

# ISOTHERM AND KINETIC STUDIES OF SELECTIVE PHOSPHATE AND NITRATE REMOVAL USING POLYETHYLENEIMINE-FUNCTIONALIZED IRON-BASED METAL ORGANIC FRAMEWORKS

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| ABSTRACT                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             | KEYWORDS                                                                                                                                                               |
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| <p>Nutrient pollution caused by excessive nitrate and phosphate discharge into aquatic environments remains a major environmental challenge due to its role in eutrophication and water quality deterioration. Conventional wastewater treatment methods often suffer from low selectivity, limited adsorption efficiency, and poor regeneration performance. This study developed a structurally optimized and functionally enhanced iron-based metal–organic framework (Fe-UPH.COHSE–NH<sub>2</sub>) for selective nutrient removal from aqueous solutions. The synthesis was carried out using a controlled solvothermal method and optimized by varying the precursor ratio of Iron (III) (Fe<sup>3+</sup>) to 1,4-benzenedicarboxylic acid (H<sub>2</sub>BDC). Batch adsorption studies integrated with isotherm, kinetic and statistical error analyses were conducted to investigate adsorption mechanisms. The Fe-UPH.COHSE–NH<sub>2</sub> exhibited a high phosphate adsorption capacity of 272.9 mg·g<sup>−1</sup> and nitrate uptake of 53.4 mg·g<sup>−1</sup> with a maximum BET surface area of 533.94 m<sup>2</sup> g<sup>−1</sup>. Isotherm correlation showed phosphate adsorption fitted best into Temkin model (R<sup>2</sup> = 0.9978), while nitrate adsorption fitted to Freundlich/Halsey models (R<sup>2</sup> = 0.9745), indicating heterogeneous adsorption behaviour. Kinetic studies confirmed pseudo-second-order behaviour with high correlation coefficient of R<sup>2</sup> = 1, suggesting chemisorption governed by electrostatic interactions, Fe–ligand surface complexation and hydrogen bonding. In conclusion, Fe-UPH.COHSE–NH<sub>2</sub> exhibits high adsorption capacity for phosphate and strong potential for sustainable and scalable water treatment applications.</p> | <p>Iron metal–organic framework (Fe-MOF); polyethyleneimine; phosphate adsorption; nitrate removal; adsorption isotherms; kinetic modelling; wastewater treatment.</p> |

## Introduction

The contamination of aquatic environments by nutrient species, particularly nitrate ( $\text{NO}_3^-$ ) and phosphate ( $\text{PO}_4^{3-}$ ), has emerged as a critical global environmental challenge driven by intensive agricultural practices, industrial discharge, and urban wastewater effluents. Elevated concentrations of these anions contribute significantly to eutrophication, leading to algal bloom proliferation, dissolved oxygen depletion, and severe disruption of aquatic ecosystems Eutrophication (Smith *et al.*, 2019; Wang *et al.*, 2023). In addition to ecological degradation, nitrate exposure in drinking water has been associated with serious human health risks, including methemoglobinemia and potential carcinogenic effects (Ward *et al.*, 2018), thereby reinforcing the urgency of developing efficient remediation technologies.

Conventional treatment methods such as biological denitrification, chemical precipitation, and membrane filtration have been widely implemented. However, their practical application remains constrained by intrinsic limitations. Biological processes require tightly controlled operational conditions and exhibit sensitivity to environmental fluctuations. Chemical precipitation generates large volumes of secondary sludge, increasing disposal costs and environmental burden. Membrane-based processes, although effective in ion separation, suffer from high energy demand and membrane fouling issues that limit long-term stability (Zhang *et al.*, 2021). Consequently, adsorption has emerged as a promising alternative due to its operational simplicity, cost-effectiveness, and potential for adsorbent regeneration (Crini and Lichtfouse, 2019). Nevertheless, adsorption efficiency is fundamentally governed by the physicochemical properties of the adsorbent, necessitating the development of advanced materials with high affinity, selectivity, and stability toward target anions.

Metal organic frameworks (MOFs) represent a class of crystalline porous materials constructed from metal nodes and organic linkers, characterized by exceptionally high surface areas, tunable pore architectures, and modular chemical functionality. These features enable precise engineering of adsorption sites and host–guest interactions, making MOFs superior to conventional porous materials such as activated carbon and zeolites for environmental applications (Li *et al.*, 2020; Wang and Wang, 2020; Furukawa *et al.*, 2013).

Among the diverse family of MOFs, iron-based MOFs (Fe-MOFs) have attracted increasing attention for water purification due to their low toxicity, environmental compatibility, and abundance of iron precursors. The presence of coordinatively unsaturated  $\text{Fe}^{3+}$  sites promote ligand exchange and surface complexation, which are critical mechanisms for anion adsorption. Furthermore, Fe-MOFs generally exhibit good structural stability in aqueous environments, making them suitable for practical water treatment applications (Hu *et al.*, 2019).

Despite these advantages, pristine Fe-MOFs often exhibit limited adsorption performance toward anionic contaminants due to insufficient surface charge density and a lack of specific binding functionalities. To overcome these limitations, post-synthetic modification strategies have been widely explored. In particular, amine-rich polymers such as polyethyleneimine (PEI) have been shown to significantly enhance anion uptake through electrostatic attraction, hydrogen bonding, and coordination interactions, thereby improving overall adsorption efficiency (Zhao *et al.*, 2018).

Recent studies have demonstrated the potential of MOFs-based materials for nutrient remediation, with Fe-MOFs systems exhibiting phosphate adsorption capacities exceeding  $70 \text{ mg g}^{-1}$  under optimized conditions (Sun *et al.*, 2021). Additionally, the development of magnetic MOFs composites and hybrid

architectures has improved material recyclability and facilitated solid–liquid separation processes (Liang et al., 2022). Lanthanide-based MOFs have also shown promising phosphate affinity, highlighting the influence of metal centers on adsorption selectivity and mechanism (Wu *et al.*, 2020). This study aims to calibrate adsorption data with adsorption isotherms and kinetic models to determine performance for nitrate and phosphate removal in aqueous solution using structurally functionalized and optimized iron-based MOFs (Fe-UPH.COHSE-NH<sub>2</sub>). The study would elucidate the adsorption capacity of Fe-UPH.COHSE-NH<sub>2</sub>, the nature, mechanism and rate of adsorption for nitrate and phosphate removal in aqueous solution.

