; reusable adsorbent; wastewater treatment.

responsible for the small decreases in adsorption capability after successive regeneration processes. The adsorbent recovered from successive regeneration processes retained its heterogeneous active sites and favorable adsorption thermodynamics as revealed by the kinetic and isotherm studies. Finally, it can be stated that the findings indicate that Fe-UPH.COHSE-NH_2 is a sustainable adsorbent with high regeneration capability and stability, which makes it an excellent candidate for nutrient removal and wastewater treatment.

Introduction

Excessive discharge of phosphate and nitrate into aquatic systems remains one of the most pressing environmental challenges associated with industrial effluents, agricultural runoff, municipal wastewater, and fertilizer leaching. Some of the threats that arise as a result of elevated nutrients include eutrophication, harmful algal blooms, hypoxia, and many others (Smith et al., 2019; Paerl & Otten, 2020; Conley et al., 2021). Sustainable management of water resources is a very important issue on a global scale, and one of the biggest factors that contribute to it is the contamination of water bodies by nutrients (Wang et al., 2021; Xu et al., 2022).

Conventional nutrient removal technologies include biological processes, ion exchange, membrane filtration, and chemical precipitation. Nevertheless, these processes tend to be inefficient when there are low concentrations of nutrients in water, produce a large amount of sludge, and require high energy consumption (Correll, 2020; Zhao et al., 2021; Li et al., 2022). The inability to distinguish between phosphate and nitrate ions in wastewater makes such technologies useless (Kumar et al., 2023; Zhang et al., 2022).

As stated by Foo & Hameed (2010), Wang & Chen (2020), and Tran et al. (2021), adsorption technique is one of the most efficient and sustainable technologies for nutrient remediation due to its easy regeneration, efficiency, operability, and simplicity. In recent years, much attention has been paid to the application of novel porous materials for water treatment, such as biochar, nanocomposite, and metal-organic framework (MOF) (Furukawa et al., 2013; Li et al., 2020; Zhao et al., 2020).

Metal–organic frameworks (MOFs) consists of organic ligands bound with metal ions or clusters, and they represent crystalline porous materials characterized by an exceptionally large specific surface area, a controllable pore structure, and adjustable surface functionality (Furukawa et al., 2013; Yaghi et al., 2019; Li et al., 2020). As reported by Zhang et al. (2021), Liu et al. (2022), and Wang et al. (2023), MOFs have proven themselves ideal materials for selective removal of ionic contaminants, including phosphate and nitrate ions. Their environmental benignity, low toxicity, abundance, and high affinity toward oxyanions distinguish iron-based MOFs (Fe-MOFs) from other MOFs (Chen et al., 2021; Huang et al., 2022; Gao et al., 2023).

Fe-MOFs demonstrate strong adsorption performance primarily as a result of phosphate ion complexation and ligand exchange due to surface Fe-OH groups (Shimizu & Matubayasi, 2023; Luo et al., 2024). Electrostatic interactions and adsorption selectivity for nutrient ions are both enhanced in the case of amino-functionalized Fe-MOFs (Zhao et al., 2021; Wang et al., 2022). Nevertheless, further investigations into the regenerative properties, stability, and durability in the presence of repetitive adsorption-desorption processes should be conducted (Li et al., 2022; Zhang et al., 2023).

Regarding the sustainability and feasibility of adsorption processes, adsorbent regeneration becomes an important issue. Foo & Hameed (2010), Tran et al. (2021), and Chen et al. (2022) concur that regeneration promotes the material's reusability, reduces operating costs, and avoids the formation of additional waste products. However, structural fatigue caused by repetitive adsorption processes may lead to pore blockage, structural degradation, or loss of active sites (Wang et al., 2022; Liu et al., 2023). The regeneration behaviour of Fe-MOFs is highly dependent on surface chemistry and adsorption phenomena. Selectivity and difficulty in desorption are common features of phosphate adsorption due to the presence of strong inner-sphere complexation and ligand exchange with Fe^{3+} sites (Shimizu & Matubayasi, 2023; Luo et al., 2024). According to Wang et al. (2023) and Huang et al. (2022), nitrate adsorption is mainly driven by weak electrostatic attraction and outer-sphere interactions, making the process more easily reversible but less stable.

