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# Kinetic and Isotherm Analysis of $TiO_2/UiO-66-NH_2$ Composites for Treating Produced Water Contaminants

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**Abstract** - The  $TiO_2/UiO-66-NH_2$  composites synthesized through a hydrothermal method, demonstrated a significant enhancement in photocatalytic activity under visible light, offering a promising solution for the treatment of pollutants in produced water. These composites exhibited exceptional photocatalytic adsorption and degradation capabilities, efficiently removing various contaminants. The adsorption process during pollutant removal was effectively modeled by both the Freundlich and Langmuir isotherms, indicating the heterogeneous nature of the adsorption sites and the monolayer adsorption behavior, respectively. The composites achieved impressive removal efficiencies of 88.46% for NH<sub>3</sub>-N and 81.97% for total dissolved solids (TDS), underscoring their potential to address common pollutants in produced water. UV-vis spectroscopy analysis revealed a band gap energy of 2.28 eV for the  $TiO_2/UiO-66-NH_2$  composites, which is lower than that of pure  $TiO_2$ , contributing to enhanced photocatalytic performance under visible light. This reduced band gap improves the material's ability to absorb visible light, thereby facilitating more efficient degradation of organic pollutants. Furthermore, the pseudo-second-order kinetic model best described the adsorption process for both  $TiO_2$  and  $TiO_2@UiO-66-NH_2$  composites, suggesting that chemisorption is the dominant mechanism for  $NH_3$ -N removal. This indicates that the composites exhibit a high affinity for  $NH_3$ -N, effectively removing it from produced water. Overall, the  $TiO_2/UiO-66-NH_2$  composites provide a promising approach for mitigating contaminants in produced water, demonstrating their potential for use in both environmental and industrial water treatment applications.

Keywords – Produced water, TiO<sub>2</sub>, UiO-66-NH<sub>2</sub>, photocatalytic, adsorption.

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#### 1. Introduction

Produced water, the largest by-product of oil and gas extraction, represents a significant environmental concern due to its complex and often toxic composition (Farnan et al., 2023). It typically contains a mixture of hydrocarbons, salts, heavy metals, radioactive materials, and a range of organic and inorganic contaminants (Zhuang et al., 2023). The improper disposal of produced water can result in severe environmental degradation, contaminating soil and water resources, and threatening both ecosystems and public health. The challenge of managing and treating produced water has thus become a focal point in addressing environmental sustainability, particularly in light of the United Nations Sustainable Development Goals (SDGs) (Obaideen et al., 2022). Specifically, SDG 6 (Clean Water and Sanitation) emphasizes the importance of ensuring clean water access, while SDG 12 (Responsible Consumption and Production) advocates for minimizing industrial waste and improving resource efficiency. Effective treatment of produced water is thus crucial for mitigating environmental

risks, enhancing water recovery, and ensuring the sustainable use of water resources in industrial sectors (David et al., 2023).

Conventional methods for treating produced water, such as coagulation, adsorption, and reverse osmosis, often face limitations in terms of cost, energy consumption, and the ability to remove a broad spectrum of contaminants (César et al., 2024). In recent years, photocatalysis has emerged as a promising alternative for the treatment of wastewater, including produced water (Mishra & Sundaram, 2023). Photocatalysis offers several advantages, such as mild operational conditions, the use of sunlight as a renewable energy source, and the potential for mineralizing organic pollutants into less harmful compounds (Chakravorty & Roy, 2024). Titanium dioxide (TiO<sub>2</sub>) is one of the most widely studied photocatalysts due to its stability, non-toxicity, and high photocatalytic activity under ultraviolet (UV) light (Pelaez et al., 2012). However, the effectiveness of  $TiO_2$  is limited by its poor absorption in the visible light spectrum, which constitutes a significant portion of solar energy (Etacheri et al., 2015). To address this limitation, researchers have increasingly focused on enhancing TiO<sub>2</sub> photocatalytic properties by integrating it with other materials, thereby expanding its light absorption range and improving its catalytic efficiency(Khan & Shah, 2023). One such material is UiO-66-NH<sub>2</sub>, a metal-organic framework (MOF) known for its high surface area, large pore volume, and excellent adsorption capacity (Lei et al., 2023). The incorporation of amine functional groups in UiO-66-NH<sub>2</sub> enhances the interaction with organic contaminants, improving the overall photocatalytic degradation process (Chen et al., 2021). Furthermore, the unique structural features of MOFs, such as tunable pore sizes and the ability to create stable, highly porous composites, offer significant advantages in enhancing the photocatalytic activity of TiO<sub>2</sub> (Kumar et al., 2024). The combination of  $TiO_2$  with UiO-66-NH<sub>2</sub> has been shown to produce composites that enhance the degradation efficiency of organic pollutants and extend light absorption into the visible spectrum, increasing their effectiveness under sunlight (Man et al., 2022).