## 2. Materials and Methods

All chemicals used were of analytical grade and used without further purification. Iron (III) chloride hexahydrate (FeCl<sub>3</sub>·6H<sub>2</sub>O) (≥99%) served as the metal precursor, while 1,4-benzenedicarboxylic acid (H<sub>2</sub>BDC) (≥98%) was used as the organic linker. N, N-dimethylformamide (DMF) (≥99.8%) was employed as the synthesis solvent due to its high polarity and strong coordination capability, facilitating metal–ligand assembly. Ethanol (≥99.5%) was used for washing and solvent exchange. Polyethyleneimine (PEI) with average molecular weight of 600 (Da) was used as a post-synthetic modifier to introduce amine (–NH<sub>2</sub>) functional groups. Sodium nitrate (NaNO<sub>3</sub>) and potassium dihydrogen phosphate (KH<sub>2</sub>PO<sub>4</sub>) were used for preparation of nitrate and phosphate stock solutions, respectively. All solutions were prepared using deionized water (18.2 MΩ·cm).

The Fe-MOF was synthesized via a controlled solvothermal method with FeCl<sub>3</sub>·6H<sub>2</sub>O, H<sub>2</sub>BDC and DMF. It was then functionalized with polyethyleneimine (PEI) to introduce amine-rich active sites and then optimized the synthesis parameters, using a Doehlert experimental design, at metal-to-ligand ratio of 2:1.5 (FeCl<sub>3</sub>·6H<sub>2</sub>O to H<sub>2</sub>BDC). This gave a final product designated as Fe-UPH.COHSE–NH<sub>2</sub>. All functionalization experiments were conducted under identical conditions to ensure reproducibility.

### 2.1 Equilibrium Adsorption Studies of Fe-UPH.COHSE-NH<sub>2</sub>

Batch equilibrium adsorption experiments were performed to evaluate the maximum adsorption capacity and behaviour of Fe-UPH.COHSE–NH<sub>2</sub> toward nitrate (NO<sub>3</sub><sup>–</sup>) and phosphate (PO<sub>4</sub><sup>3–</sup>) removal. This would provide the basis for modelling adsorption isotherms, which describe the relationship between the amount of solute adsorbed and its concentration in solution at equilibrium. For this study, the equilibrium adsorption capacities of phosphate (PO<sub>4</sub><sup>3–</sup>) and nitrate (NO<sub>3</sub><sup>–</sup>) ions onto Fe-UPH.COHSE–NH<sub>2</sub> were evaluated using varying adsorbent dosages. To determine the adsorption equilibrium behaviour, each glass of 100 mL beaker was filled with either 60 mL of 500 mg/L phosphate or 100mg/L nitrate solutions from the stock solutions prepared by dissolving known quantities of dry KH<sub>2</sub>PO<sub>4</sub> and NaNO<sub>3</sub> in deionized water. The pH of each adsorbate solution was adjusted to optimum pH value of 6.

Different adsorbent (Fe-UPH.COHSE–NH<sub>2</sub>) dosages of 0.1, 0.2, 0.4, 0.6, 0.8, 1.0 and 1.2 g, were added into the different breakers. Each mixture was placed on a mechanical shaker and agitated at 150 rpm for 90 minutes (optimum time for phosphate) and 60 minutes (optimum time for nitrates). The mixtures were then filtered using Whatman No. 1 (0.45 μm) filter paper to remove the spent adsorbent. The residual concentrations of phosphate and nitrate in the filtrates were measured using a UV–Visible spectrophotometer at their respective absorbance wavelengths. The equilibrium adsorption capacity

( $q_e$ ) of Fe-UPH.COHSE-NH<sub>2</sub> for each adsorbate was calculated using Equation 1 while Removal efficiency of the adsorbates was calculated using expression shown in Equation 2: This dataset formed the basis for subsequent isotherm model fitting.

$$q_e = \frac{(C_i - C_e)}{m} V \quad (1)$$

Where:

- $q_e$  is equilibrium adsorption capacity (mg/g)
- $C_i$  is initial concentration of adsorbate (mg/L)
- $C_e$  is concentration of adsorbate at equilibrium (mg/L)
- $V$  is volume of solution (L)
- $m$  is mass of adsorbent (g)

$$\text{Recovery efficiency (\%)} = \frac{C_0 - C_e}{C_0} \times 100 \quad (2)$$

## 2.2 Application of Adsorption Isotherm Models to Fe-UPH.COHSE-NH<sub>2</sub> Adsorption Data

Adsorption is usually described through isotherms which is, the amount of adsorbate on the adsorbent as a function of its concentration at constant temperature. Adsorption isotherms provide insights into the nature of the interaction between the adsorbates and Fe-UPH.COHSE-NH<sub>2</sub>. Different isothermal adsorption relations have been used to describe the adsorption data to understand surface properties, adsorption mechanism, and adsorbent capacity:

### 2.2.1 Langmuir Isotherm

Langmuir isotherm as shown in Equation 3 is used for single-layer adsorption, which assumes maximum adsorption corresponding to a saturated monolayer of molecules on the surface of the carbon where the energy of adsorption is considered to be constant.

$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e} \quad (3)$$

Where:

- $q_e$  is Equilibrium adsorption capacity (mg g<sup>-1</sup>)
- $q_{max}$  is Maximum monolayer adsorption capacity (mg g<sup>-1</sup>)
- $K_L$  is Langmuir constant (affinity constant) (L mg<sup>-1</sup>)
- $C_e$  is Equilibrium concentration of adsorbate in solution (mg L<sup>-1</sup>)

Linearized plot of  $C_e/q_e$  vs  $C_e$  was used to estimate maximum monolayer adsorption and Langmuir constant where slope =  $\frac{1}{q_m}$  and intercept =  $\frac{1}{q_m K_L}$ . The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant, commonly known as separation factor ( $R_L$ ) as represented in Equation 4.

$$R_L = \frac{1}{1 + K_L C_0} \quad (4)$$

Where:

- $R_L$  is Separation factor (dimensionless)
- $K_L$  is Langmuir constant (L mg<sup>-1</sup>)

$C_0$  is Initial concentration of adsorbate ( $\text{mg L}^{-1}$ )

The value of  $R_L$  indicates the type of the isotherm to be either unfavourable ( $R_L > 1$ ), linear ( $R_L = 1$ ), favourable ( $0 < R_L < 1$ ) or irreversible ( $R_L = 0$ ). Thus, lower  $R_L$  value reflects that adsorption is more favourable.