Surface heterogeneity, pore structure, and distribution of functional groups significantly affect the adsorption properties of Fe-MOFs. These characteristics can be attributed to kinetic and isotherm models such as the Langmuir, Freundlich, Temkin, Halsey, Henry, and Jovanovic models (Foo & Hameed, 2010; Wang et al., 2021; Zhao et al., 2022). The kinetics and mechanisms of adsorption capacity, multilayer formation, and adsorbate-adsorbent interactions are clarified by all these models put together.

Therefore, With the aid of repetitive cycles of phosphate and nitrate adsorption, this work explores the efficacy and stability of Fe-UPH.COHSE-NH_2 upon regeneration. The specific objectives are to (i) test the adsorption performance after several regeneration cycles; (ii) determine the structural and physicochemical stability of the regenerated Fe-MOF; (iii) investigate the effect of regeneration on the kinetics and equilibrium of adsorption; and (iv) elucidate the role of adsorption mechanisms in the stability and reusability of the MOF. The outcomes of this work will open new directions of investigation related to nutrient removal by means of environment-friendly approaches and development of MOF-based adsorbents for water purification.

2.0 Materials and Methods

2.1 Synthesis of Fe-UPH.COHSE–NH_2

All chemicals and reagents used in this study were of analytical grade and employed without further purification. The Fe-based metal-organic framework (Fe-MOF) was prepared using iron (III) chloride hexahydrate ($FeCl_3 \cdot 6H_2O$, ≥99%) as the metal precursor and 1,4-benzenedicarboxylic acid (H_2BDC, ≥98%) as the organic linker. DMF (N,N-Dimethylformamide, ≥99.8%) was chosen as the solvent in the solvothermal process due to its coordinating ability and polarity, providing effective interaction between the metal and ligand during the synthesis process. Ethanol (≥99.5%) was used in washing the synthesised product in order to eliminate any unreacted precursors or solvent molecules remaining in the structure. For increasing adsorption affinity towards nutrient ions, modification of the MOF surface with amine-rich (-NH_2) groups using polyethyleneimine (PEI) as a post-synthetic functionalisation reagent was performed. PEI is a polymer molecule with an average molecular weight of 600 Da. Deionised water (resistivity 18.2 MΩ·cm) was used in all aqueous solutions and experimental procedures in order to avoid any contamination or purity issues in adsorption processes.

2.2 Adsorption Experiments

Batch adsorption experiments were conducted using phosphate and nitrate solutions prepared from analytical-grade salts. The adsorption studies were performed under optimized conditions of pH, contact time, adsorbent dosage, and initial nutrient concentration. Residual nutrient concentrations were determined using UV–Vis spectrophotometric methods.
The adsorption capacity was calculated using:

$$q_e = \frac{(C_0 - C_e)V}{m} \qquad (1)$$

where q_e is the adsorption capacity (mg g^{-1}), C_0 and C_e are the initial and equilibrium concentrations (mg L^{-1}), V is solution volume (L), and m is adsorbent mass (g).

2.3 Regeneration and Reusability Studies

Adsorption–desorption cycles were performed to evaluate regeneration efficiency and long-term stability. Following adsorption, the spent adsorbent was separated and regenerated using dilute alkaline (NaOH) desorbing solutions under controlled agitation of 150 rpm. Following that, the adsorbent was washed with ethanol, dried, and then used again for further cycles.

Regeneration efficiency (%) was calculated as:

$$Regeneration\ Efficiency, RE\ (\%) = \frac{q_n}{q_1} \times 100 \qquad (2)$$

where q_n is the adsorption capacity during the first cycle and the adsorption capacity after n number of cycles is denoted by q_^{1}.