In this context, TiO<sub>2</sub>/UiO-66-NH<sub>2</sub> composites represent a highly promising approach for the treatment of produced water. The synergy between TiO<sub>2</sub> and UiO-66-NH<sub>2</sub> allows for enhanced photocatalytic performance, reduced toxicity of contaminants, and improved stability of the photocatalyst, offering a sustainable and efficient solution for water treatment. The use of TiO<sub>2</sub>/UiO-66-NH<sub>2</sub> composites also aligns with the principles of circular economy and environmental sustainability by promoting the reuse of water in industrial processes and reducing the environmental footprint of oil and gas operations. This study aims to investigate the synthesis, characterization, and photocatalytic performance of TiO<sub>2</sub>/UiO-66-NH<sub>2</sub> composites for the treatment of produced water, focusing on their potential to meet the growing demand for sustainable water management technologies. The findings from this research are expected to contribute significantly to advancing the development of eco-friendly and efficient water treatment methods in line with the global SDGs.

#### 2. Materials and Methods

#### 2.1 Materials

Zirconium chloride (ZrCl<sub>4</sub>, 99.5%), titanium dioxide (TiO<sub>2</sub>), 2-aminoterephthalic acid, methanol, acetic acid, and dimethylformamide (DMF) were obtained from Sigma-Aldrich, Singapore. HI3824-025 test kit reagents, and potassium dichromate. Deionized water was used throughout the experimental procedures to ensure purity and prevent contamination. These reagents were employed in the synthesis of materials and the subsequent preparation steps for photocatalytic experiments. The produced water sample was sourced from the Oil and Gas facility in Cirebon, West Java, Indonesia. A detailed description of the effluent characteristics is provided in Table 1.

#### 2.2 Characterization of produced water

The preliminary analysis of the produced water focused on its physical characteristics and chemical. pH measured with a pH meter, model Y98, China, and total dissolved solids (TDS) measured with a TDS meter, model E-01, China. Chemical Oxygen Demand (COD) was determined using a UV-Vis spectrophotometer in accordance with SNI 6989.2:2019. Total Suspended Solids (TSS) were analyzed following the protocol outlined in SNI 6989.3:2019, while Biochemical Oxygen Demand (BOD) was measured as per SNI 6989.72:2009. Ammonia levels were quantified based on the guidelines of SNI 06-6989.30-2005. Table 1. shows the initial characteristics of produced water.

Table 1. Initial characteristics of produced water					
No.	Parameter	Unit	Value		
1	pН	-	8.3		
2	TDS	ppm	4,000		
3	TSS	ppm	30		
4	COD	ppm	72.3		
5	BOD	ppm	30.4		
6	Amonia	ppm	24		

#### 2.3 Fabrication of TiO<sub>2</sub>/UiO-66-NH<sub>2</sub> composite

360 mg of TiO<sub>2</sub> was dispersed in 60 mL of water and sonicated for 10 minutes. Then, 40 mg of MOF (to achieve 10 wt UiO-66-NH<sub>2</sub>) was added, and the mixture was sonicated for an additional 10 minutes. The pH was adjusted, and the solution was stirred at room temperature until the solvent evaporated. The resulting powder was dried at 100 °C for 24 hours.

#### 2.4 UV-VIS DRS analysis and adsorption studies

The optical properties of the nanofiller photocatalyst were analyzed using UV-Vis spectroscopy. The absorption spectrum was recorded over the wavelength range of 200–800 nm to evaluate the material's light absorption capabilities. A UV-Vis spectrophotometer equipped with an integrating sphere was used to ensure accurate diffuse reflectance measurements. The band gap energy (Eg) of the material was determined using the Tauc method, as represented in (Eq. 1).

$$\alpha hv = A \left( hv - E_g \right)^{\frac{n}{2}} \tag{1}$$

Where  $\alpha$ , h, v, A, and  $E_g$  represent the optical absorption coefficient, Planck's constant, photon frequency, a proportionality constant, and the band gap energy of the material, respectively. The parameter "n" is used to indicate the type of electronic transition occurring within the material, where n=1n = 1n=1 corresponds to a directly allowed transition.