### 2.2.2 Freundlich Isotherm

Freundlich isotherm, as expressed in Equation 5, is commonly used to describe adsorption on heterogeneous surfaces. The model assumes that adsorption sites possess non-uniform energies and are exponentially distributed with respect to the heat of adsorption, thereby accounting for multilayer adsorption behaviour on heterogeneous adsorbents (Amrutha *et al.*, 2023; Shimizu & Matubayasi, 2023). The linearized form of the Freundlich isotherm is expressed in Equation 6, where plots of  $\log q_e$  versus  $\log C_e$  yield a straight line with slope equal to  $\frac{1}{n}$  and intercept equal to  $\log K$ .

$$q_e = K_F C_e^{1/n} \quad (5)$$

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (6)$$

Where:

$q_e$  is mass of solute adsorbed per unit mass of adsorbent

$C_e$  is equilibrium concentration of the adsorbate

$K_f$  is constants representing the adsorption capacity

$n$  is adsorption intensity

### 2.2.3 Temkin Isotherm

The Temkin model accounts for adsorbate–adsorbent interactions and assumes that the heat of adsorption decreases linearly with increasing surface coverage. The model is particularly suitable for describing adsorption processes occurring on heterogeneous surfaces and provides insight into the influence of indirect adsorbate interactions during adsorption equilibrium (Hu *et al.*, 2023; Wang & Guo, 2023). This relationship is expressed linearly in Equation 7, where plots of  $q_e$  versus  $\ln C_e$  enable the determination of the isotherm constants  $b_T$  and  $A_T$  from the slope and intercept, respectively. Note that slope =  $B$  and intercept =  $A_T$ .

$$q_e = B * \ln A + B * \ln C_e \quad (7)$$

Where:

$q_e$  is amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium

$C_e$  is equilibrium concentration of adsorbate

$B$  is  $\frac{RT}{b}$ , with  $R$  = universal gas constant (8.314),

$T$  is temperature ( $K$ ), and

$b_T$  is Temkin constant related to heat of adsorption ( $\text{J/mol}$ ).

$A_T$  is Temkin equilibrium binding constant ie measure of the equilibrium binding energy or maximum binding energy

### 2.2.4 Henry's Isotherm

This assumes that adsorption is reversible and occurs without any interaction between adsorbed molecules, and that the surface of the adsorbent provides an unlimited number of identical and energetically equivalent sites at low concentrations. The model implies that the adsorbent remains unsaturated and that the adsorption process is governed by a linear partitioning mechanism rather than saturation-driven kinetics. A good correlation with the Henry isotherm suggests that the adsorbent surface has not reached saturation capacity and that adsorption occurs predominantly under dilute and ideal conditions, which are commonly associated with physical adsorption (physisorption) governed by weak intermolecular interactions (Azizian *et al.*, 2022; Shimizu & Matubayasi, 2023). Under such conditions, the adsorption process exhibits a linear relationship between adsorbate concentration and adsorption capacity, indicating low surface coverage and reversible adsorbate–adsorbent interactions. The Henry isotherm is linearly expressed in Equation 8:

$$q_e = K_H C_e \quad (8)$$

Where:

$q_e$  (mg/g) is the amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium,

$C_e$  (mg/L) is the equilibrium concentration of the adsorbate in solution, and

$K_H$  (L/g) is Henry's constant, which represents the distribution coefficient and reflects the strength of the adsorbate-adsorbent interaction in the linear region.

Note that Henry's constant  $K_H$  is a measure of the adsorbent's affinity for the adsorbate. A higher  $K_H$  value indicates stronger adsorption. The Henry isotherm assumes that adsorption is reversible and adsorbent surface is homogeneous. It also assumes that adsorbate-adsorbent interaction is weak. Henry isotherm is useful for describing adsorption processes at low adsorbate concentrations where the adsorbent surface remains far from saturation. The model assumes a linear relationship between the amount adsorbed and the equilibrium concentration of the adsorbate, making it particularly suitable for dilute solutions and low-pressure gas adsorption systems (Shimizu & Matubayasi, 2023; Azizian *et al.*, 2022). Owing to its simplicity, the Henry isotherm is frequently applied as a fundamental model for evaluating initial adsorption behaviour and adsorbate–adsorbent affinity in dilute aqueous and gaseous systems.

### 2.2.5 Halsey Isotherm

The key feature in Halsey Isotherm is its ability to reflect surface heterogeneity through the value of the exponent  $nH$ . Specifically, lower values of  $nH$  signify higher surface heterogeneity, indicating a wider range of adsorption energies across the material surface. The model assumes that adsorption occurs in multiple layers, particularly under conditions involving weak adsorbate–adsorbent interactions that are characteristic of physisorption processes (Shimizu & Matubayasi, 2023; Foo & Hameed, 2022). In multilayer adsorption systems, adsorbate molecules initially occupy the primary surface sites and subsequently form additional layers through intermolecular interactions, making such models suitable for heterogeneous porous materials and weakly bonded adsorption systems. The Halsey isotherm is represented in its linear and exponential forms as shown in Equation 9 and 10 respectively:

$$\ln q_e = \ln K_H + \frac{1}{n_H} \ln C_e \quad (9)$$

Or equivalently,

$$q_e = K_H \cdot C_e^{-1/n_H} \quad (10)$$

Where:

$q_e$  (mg/g) is the amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium,

$C_e$  (mg/L) is the equilibrium concentration of the adsorbate in solution,

$K_H$  is the Halsey constant, which reflects the adsorption capacity of the material, and

$n_H$  is the Halsey exponent, which provides an indication of the degree of surface heterogeneity.

### 2.2.6 Jovanovic Isotherm

A good fit to the Jovanovic isotherm suggests that the adsorption process is localized and monolayer-dominated, but may also involve mechanical or pore-related influences, such as swelling, compression, or rearrangement of surface structure. This model is especially valuable in systems where adsorbate-adsorbent interactions, surface heterogeneity, and non-ideal adsorption behavior are significant, as it provides a more realistic and nuanced description of adsorption mechanisms than strictly idealized models (Foo & Hameed, 2022; Shimizu & Matubayasi, 2023). By accounting for deviations from ideality, such models improve the interpretation of equilibrium data in complex environmental adsorption systems, particularly for heterogeneous porous materials. The Jovanovic isotherm in linear form is expressed in Equation 11:

$$\ln q_e = \ln q_{\max} - K_J C_e \quad (11)$$

Where:

$q_e$  (mg/g) is the amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium,

$C_e$  (mg/L) is the equilibrium concentration of the adsorbate in solution,

$q_{\max}$  (mg/g) is the maximum adsorption capacity, and

$K_J$  (L/mg) is the Jovanovic constant, which is related to the adsorption energy.

A plot of  $\ln q_e$  versus  $C_e$  enables the determination of the isotherm constants  $K_J$  and  $q_{\max}$  from the slope and intercept respectively. Note that slope =  $-K_J$  and intercept =  $\ln q_{\max}$ . Jovanovic isotherm is useful for describing adsorption on heterogeneous surfaces and can be applied to various adsorbent-adsorbent systems.

### 2.3 Application of Kinetic Models to Fe-UPH.COHSE-NH<sub>2</sub> Adsorption Data

Kinetic models were applied to identify the mechanism controlling the rate of adsorption. Understanding the adsorption kinetics of Fe-UPH.COHSE-NH<sub>2</sub> is critical for evaluating its performance in the removal of phosphate (PO<sub>4</sub><sup>3-</sup>) and nitrate (NO<sub>3</sub><sup>-</sup>), from aqueous solutions. Kinetic modelling aids in identifying the mechanism of adsorption, the rate-limiting step, and the time needed to attain equilibrium. This information is essential for process design, scale-up, and optimization of adsorption systems.