2.4 Characterization of Regenerated Fe-MOF

The structural stability of the regenerated Fe-MOF was extensively studied by means of advanced characterization techniques, including Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), scanning electron microscopy (SEM), Brunauer-Emmett-Teller (BET) surface area analysis, and thermogravimetric analysis (TGA). The functional properties, crystalline structure, morphology, porosity, and thermal characteristics of the regenerated material were studied using the above techniques in regard to its adsorption-desorption behavior.
Fourier transform infrared spectroscopy (FTIR) was used for identifying the functional groups present on the surface and for studying any changes in the chemical bonding after regeneration. It was important to retain the functional groups such as amino group (-NH_2), carboxylate group (-COO·⁚·), and iron-oxygen (Fe-O) coordination bonds because these functional groups facilitate the adsorption of nutrients through electrostatic attraction, ligand exchange, and surface complexation mechanisms.
X-ray diffraction (XRD) analysis was done to examine the crystallinity and structural stability of the new Fe-MOF structure. Structural collapse, phase change, or even loss of long-range crystallinity could be attributed to multiple adsorption/desorption cycles, which were established from the comparison of

the diffraction pattern before and after regeneration. The ability of the Fe-MOF to maintain its crystallinity and structural stability even after undergoing multiple cycles is indicated by the presence of major diffraction peaks.

Scanning electron microscopy (SEM) was to analyze the influence of the restoration process on surface morphology, particle distribution, and texture variation. The structural deformation, surface roughness, pore accessibility, and agglomeration of the particles after several adsorption cycles were monitored using SEM images. "The reusability of the adsorbent can be proven through the retention of porous and dispersed particles."

Brunauer–Emmett–Teller (BET) surface area analysis was used to determine the specific surface area, pore volume, and pore size distribution of the regenerated Fe-MOF. The BET method is essential when investigating the availability of adsorption sites and the level of pore clogging due to repetitive adsorption/desorption cycles. The mass transfer characteristics and long-term adsorption capacity of the regenerated material were examined through pore volume and surface area change measurements.

Thermogravimetric analysis (TGA) was carried out to evaluate the thermal stability and decomposition of the regenerated Fe-MOF. In the process of regeneration, the thermal decomposition pattern indicated the stability of the adsorbent against heat stress. The prepared Fe-MOF proved to be durable and sustainable for adsorption purposes based on its thermal stability.

The regenerated Fe-MOF has been proven to be stable structurally and physicochemically due to the comprehensive data obtained from these analyses. This enables it to be applied in long-term environmental purification and repeated adsorption of nutrients.

2.5 Kinetic and Isotherm Modelling

Kinetic and equilibrium adsorption models these methods allowed us to determine the surface interaction properties, adsorption mechanisms, and rate behavior of adsorption after regeneration cycles. With the help of this model, we were able to determine if the regenerated Fe-MOF was still efficient in adsorption and maintained the same mechanism even after several nutrient uptakes.

Pseudo-first-order (PFO), pseudo-second-order (PSO), and Elovich kinetic models were employed to analyse the adsorption kinetics of phosphate and nitrate onto the regenerated Fe-MOF. The pseudo-first-order model was used to evaluate adsorption processes primarily governed by physisorption and diffusion-controlled mechanisms. In contrast, the pseudo-second-order model was applied to investigate chemisorption-controlled adsorption involving electron sharing or electron exchange between nutrient ions and active sites on the Fe-MOF surface. The Elovich model was further used to assess adsorption behaviour on energetically heterogeneous surfaces and to examine the influence of surface activation and desorption processes.

The kinetic parameters obtained from these models were used to identify the dominant rate-controlling mechanisms and to determine the extent to which adsorption behaviour changed after repeated regeneration cycles. Comparison between experimental and calculated adsorption capacities also provided additional validation of the suitability and predictive reliability of the selected kinetic models.

Equilibrium adsorption data were adsorption capacity, surface heterogeneity, and mechanism of interaction between adsorbate and adsorbent have been evaluated through Langmuir, Freundlich, Temkin, Halsey, Henry, and Jovanovic isotherm models. The monolayer adsorption on homogeneous surface adsorbents has been evaluated using Langmuir isotherm model. Behaviour of adsorption in heterogeneous and multilayer adsorption systems has been evaluated using Freundlich model while the variation in surface coverage in adsorption heat and effect of interaction between adsorbate and adsorbent has been evaluated using Temkin model.