#### 2.5 Adsorption kinetics

The adsorption rate at the active sites of the  $TiO_2/UiO-66-NH_2$  composite governs the removal of pollutants from the solution. To elucidate this process, several kinetic models were utilized, including pseudo-first-order, pseudo-

second-order, intraparticle diffusion, Elovich, mass transfer, and Bangham's models (Kusworo et al., 2024). These models provide valuable insights into the mechanisms and factors influencing pollutant adsorption, offering distinct perspectives on the process dynamics. The mathematical expressions for these models (Eq. 2-7).

$$\frac{t}{\rho_{\rm c}} = \frac{1}{K_{\rm c} \rho^2} - \frac{t}{\rho_{\rm c}}$$
(2)

 $Q_t = K_{2i} \frac{1}{t^2} + C_i$   $Q_t = K_{dit} \frac{1}{t^2} + C_i$ (3)  $Q_t = K_{dit} \frac{1}{t^2} + C_i$ (4)

$$Q_{t} = \frac{1}{2} \ln(\alpha \beta) + \frac{1}{2} \ln t$$
(1)

$$\ln (C_0 - C_t) = \ln (D) - k_0 t$$
(6)

$$\operatorname{Log}\left[\operatorname{Log}\left(\frac{c_0}{c_0 - mq_t}\right) = \operatorname{Log}\left(\frac{m K_b}{2.303 V}\right) + \alpha \operatorname{Log}\left(t\right)$$
(7)

Where  $Q_t$  and  $Q_e$  represent the pollutant adsorption capacity at a specific time and at equilibrium, respectively (both in mg/g). The parameters  $K_1$ ,  $K_2$ ,  $K_i$ ,  $C_i$ , K,  $K_0$ , and  $k_b$  are the kinetic constants for various models, including pseudofirst-order (min<sup>-1</sup>), pseudo-second-order (g.mg<sup>-1</sup>.min<sup>-1</sup>), intraparticle diffusion (mg (g min)<sup>-1/2</sup>), Elovich (g.mg<sup>-1</sup>), mass transfer (min<sup>-1</sup>), and Bangham's model (L. g<sup>-1</sup>).

#### 2.6 Adsorption Isotherm

This study explores adsorption isotherms to understand the relationship between adsorbate quantity and its initial concentration on the TiO<sub>2</sub>/UiO-66-NH<sub>2</sub> composite. The Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich models (Kusworo et al., 2024) were evaluated using (Eq. 8–11).

$$\frac{1}{Q_e} = \frac{1}{K_L Q_m C_e} + \frac{1}{Q_m}; R_L = \frac{1}{1 + K_L C_o}$$
(8)

$$\begin{array}{l} \log Q_e = \log K_F + -\log C_e \\ Q_e = \frac{RT}{h} \ln K_T + \frac{RT}{h} \ln C_e \end{array} \tag{9}$$

$$Q_e = q_m e^{-K\epsilon^2}$$
(11)

Where  $Q_e$ ,  $Q_m$ ,  $C_o$ , and  $C_e$  represent the equilibrium and maximum adsorption capacities (mg/g), and the initial and equilibrium pollutant concentrations (mg/L), respectively.  $K_L$ ,  $K_F$ , n,  $K_T$ , and  $b_T$  are the constants for the Langmuir, Freundlich, and Temkin adsorption models.



#### 3. Results and Discussion 3.1 UV-VIS DRS analysis

The UV-Vis spectra and Tauc plot analysis provide critical insights into the optical properties and band gap energies of various photocatalytic materials, including TiO<sub>2</sub>, UiO-66-NH<sub>2</sub>, and TiO<sub>2</sub>@UiO-66-NH<sub>2</sub> composites. The UV-Vis spectra reveal that all three materials exhibit substantial light absorption capabilities across a broad spectral range 200-800 nm. Figure 2 presents a comprehensive analysis of the composite material's optical properties through (a) UV-Vis diffuse reflectance spectroscopy (DRS) and (b) the corresponding Tauc plot. The TiO<sub>2</sub>@UiO-66-NH<sub>2</sub> photocatalyst displays a broader absorbance profile compared to pure TiO<sub>2</sub>, indicating enhanced efficiency in utilizing visible light energy. This phenomenon is further corroborated by the red shift of the absorption edge and the reduction in band gap energy, as revealed by Tauc plot analysis. The band gap energies of TiO<sub>2</sub>, UiO-66-NH<sub>2</sub>, and  $TiO_2@UiO-66-NH_2$  are determined to be 3.07 eV, 2.61 eV, and 2.28 eV, respectively. Notably, the band gap values of UiO-66-NH<sub>2</sub> and TiO<sub>2</sub>@UiO-66-NH<sub>2</sub> are significantly lower than those of pure  $TiO_2$  in its various crystalline forms, including anatase (3.2 eV), rutile (3.0 eV), and brookite (3.4 eV) (Sadia et al., 2024; Y. L. Wang et al., 2021)