Batch adsorption experiments were carried out by varying contact time (10 –180 minutes) while keeping other parameters constant. The procedures of kinetic experiments were basically identical to

those of equilibrium test. 0.1g of Fe.UPH.COHS- $\text{NH}_2$  were mixed with 60ml of 500mg/l phosphate and 100mg/l nitrate and then added into two breakers. Each mixture was placed on a mechanical shaker and agitated at 150 rpm. The samples were taken at preset time intervals (10, 20, 40, 70, 100, 150 and 180mins) and filtered. The concentrations of phosphate and nitrate at these time intervals were measured. The adsorption capacity ( $q_t$ ) of the adsorbents at preset time  $t$ , was calculated from Equation 12.

$$q_t = \frac{(C_0 - C_t)V}{M} \quad (12)$$

where:

$C_0$  is the initial concentrations of the adsorbates (mg/l),

$C_t$  is the concentration of the adsorbate at any time  $t$  (mg/l),

$V$  is the volume of the solution used (L) and

$M$  is the mass of adsorbent used.

The resulting data were analysed using three standard kinetic models: the pseudo-first-order, pseudo-second-order, and Elovich kinetics models.

### 2.3.1 Pseudo-First-Order Kinetic Model

The pseudo-first-order kinetic model, proposed by Lagergren, assumes that the rate of adsorption is directly proportional to the number of unoccupied adsorption sites. The linear form of this model is expressed in Equation 13. A plot of  $\ln(q_e - q_t)$  versus  $t$  yields a straight line if the model applies. The slope and intercept of the plot were used to calculate  $k_1$  and  $q_e$  respectively.

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (13)$$

Where:

$q_e$  is amount of adsorbate adsorbed at equilibrium (mg/g)

$q_t$  is amount adsorbed at time  $t$  (mg/g)

$k_1$  is pseudo-first-order rate constant ( $\text{min}^{-1}$ )

$t$  is contact time (min)

### 2.3.2 Pseudo-Second-Order Kinetic Model

Pseudo-second-order equation is based on the adsorption capacity of the solid phase which predicts the behaviour over the whole range of data. This model assumes that chemisorption (involving valence forces through sharing or exchange of electrons) governs the adsorption rate (Ho *et al.*, 2005). The linearized form is given in Equation 14:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_t} \quad (14)$$

Where:

$k_2$  is pseudo-second-order rate constant (mg/min)

let  $h = k_2 q_e^2$  (15)

Then Equations (14) become:

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e} t \quad (16)$$

Equation (16) does not have the disadvantage of the problem with assigning an effective  $q_e$ . If Pseudo-second order kinetics is applicable, the plot of  $t/q_t$  against  $t$  of Equation (16) should give a linear relationship from which  $q_e$  and  $h$  values will be determined from the slope and intercept of the plot respectively and there is no need to know any parameter beforehand (Ho & McKay, 1998).  $k_{p2}$  will then be determined from Equation (15).

### 2.3.3 Elovich Kinetic Model

The Elovich equation is a kinetic model used to describe the adsorption of solutes or gases onto solid surfaces. It is often applied to chemisorption processes, where the rate of adsorption decreases with time due to surface coverage. The Elovich equation is expressed in Equation 17:

$$q^t = \left(\frac{1}{\beta}\right) * \ln(\alpha\beta t + 1) \quad (17)$$

Where;

$q_t$  is amount of adsorbate adsorbed at time  $t$

$\alpha$  is initial adsorption rate (mg/g/min)

$\beta$  is the desorption constant (g/mg) and is related to the extent of surface coverage and the activation energy for chemisorption (mg/g/min).

$t$  is time (min)

Elovich equation assumes that the adsorption rate decreases exponentially with increasing surface coverage. It also assumes that adsorption process is controlled by chemisorption. It can be used to model the adsorption of pollutants onto adsorbents and analyze the effects of surface heterogeneity on adsorption kinetics. The linear form of Elovich equation is expressed in Equation 18:

$$(q_t = \left(\frac{1}{\beta}\right) (\alpha\beta) * \ln \left(\frac{1}{\beta}\right) + * \ln (t) \quad (18)$$

This can be rearrange as shown in Equation 19 as

$$q_t = a + b * \ln (t) \quad (19)$$

where;

$$a = \left(\frac{1}{\beta}\right) * \ln (\alpha\beta)$$

$$b = \left(\frac{1}{\beta}\right)$$

If the adsorption process fits into Elovich equation, a plot of  $q_t$  against  $\ln t$  would yield a linear relationship with slope =  $(1/\beta)$  and an intercept =  $[1/\beta \ln (\alpha\beta)]$ .

### 2.4 Model Validation

The isotherm and kinetic model performance was validated using the coefficient of determination ( $R^2$ ), root mean square error (RMSE), sum of squared errors (SSE), and Akaike information criterion (AIC).

The best-fitting model was selected based on the highest  $R^2$  and the lowest RMSE, SSE, and AIC values. The RMSE was calculated as shown in Equation 20:

$$RMSE = \sqrt{\frac{1}{n} \sum_{i=1}^n (q_{e,exp} - q_{e,cal})^2} \quad (20)$$

The SSE was calculated as shown in Equation 21

$$SSE = \sum_{i=1}^n (q_{e,exp} - q_{e,cal})^2 \quad (21)$$

The AIC was calculated as shown in Equation 22

$$AIC = n \ln \left( \frac{SSE}{n} \right) + 2k \quad (22)$$

where n is the number of observations and k is the number of model parameters.

### 3. Results and Discussions

#### 3.1 Equilibrium Adsorption of Fe-UPH.COHSSE-NH<sub>2</sub>

The equilibrium adsorption performance of Fe-UPH.COHSSE-NH<sub>2</sub> toward phosphate and nitrate removal from aqueous solution was evaluated as a function of adsorbent dosage, as illustrated in Figures 1 and 2. Their adsorption capacities ( $q_e$ ), calculated using Equation (1), decreased with increasing adsorbent dosage whereas the removal efficiency, determined using Equation (2), increased with increasing adsorbent dosage. Highest adsorption capacities of 292.9 and 53.4 (mg/g) at 0.2g dosage was recorded for phosphate and nitrate respectively. Also, highest removal efficiency of 11.88 and 11.0% was observed for phosphate and nitrate respectively at 0.2g dosage.