The **Halsey isotherm model** represent the theory that has been mainly used to describe multilayer adsorption in the presence of heterogeneous surfaces with multiple types of active sites. Based on its practical application, adsorption occurs in multiple layers of surfaces whereby molecules migrate to more energetic places with time. The phosphate and nitrate ions bind with multiple layers of adsorption sites in terms of Fe-MOF adsorption, as indicated by the presence of a porous system with heterogeneous energy distribution and variable sizes of pores as per a reasonable fit with Halsey isotherm model. It represents a typical case of the type of behavior observed in multilayer adsorption in non-uniform energy surfaces whereby individual site energies are not the same but increase as the adsorption continues in multiple layers. This is common for meso- and microporous systems such as metal-organic frameworks (Foo & Hameed, 2010; Li et al., 2020; Wang et al., 2021; Zhang et al., 2021). Porous network structures in such materials offer an opportunity for adsorbates to diffuse and build up in multiple layers. Anions that bind through electrostatic attraction and surface complexation are well described in the behavior of multilayer adsorption in Fe-based MOFs with hierarchical porous domains in accordance with Halsey isotherm theory (Liu et al., 2022; Wang et al., 2023; Zhao et al., 2022).

Therefore, the Halsey equation indicates that there is surface heterogeneity and multilayer adsorption, particularly for nitrate ions that typically show weak and less homogeneous surface interactions.

The **Henry isotherm model** represents the simplest adsorption process where there is no saturation of adsorption sites and which is often observed at low concentrations of solutes. In this case, the quantity of the adsorbed substance is linearly related to the concentration of the adsorbate in solution, implying that the ratio of liquid to solid phase is always constant. The Henry model, which is well-fitted, implies that adsorption occurs at an early stage, when site competition and saturation are not yet important factors. At low equilibrium concentrations of Fe-UPH.COHSE-NH_2, the Henry model implies that the adsorption of phosphates and nitrates is proportional and takes place on the active sites. Surface complexation and electrostatic interactions account for the initial high affinity of the adsorbent surface towards the nutrient ions. At higher concentrations, site saturation and heterogeneous energy distribution are more important in adsorption, as seen in the deviations from Henry behavior.

The **Jovanovic isotherm model** helps us understand adsorption through its mechanical approach that looks at the force between adsorbate and adsorbent surfaces, with adsorption being localized on a monolayer level with the possibility of surface deformations. Two main aspects where it performs excellently include assessment of physical constraints on the surface of the adsorbent as well as its maximum adsorption capacity. Based on the Jovanovic model, which fits nicely, most adsorption processes happen on a monolayer level; however, surface accommodation and structural rearrangement take place. This implies that in the case of Fe-MOF, phosphate and nitrate ions get accommodated on certain active sites up to a maximum possible level after which adsorption doesn’t happen anymore. Using this model, we can predict the maximum capacity of adsorbents for ions and how stiffness and structural properties affect the process.

Collectively, the models explain the underlying principles of the adsorption system in great detail. In particular, the limiting monolayer capacity and surface interactions are explained by Jovanovic;

multilayer adsorption on heterogeneous surfaces is explained by Halsey; and the linear uptake phase is explained by Henry. In all, the findings indicate that the mechanisms controlling the phosphate and nitrate adsorption onto Fe-UPH.COHSE-NH2 involve electrostatic attraction, surface complexation, and heterogeneous multilayer adsorption. Phosphate adsorption is highly site-specific and strong, whereas nitrate adsorption is relatively more diffuse and weaker.

The understanding of the adsorption capacity of the regenerated Fe-MOF was improved significantly by the analysis of kinetics and isotherms together.

3.0 Results and Discussion

3.1 Regeneration Performance of Fe-UPH.COHSE–NH_2

The regeneration experiments demonstrated that Fe-UPH.COHSE–NH_2 retained high adsorption efficiency during repeated nutrient adsorption cycles. The stability of the adsorbent is evidenced by the fact that the phosphate removal efficiency remained higher than 85% despite several regeneration cycles. Figures 1 and 2 present the recyclability of phosphate and nitrate adsorption over three regeneration cycles, respectively. Repeated adsorption-desorption cycles have not affected the relatively high adsorption capacity, meaning that the Fe-based active centers remained accessible enough for phosphate ions' adsorption.

It is possible that due to the ligand exchange and inner-sphere complexation, the high affinity of phosphate ions towards Fe^{3+} active centers could result in such high phosphate retention properties. While increasing adsorption selectivity, those interactions lead to partial irreversibility of adsorption during the process of regeneration. It has been established that the adsorption capacity decreases gradually with each cycle.