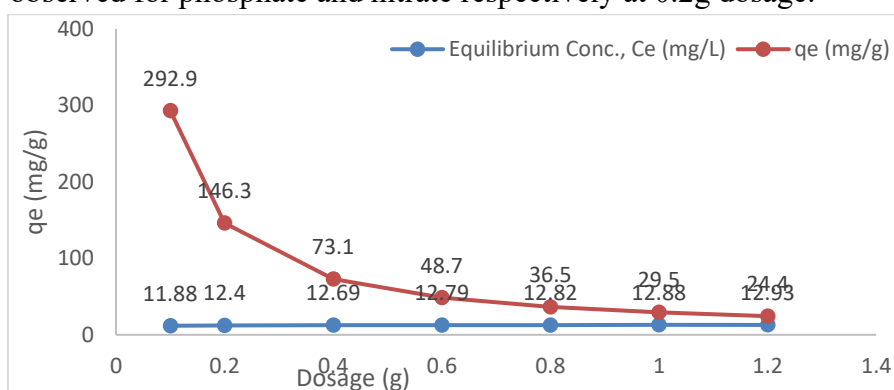


Figure 1: Equilibrium Concentration (Ce) and Adsorption Capacity (qe) for Phosphate across various adsorbent dosages

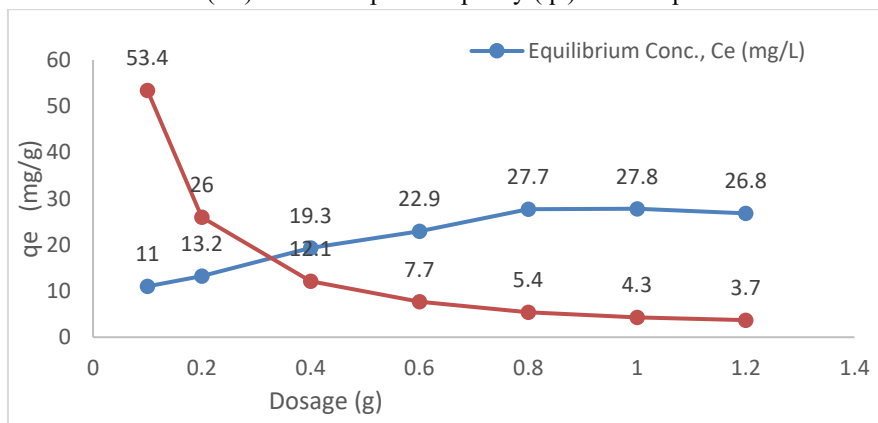


Figure 2: Equilibrium Concentration (Ce) and Adsorption Capacity (qe) for Nitrate across various adsorbent dosages.

This inverse relationship between  $q_e$  and removal efficiency for both phosphate and nitrate adsorption reflects the fundamental distinction between adsorbate mass uptake and overall contaminant removal. At lower adsorbent dosages, the limited number of active sites may result in higher adsorption capacity per unit mass due to the efficient utilization of available binding sites. However, at higher dosages, although additional active sites become available, the fixed amount of adsorbate is distributed across a larger adsorbent mass, leading to reduced equilibrium adsorption capacity ( $q_e$ ) as a result of partial site underutilization, particle aggregation, and possible overlap of adsorption sites (Zhang *et al.*, 2023; Alqadami *et al.*, 2022). This behaviour is commonly observed in adsorption systems where an increase in adsorbent dosage improves removal efficiency but decreases adsorption capacity per unit mass due to unsaturated adsorption sites. This effect, combined with a reduced adsorbate-to-adsorbent ratio, weakens the concentration gradient and mass transfer driving force, further contributing to the decrease in adsorption capacity (Ho and McKay, 1999; Liu *et al.*, 2022).

Importantly, the consistently high removal efficiencies observed across all dosages may be attributed to the optimized porous structure of Fe-UPH.COHS- $\text{NH}_2$ , particularly at the 2:1.5 synthesis ratio, with a high surface area of  $533.94 \text{ (m}^2 \text{ g}^{-1}\text{)}$  and abundant accessible adsorption sites. This structural advantage enhances pollutant uptake by facilitating diffusion and increasing active site availability (Furukawa *et al.*, 2013; Li *et al.*, 2020). A comparative evaluation of both ions reveals that phosphate consistently exhibits higher adsorption capacity and removal efficiency than nitrate across all dosages, indicating stronger interaction with  $\text{Fe}^{3+}$  active sites. This enhanced affinity is attributed to the ability of phosphate to form stronger inner-sphere complexes with metal centers, whereas nitrate primarily interacts through weaker electrostatic forces. Therefore, the adsorption behaviour observed in Figures 1 and 2 confirms that performance is governed by a synergistic interplay between synthesis-controlled surface properties, active site availability, and mass transfer dynamics. These findings demonstrate that both material design (metal–ligand ratio optimization) and operational conditions (adsorbent dosage) collectively determine adsorption efficiency, consistent with previously reported behaviour of MOF-based adsorbents (Wang and Wang, 2020; Kumar *et al.*, 2024).

### 3.2 Modelling Adsorption Data with Adsorption Isotherms

The equilibrium adsorption data for phosphate and nitrate removal using Fe-UPH.COHS- $\text{NH}_2$  were analysed using classical isotherm models, including Langmuir, Freundlich, Temkin, Henry's, Halsey, and Jovanovic models (Equations 3–8). These models were applied to interpret adsorption mechanisms, surface heterogeneity, energy distribution, and adsorbate–adsorbent interactions governing nutrient uptake. Linearized forms of the models were fitted to experimental equilibrium data, and the resulting parameters are summarized in Table 1.

**Table 1: Isotherm Parameters and Statistical Performance validation for Phosphate and Nitrate adsorption onto Fe.UPH.COHS-E-NH<sub>2</sub>**