Unlike phosphate adsorption, nitrate adsorption demonstrated much lower regeneration stability due to weaker interactions. Weaker electrostatic binding and lower surface affinity are indicated by the sharper decrease in nitrate removal efficiency upon repeated adsorption-desorption cycles. Such action is consistent with the adsorption mechanism of nitrate uptake, which is outer-sphere adsorption.

It is clear from the results of regeneration that, compared to nitrate adsorption, phosphate adsorption is more stable and selective with Fe-UPH.COHSE-NH_2.

Table 1. Phosphate Adsorption Recyclability over 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

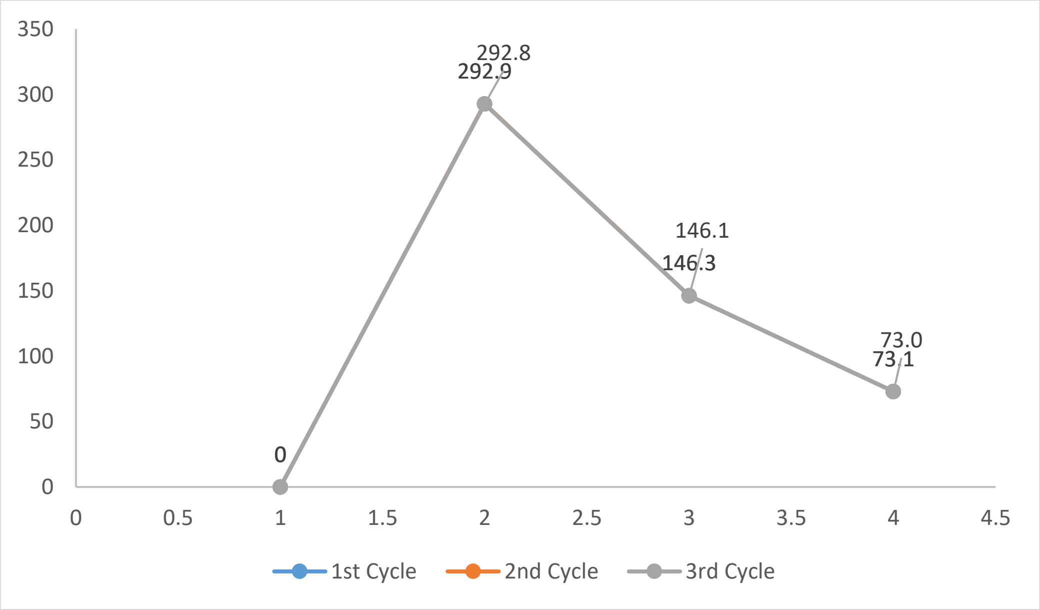

Figure 1: Regenerated Fe-UPH.COHSE–NH₂ phosphate adsorption capacity cycles

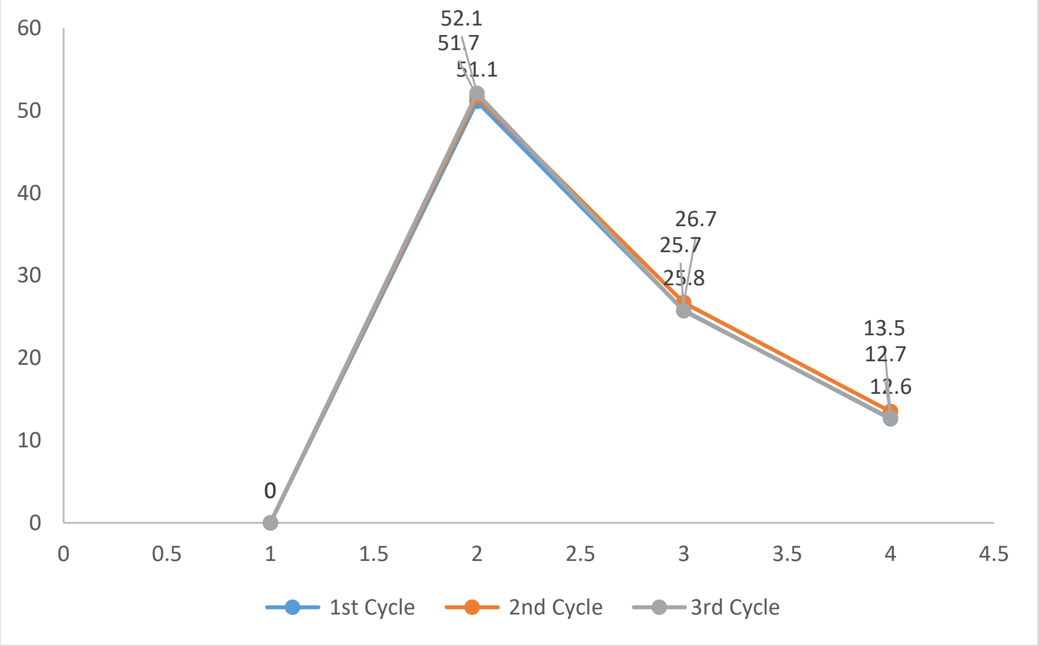

Figure 2: Regenerated Fe-UPH.COHSE–NH₂ nitrate adsorption capacity cycles

Results of Real-World Application of Fe-MOFs in Waste Matrices**:** The physicochemical parameters of the actual wastewater samples are shown in Table 3. The varying environmental conditions associated with the nutrient pollution scenario were represented by the different characteristics of the wastewater samples. Table 4 shows the efficiency of phosphate and nitrate adsorption obtained for the actual water samples.

Table 3: Physicochemical Properties of the Real Water Samples from Various Sources

Parameter	Rain Runoff	Domestic Effluent	Surface Water	Industrial Effluent
pH	6.5	6.0	6.7	10.5
TDS (mg/L)	207	373	381	2160
Conductivity (µS/cm)	324	583	595	3373
Phosphate (mg/L)	2.01	8.80	10.50	6.50
Nitrate (mg/L)	5.79	11.84	7.79	7.73

Table 4: Phosphate and nitrate removal efficiency in real-world samples.

Sample	Phosphate		Nitrate	
	Removal Efficiency (RE %)	qe (mg/g)	Removal Efficiency (RE %)	qe (mg/g)
Rain Runoff	15.5	0.22	79.5	2.75
Domestic Effluent	21.5	1.45	33.8	2.39
Surface Water	6.2	0.39	62.3	2.95
Industrial Effluent	10.6	0.46	81.7	3.74

3.2 Structural Stability After Repeated Adsorption Cycles