| Isotherm Model | Linear Model and Isotherm Parameters for Phosphate | Isotherm Model and Isotherm Parameters for Nitrate |
|----------------|----------------------------------------------------|----------------------------------------------------|
|                | Parameters for Phosphate                           |                                                    |
| Langmuir       | $Y = 0.4129x - 4.9478$                             | $Y = 0.3819x - 4.6671$                             |
|                | $q_{\max} = 2.422 \text{ (mg/g)}$                  | $q_{\max} = 2.6185 \text{ (mg/g)}$                 |
|                | $K_L = 0.834 \text{ (L/g)}$                        | $K_L = -0.0818 \text{ (L/g)}$                      |
|                | $R_L = 0.0024$                                     | $R_L = -0.1393$                                    |
|                | $R^2 = 0.7045$                                     | $R^2 = 0.8657$                                     |
|                | RMSE = 123.31                                      | RMSE = 29.39                                       |
|                | SSE = 106,431.65                                   | SSE = 6046.20                                      |
|                | AIC = 71.41                                        | AIC = 23.46                                        |
|                | $Y = -29.147x + 33.904$                            | $Y = -0.3745x + 3.8686$                            |
|                | $1/n = -29.147$                                    | $1/n = -0.3745$                                    |
| Freundlich     | $n = -0.034$                                       | $n = -0.384$                                       |
|                | $K_F = 8.016 \times 10^{33} \text{ (mg/g)}$        | $K_F = 81.2312 \text{ (mg/g)}$                     |
|                | $R^2 = 0.9230$                                     | $R^2 = 0.9745$                                     |
|                | RMSE = 33.19                                       | RMSE = 2.50                                        |
|                | SSE = 7,709.87                                     | SSE = 43.67                                        |
|                | AIC = 53.03                                        | AIC = -14.69                                       |
|                | $Y = -3255.5x + 8349.5$                            | $Y = -0.0194x + 3.3121$                            |
|                | $A_T = 0.0769 \text{ (L/g)}$                       | $A_T = 0.2328 \text{ (L/g)}$                       |
|                | $b_T = -0.7612 \text{ (J/mol)}$                    | $b_T = -23.8045 \text{ (J/mol)}$                   |
|                | $R^2 = 0.9978$                                     | $R^2 = 0.8753$                                     |
| Temkin         | RMSE = 4.21                                        | RMSE = 2.50                                        |
|                | SSE = 124.85                                       | SSE = 43.67                                        |
|                | AIC = 24.75                                        | AIC = -3.02                                        |
|                | $Y = -29.147x + 78.066$                            | $Y = -2.602x + 10.125$                             |
|                | $n_H = -0.034$                                     | $n_H = -0.3843$                                    |
|                | $K_H = 3.244$                                      | $K_H = 48.9598$                                    |
|                | $R^2 = 0.9230$                                     | $R^2 = 0.9745$                                     |
|                | RMSE = 24.18                                       | RMSE = 4.67                                        |
|                | SSE = 4,088.63                                     | SSE = 152.73                                       |
|                | AIC = 48.67                                        | AIC = -0.10                                        |
| Halsey         | $Y = -262.35x + 3408$                              | $Y = -2.3422x + 65.84$                             |
|                | $K_H = -262.35$                                    | $K_H = -2.342$                                     |
|                | $R^2 = 0.9969$                                     | $R^2 = 0.8068$                                     |
|                | RMSE = 5.03                                        | RMSE = 5.94                                        |
|                | SSE = 176.92                                       | SSE = 247.26                                       |
|                | AIC = 26.61                                        | AIC = 48.82                                        |
|                | $Y = -2.3568x + 33.925$                            | $Y = -0.1395x + 5.2806$                            |
|                | $K_J = 2.357$                                      | $K_J = -0.1395$                                    |
|                | $q_{\max} = 5.41 \times 10^{14} \text{ (mg/g)}$    | $q_{\max} = 196.488 \text{ (mg/g)}$                |
|                | $R^2 = 0.9284$                                     | $R^2 = 0.9613$                                     |
| Jovanovic      | RMSE = 28.74                                       | RMSE = 14.47                                       |
|                | SSE = 5,129.56                                     | SSE = 1469.85                                      |
|                | AIC = 50.91                                        | AIC = 14.06                                        |
|                |                                                    |                                                    |

Model performance was assessed using statistical indicators, namely the coefficient of determination ( $R^2$ ), root mean square error (RMSE), sum of squared errors (SSE), and Akaike Information Criterion (AIC) (Equations 20–22). This multi-metric approach ensured robust evaluation beyond reliance on  $R^2$  alone, improving confidence in model selection and interpretation.

For phosphate adsorption, the equilibrium data showed strong agreement with Freundlich, Temkin, Henry's, Halsey, and Jovanovic models. However, the Temkin and Henry isotherms provided the best overall fit, exhibiting the lowest error values and highest statistical reliability. The Temkin model achieved an excellent correlation ( $R^2 = 0.9978$ ), indicating that phosphate uptake is strongly influenced by adsorbate–adsorbent interactions on a heterogeneous surface.

The suitability of the Temkin model suggests that adsorption heat decreases linearly with surface coverage due to indirect adsorbate–adsorbate interactions. This behaviour is characteristic of chemisorption on energetically non-uniform surfaces where binding sites vary in affinity. The negative Temkin constant further indicates strong electrostatic attraction and possible inner-sphere complexation between phosphate ions and  $\text{Fe}^{3+}$  active sites on the adsorbent. Similar mechanisms have been widely reported for phosphate uptake on iron-based materials involving ligand exchange and surface complex formation (Foo & Hameed, 2022; Shimizu & Matubayasi, 2023).

Henry's model also showed excellent agreement ( $R^2 = 0.9969$ ), suggesting partial linear partitioning at low concentrations where adsorption sites are not fully saturated. This indicates that phosphate uptake initially follows a proportional distribution between solution and solid phases. Nevertheless, the superior performance of the Temkin model confirms that surface interactions and chemisorption remain dominant.

Although Freundlich, Halsey, and Jovanovic models also showed relatively good fits, their higher RMSE, SSE, and AIC values indicate lower predictive accuracy. The Freundlich and Halsey models suggest multilayer adsorption on heterogeneous surfaces, but deviations in parameter values (such as negative  $1/n$ ) indicate non-ideal adsorption behaviour of exothermic reaction arising from adsorption energy decreasing linearly with surface coverage. The Jovanovic model produced unrealistically high  $q_{\text{max}}$  values, reducing its physical reliability despite acceptable statistical fit.

For nitrate adsorption, the equilibrium data showed strong agreement with the Freundlich, Halsey, Temkin, and Jovanovic models, with the Freundlich and Halsey model exhibiting the best statistical performance. The Freundlich and Halsey isotherm produced the highest correlation coefficient ( $R^2 = 0.9745$ ) alongside the lowest AIC value ( $-14.69$  and  $-3.02$  respectively) indicating superior fitting accuracy and predictive reliability. Freundlich model is limited as it describes the lower concentration only, while Halsey also covers at higher concentrations. This result confirms that nitrate adsorption onto Fe.UPH.COHS- $\text{NH}_2$  occurred predominantly on a heterogeneous surface containing adsorption sites with non-uniform energy distributions. The Freundlich behaviour also suggests multilayer adsorption and variable binding affinities, likely arising from porous structure, amino functional groups, and Fe-based active sites in Fe.UPH.COHS- $\text{NH}_2$ . The Halsey model further supports multilayer adsorption and heterogeneous pore distribution. The Temkin model showed moderate fit ( $R^2 = 0.8753$ ), indicating that adsorbate–adsorbent interactions contribute to nitrate uptake but are weaker compared to phosphate. This may be attributed to the relatively weak electrostatic attraction between nitrate ions and Fe sites. Unlike phosphate, nitrate typically forms outer-sphere

complexes and is mainly governed by electrostatic interactions rather than strong chemisorption. Similar trends have been reported in Fe-based adsorption systems (Wang et al., 2023).