The FTIR study of the regenerated adsorbent showed that the main functional groups associated with the amino ligands and Fe-O bonding were generally not affected despite repeated adsorption cycles. The surface interaction of nutrients with active functional groups may be inferred from the slight shift in characteristic peaks without any sign of significant structural degradation.

Additionally, XRD study confirmed that the crystalline structure of the Fe-MOF was retained for the most part after regeneration. Structural stability of the framework during the numerous adsorption/desorption cycles can be attributed to the presence of sharp diffraction peaks. Framework distortion or the buildup of adsorbates within the pores may account for the slight decrease in peak intensity after some number of cycles.

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3.3 Regeneration Mechanisms

The remarkable structural stability and reusability of Fe-UPH.COHSE-NH_2 during multiple adsorption and desorption processes have been evidenced by the regeneration and reusability findings. The adsorption capacities of phosphate were relatively constant in all the three cycles of regeneration, as presented in Table 4.8. In particular, there were no changes in the qe values of 292.9, 292.9, and 292.8 mg/g during the first, second, and third cycles of regeneration at the optimal dosage of 0.1 g. Moreover, the nitrate adsorption capacities showed insignificant variation in the dosage range of 51.1-52.1 mg/g. These findings confirm the high regeneration capacity and stability of the synthesised Fe-MOF over the long term.

The stability of active adsorption sites and porous structure of the Fe-UPH.COHSE-NH_2 framework during the regeneration process is evidenced by the slight decrease in adsorption properties during regeneration cycles. It should be noted that the adsorbent's thermal stability, porosity, crystalline nature, and functional groups were confirmed by the PXRD, FTIR, BET, SEM, and TGA analyses. The high degree of reusability indicates that the regeneration process does not cause significant damage to the amino-functionalized adsorption sites involved in nutrients' absorption or Fe-O coordination bonds.