Generally, isotherm analysis indicates that both phosphate and nitrate adsorption occur on heterogeneous surfaces, but with different dominant mechanisms. Phosphate adsorption is primarily governed by chemisorption and surface complexation, strongly supported by Temkin and Henry models. In contrast, nitrate adsorption follows Freundlich behaviour, indicating multilayer adsorption with weaker interaction energies.

Despite these differences, the strong applicability of the Temkin model for both nutrients highlights the importance of adsorbate–adsorbent interactions, particularly involving  $\text{Fe}^{3+}$  functional sites. This confirms that nutrient uptake is largely controlled by surface-specific interactions across heterogeneous active sites. The corresponding linear plots validating these models are presented in Figures 3–5.

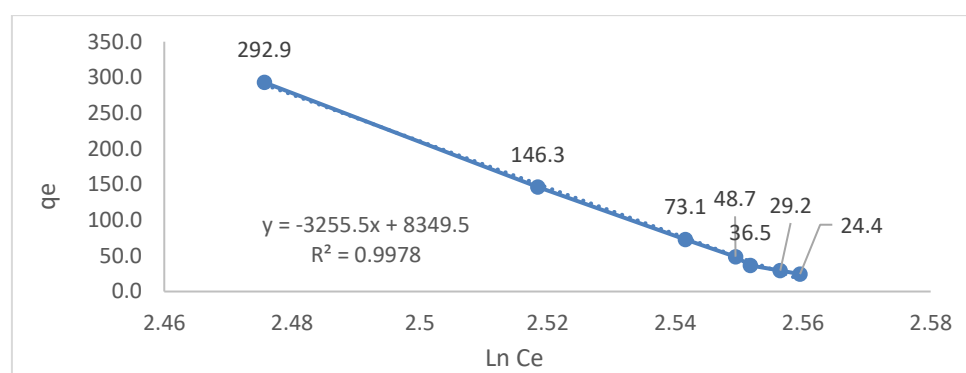


Figure 3: Temkin Isotherm Model for Phosphate Adsorption onto Fe-UPH.COHS-E-NH<sub>2</sub>

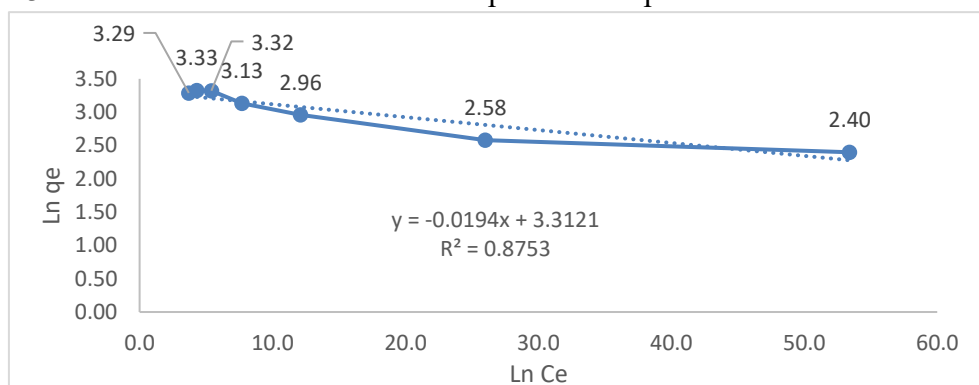


Figure 4: Temkin Isotherm Model for Nitrate Adsorption onto Fe-UPH.COHS-E-H<sub>2</sub>

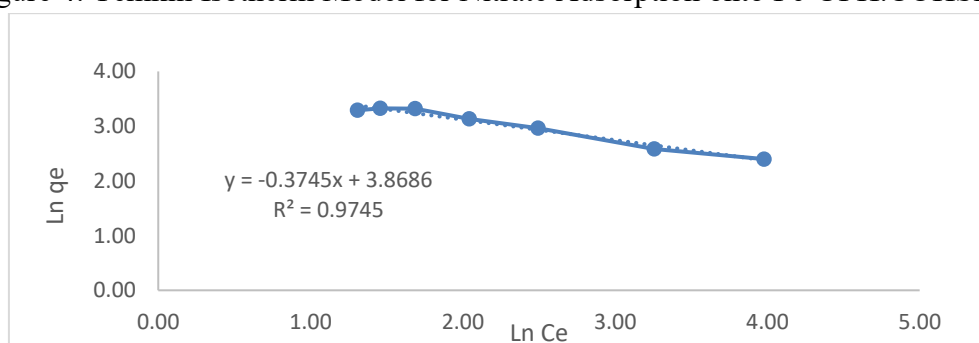


Figure 5: Freundlich Isotherm Model for Nitrate Adsorption onto Fe-UPH.COHS-E-NH<sub>2</sub>

### 3.3 Verification of Isotherm Models

To validate model reliability, interpolated and extrapolated equilibrium concentrations ( $C_e$ ) were used to calculate theoretical adsorption capacities ( $q_e^{cal}$ ), which were compared with experimental values ( $q_e^{exp}$ ). The close agreement between both datasets confirms the predictive accuracy of the selected isotherm models. Minimal deviations between experimental and calculated values demonstrate that the Temkin model (for phosphate) and Halsey/Freundlich model (for nitrate) accurately describe adsorption behaviour. This strong agreement supports the conclusion that adsorption is governed by surface-controlled processes involving heterogeneous active sites.

Overall, the verification results confirm that chemisorption, electrostatic attraction, and surface complexation are the dominant mechanisms controlling nutrient removal by Fe.UPH.COHSSE-NH<sub>2</sub>.

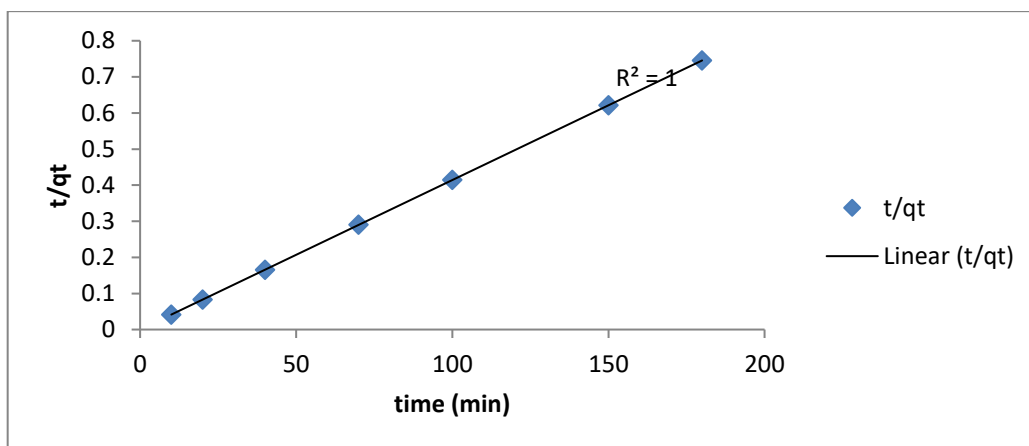
### 3.4 Application of Kinetic Models to Adsorption Data

Kinetic modelling of phosphate and nitrate adsorption onto Fe-UPH.COHSSE-NH<sub>2</sub> was performed using the pseudo-first-order, pseudo-second-order, and Elovich models to evaluate adsorption rates and elucidate the underlying rate-controlling mechanisms. The kinetic expressions (Equations 13–19) were applied to the experimental data, and the resulting parameters are presented in Table 2. Model validation was further supported using statistical error functions as defined in the governing equations.