The surface complexation between the phosphate ions and the active centers of Fe^{3+} along with ligand exchange are the principal elements involved in the regeneration process of phosphate adsorption. The chemisorption interactions enable the formation of strong inner sphere complexes by phosphate ions with the surface groups of Fe-OH and Fe-O during the adsorption process. During the regeneration process, the strength of these interactions is weakened by the desorbing agents, hence releasing the adsorbed phosphate without altering the framework structure. It is evident that the chemisorption interactions are structurally sustainable and partly reversible since the adsorbent retains relatively consistent adsorption capacities throughout several cycles.

The hydrogen bonding, outer sphere complexation, and weak electrostatic attractions are the major factors that determine nitrate adsorption. The nitrate adsorption capacities tend to remain constant through cycles since the weak interactions facilitate the ease of desorption during the regeneration process. Due to their poor affinity towards Fe-based active centers and being monovalent ions, nitrate ions exhibit a slightly low adsorption capacity than phosphate ions.

Moreover, the easy accessibility of active sites, mesoporous nature of the Fe-MOF and high BET surface area (533.94 m2/g) of the material could also be responsible for its good regeneration capability. SEM analysis has shown that it possesses a porous nature which makes it suitable for fast mass transport and effective utilization of adsorption sites during subsequent adsorption-desorption processes. It is also clear from the fact that it maintains its structural integrity up to temperatures around 350oC.

From the results obtained on regeneration it is clear that Fe-UPH.COHSE-NH2 is highly suitable for nutrient remediation applications due to its regenerative and durable nature.

3.4 Kinetic and Isotherm Interpretations

The adsorption kinetics of phosphate and nitrate onto Fe-UPH.COHSE-NH_2 The adsorption kinetics of phosphate and nitrate were analyzed using Elovich kinetic models, PSO, and PFO. Kinetic data shows that the PSO is the most accurate to describe the adsorption of phosphate and nitrate. Also, the correlation coefficient of the model is extremely high ($R^2 = 1.000$). Such strong agreement indicates the predominance of chemisorption as the rate-controlling mechanism. The strong interaction of phosphate ions with Fe-MOF active sites was proved by the linear relationship and high adsorption rate constant ($K_2 = 0.297$ min^{-3}) obtained from the PSO model. Fast achievement of equilibrium and high adsorption capacity (qt = 241.49 mg/g) further confirm the presence of strong inner-sphere complexation and ligand exchange mechanisms. Weak correlation coefficients of the PFO ($R^2 = 0.003$) and Elovich ($R^2 = 0.0957$) models indicate that surface diffusion and physisorption do not play an important role in adsorption.

Similarly, pseudo-second-order kinetics was noted during nitrate adsorption with a relatively higher value of K_2 (2.6014 min^{-1}) and good correlation ($R^2 = 1.000$). This PSO kinetic model confirms that there is still surface interaction between nitrate ions and Fe-modified surface during the process, despite the relatively lower adsorption capacity of nitrate compared to phosphate adsorption. Nitrate adsorption may involve weaker electrostatic attraction and outer-sphere interactions, causing a relatively lower affinity of nitrate adsorption.

For further analyses, equilibrium adsorption data was used for isotherms from Freundlich, Temkin, Halsey, Henry, and Jovanovic. Among these isotherm models, the Henry model had the second-best correlation ($R^2 = 0.9969$) for phosphate adsorption, whereas the Temkin model provided the best correlation ($R^2 = 0.9978$). Phosphate adsorption occurred on energetic heterogeneous surfaces, with decreasing adsorption enthalpy in a linear relationship with the surface coverage, according to the highly correlated Temkin isotherm. Strong adsorbate-adsorbent interactions are exhibited during chemisorption, characterized by this type of behavior.

Electrostatic attraction and surface complexation are very likely to occur between phosphate ions and Fe^{3+} centers, as evidenced by the negative Temkin constant ($bT = -0.7612$ J/mol). Proportional partitioning of adsorption could occur before surface saturation, as suggested by the Henry model.