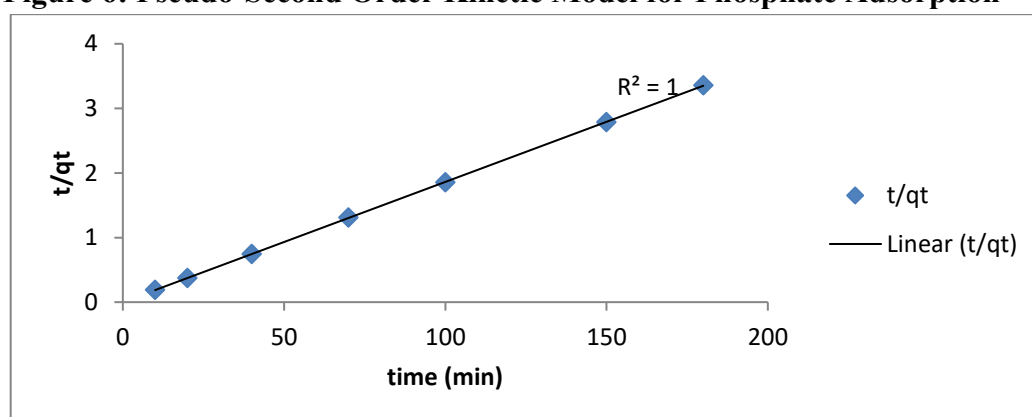
**Table 2: Kinetic Parameters and Statistical Performance validation for Phosphate and Nitrate Adsorption onto Fe.UPH.COHSSE-NH<sub>2</sub>**

| Kinetics Model                     | Linear Model and Kinetics Parameters for Phosphate                                                                                                                         | Linear Model and Kinetics Parameters for Nitrate                                                                                                                                  |
|------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Pseudo First Order Kinetics (PFO)  | $Y = -0.0019x - 4.1791$<br>$R^2 = 0.003$<br>$K_1 = -0.0019 \text{ (min}^{-1}\text{)}$<br>$q_e = -4.1791 \text{ (mg/g)}$<br>$RMSE = 3.85$<br>$SSE = 148.3$<br>$AIC = 25.37$ | $Y = -0.0032x - 1.2196$<br>$R^2 = 0.0397$<br>$K_1 = -0.0032 \text{ (min}^{-1}\text{)}$<br>$q_e = -1.2196 \text{ (mg/g)}$<br>$RMSE = 4.12$<br>$SSE = 175.2$<br>$AIC = 26.54$       |
| Pseudo Second Order Kinetics (PSO) | $Y = 0.0041x - 5 \times 10^{-6}$<br>$R^2 = 1$<br>$K_2 = 0.297 \text{ (min}^{-1}\text{)}$<br>$q_e = 0.0041 \text{ (mg/g)}$<br>$RMSE = 0.72$<br>$SSE = 12.1$<br>$AIC = 7.83$ | $Y = 0.0186x + 0.0009$<br>$R^2 = 1$<br>$K_2 = 2.6014 \text{ (min}^{-1}\text{)}$<br>$q_e = 0.0186 \text{ (mg/g)}$<br>$RMSE = 0.95$<br>$SSE = 18.7$<br>$AIC = 10.88$                |
| Elovich Kinetics                   | $Y = 0.0047x + 241.45$<br>$R^2 = 0.0957$<br>$\beta = 212.77$<br>$\alpha = 1.136 \times 10^{2205}$<br>$RMSE = 4.63$<br>$SSE = 193.4$<br>$AIC = 27.29$                       | $Y = 0.318x + 52.276$<br>$R^2 = 0.3856$<br>$\beta = 3.145 \text{ (g/mg)}$<br>$\alpha = 8.699 \times 10^{70} \text{ (mg/g/min)}$<br>$RMSE = 3.26$<br>$SSE = 74.4$<br>$AIC = 20.56$ |

The kinetic results (Table 3) show that both phosphate and nitrate adsorption are best described by the pseudo-second-order model, which yielded exceptionally high correlation coefficients ( $R^2 \approx 1.000$ ). This strong agreement indicates that the adsorption process is predominantly controlled by chemisorption involving valence forces, electron sharing, or electron exchange between the adsorbate species and Fe active sites on the adsorbent surface. Figures 6 and 7 illustrate the pseudo-second-order kinetic fits for phosphate and nitrate adsorption, respectively.



**Figure 6: Pseudo-Second Order Kinetic Model for Phosphate Adsorption**



**Figure 7: Pseudo-Second Order Kinetic Model for Nitrate Adsorption**

Further analysis confirms that phosphate adsorption consistently follows pseudo-second-order kinetics ( $R^2 \approx 0.997$ – $1.000$ ), reinforcing the conclusion that chemisorption is the dominant rate-controlling step. The close agreement between experimental and calculated equilibrium adsorption capacities ( $q_e$  values) further validates the reliability of this kinetic interpretation.

Overall, these findings indicate that phosphate uptake proceeds mainly through multilayer chemisorption, governed by strong inner-sphere complexation between phosphate ions and  $\text{Fe}^{3+}$  active centres within the Fe-UPH.COHS- $\text{NH}_2$  framework. This mechanism is consistent with established behaviour in iron-based metal–organic frameworks and functionalised adsorbents, where ligand exchange and specific surface complexation play key roles in selective phosphate removal (Furukawa et al., 2013; Liu et al., 2022; Wang et al., 2023).

#### 4. Conclusion

In conclusion, Fe-UPH.COHS- $\text{NH}_2$  exhibits strong potential as a highly efficient and selective adsorbent for phosphate removal from aqueous media. The comprehensive adsorption analysis presented in this study establishes a coherent relationship between the material's structural features, surface chemistry, and adsorption performance. This integrated mechanistic framework is consistent with well-established principles governing metal-organic framework (MOF)-based adsorption systems, particularly those involving iron-functionalised active sites and surface complexation processes (Furukawa et al., 2013; Foo & Hameed, 2010; Kumar et al., 2024).

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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.