Freundlich, Halsey, and Jovanovic models also indicated high degrees of correlation, implying the presence of various adsorption sites and possibilities for multilayer adsorption. The extremely high Freundlich adsorption constant ($Kf = 8.016 \times 10^{33}$ mg/g) of the Fe-MOF towards the phosphate ions indicates the extremely strong adsorption affinity of the adsorbent.

Multilayer heterogeneous adsorption on non-uniform energy surfaces is implied by the high correlation ($R^2 = 0.9745$) of Freundlich and Halsey adsorption isotherms for nitrate adsorption. It appears that nitrate adsorption does not occur via monolayer adsorption as indicated by poor results obtained for Langmuir and Henry models. It appears that heterogeneous weak multilayer adsorption interactions take place in the nitrate adsorption process.

The adsorption of phosphates by Fe-UPH.COHSE-NH_2 takes place mainly via chemisorption and surface complexation according to the kinetic and isotherm analysis. In contrary, adsorption of nitrates mainly takes place via heterogeneous weak multilayer interactions. The above described adsorption mechanisms persist in repeated adsorption-desorption cycles.

3.5 Environmental Implications

There are significant environmental and practical implications for sustainable wastewater treatment related to excellent regeneration properties and long-term stability of Fe-UPH.COHSE-NH_k. Operational costs of adsorbent replacement are significantly reduced since adsorbent has the ability to maintain high adsorption capacities in numerous regeneration cycles. This research demonstrates that Fe-MOFs can be used for controlling eutrophication resulting from excess nutrients discharges in water bodies due to their high phosphate adsorption capacity. The significance of high selectivity towards phosphate is explained by the fact that phosphate is one of the limiting factors of toxic algal blooms and oxygen depletion in surface waters.

The possibility of application of Fe-UPH.COHSE-NH_2 in complex environmental matrices was demonstrated with the help of practical applications tests. High adsorption capacity was maintained in case of domestic effluent, despite the reduction of phosphate removal efficiencies in actual wastewater samples because of ion competition and ionic strength effect. Maximum nitrate removal efficiencies reached 79.5% in rain runoff samples and 81.7% in industrial effluent samples, which means that these efficiencies can be considered relatively high in different water matrices.

These findings indicate that The synthesized Fe-MOF performs excellently in many physicochemical conditions like varying pH, conductivity, salinity, and contaminants concentrations. Most of the flexibility of Fe-MOF in practical environmental conditions depends on its chemically stable structure, high surface area, and mesoporous nature.

Regeneration using environmentally friendly sodium hydroxide solution is another benefit that makes the adsorption process more sustainable. Regeneration helps support the circular approach to water treatment processes by making nutrient recovery and adsorbent reuse possible, thus reducing the need to produce new adsorbents.

The current study demonstrates that Fe-UPH.COHSE-NH_2 is thermally stable, structurally strong, and durable in adsorption, and hence, can be applied in environmental remediation projects on a large scale.

4.0 Conclusion

This study demonstrates that Fe-UPH.COHSE-NH_2 is a highly effectively removes phosphate and nitrate from water-based solutions through the use of a reusable and structurally stable adsorbent. Regeneration experiments revealed that the adsorption capacity was highly stable throughout three consecutive adsorption-desorption cycles, particularly in terms of phosphate adsorption without any substantial loss.

Phosphate and nitrate adsorption followed the pseudo-second order kinetic model, according to kinetic analysis. It implies that chemisorption is responsible for the rate controlling step. Whereas nitrate adsorption adhered to Freundlich and Halsey isotherms, suggesting heterogenous multilayer adsorption, phosphate adsorption followed the Temkin and Henry models which suggested heterogenous surface complexation, according to the isotherm modeling.

A crystalline, porous, thermally stable, and chemically robust Fe-MOF framework was synthesised. Its adsorption performance was maintained even after multiple usages. The results from PXRD, FTIR, SEM, BET, and TGA have collectively proven this.

Fe-UPH.COHSE-NH_2 demonstrated great capability of phosphate and nitrate removal under various environmental conditions including fluctuations in pH levels, ionic strength, and presence of competing ions, according to the findings from real-world experiments.

Great promise is shown by this Fe-MOF in terms of sustainable nutrient remediation, wastewater treatment and environmental protection applications due to its high regeneration efficiency and adsorption capacity.

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