The reduction in band gap energy suggests that these composites possess an enhanced ability to utilize visible light, which is crucial for applications under solar irradiation. This improvement can be attributed to several mechanisms. Firstly, the introduction of new energy levels within the TiO<sub>2</sub> band gap decreases the energy required for electronic transitions (Ye & Liang, 2024). Additionally, the TiO<sub>2</sub>@UiO-66-NH<sub>2</sub> photocatalyst benefits from quantum effects arising from the reduced particle size of TiO<sub>2</sub> and synergistic interactions between the -NH<sub>2</sub> groups of UiO-66-NH<sub>2</sub> and TiO<sub>2</sub> (Monticone et al., 2000). These factors contribute to band gap reduction and improved electron transfer efficiency, effectively minimizing electron-hole pair recombination, a key factor in enhancing photocatalytic activity. The formation of composites with UiO-66-NH<sub>2</sub> yield materials with superior optical properties and reduced band gap energies, making them highly promising for various photocatalytic applications, including pollutant degradation and renewable energy utilization.

Figure 1. Illustrates the experimental setup designed for assessing photocatalytic performance.



#### 3.2 Adsorption of pollutant

Figures 3(a) and (b) illustrate an increasing trend in the percentage of NH<sub>3</sub>-N and TDS rejection with increasing contact time and catalyst dosage. Based on the analysis, a catalyst dosage of 0.3 grams was identified as the most optimal for both pollutants. This finding aligns with previous studies that highlighted catalyst dosage and contact time as two critical parameters significantly influencing the efficiency of the adsorption process (Akinyemi et al., 2024). At higher catalyst dosages, the specific surface area of the catalyst increases, offering more active sites for interaction with pollutant molecules (Sun et al., 2018). This explains the enhanced rejection efficiency observed for both NH<sub>3</sub>-N and TDS. However, when the dosage exceeds 0.3 grams, the efficiency tends to stabilize. This reduced performance at higher dosages is likely due to catalyst agglomeration, which decreases the available surface area, or the saturation of active sites by pollutant molecules (Hachemi et al., 2024). Moreover, contact time plays a pivotal role in enhancing the rejection percentage. Pollutant molecules require adequate time to diffuse onto the catalyst surface for adsorption to occur. With sufficient contact time, adsorption efficiency continues to improve until a saturation point is reached, at which all active sites are occupied by pollutant molecules. Beyond this point, increasing the contact time has minimal

to no effect on further improving efficiency, as the catalyst's adsorption capacity has already been fully utilized (Pourhakkak et al., 2021).

The observed differences in rejection patterns between NH<sub>3</sub>-N and TDS reflect the distinct physicochemical properties of these pollutants. NH<sub>3</sub>-N, being more polar, exhibits stronger interactions with the active sites of the catalyst, leading to higher rejection efficiency compared to TDS across all experimental conditions (C. Wang et al., 2022). In contrast, TDS, characterized by more complex physicochemical properties, may require longer contact times or additional mechanisms to achieve comparable adsorption efficiency. These findings have significant implications for the advancement of wastewater treatment technologies, particularly for produced water. By optimizing the catalyst dosage to 0.3 grams and establishing the appropriate contact time, treatment efficiency can be substantially improved without incurring excessive operational costs. Furthermore, these results underscore the potential for further exploration and development of novel photocatalysts with enhanced properties to address the challenges of treating other organic and inorganic pollutants.





# 3.3 Adsorption Isotherm

The adsorption performance of NH<sub>3</sub>-N on TiO<sub>2</sub> and TiO<sub>2</sub>@UiO-66-NH<sub>2</sub> was evaluated using the Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich (D-R) isotherm models, providing insights into the underlying mechanisms and efficiencies. The Langmuir model, which assumes monolayer adsorption on a homogeneous surface, revealed comparable maximum adsorption capacities (Q<sub>m</sub>) for TiO<sub>2</sub> (68.823 mg/g) and TiO<sub>2</sub>@UiO-66-NH<sub>2</sub> (68.729 mg/g). However, the higher Langmuir constant (K<sub>L</sub>) and lower separation factor (RL) for TiO<sub>2</sub> suggest stronger adsorption affinity and more favorable adsorption conditions compared to TiO<sub>2</sub>@UiO-66-NH<sub>2</sub>. The excellent R<sup>2</sup> value for TiO<sub>2</sub>@UiO-66-NH<sub>2</sub> (0.987) indicates a better fit of this model to the composite, implying significant monolayer adsorption (Pourhakkak et al., 2021; C. Wang et al., 2022)

The Freundlich model, which accounts for adsorption on heterogeneous surfaces, highlighted the superior performance of TiO<sub>2</sub>@UiO-66-NH<sub>2</sub>, with higher K<sub>f</sub> (3.383) and n<sup>-1</sup> (1.218) values compared to TiO<sub>2</sub>. These parameters indicate greater adsorption capacity and intensity for the composite. The  $R^2$  value for  $TiO_2@UiO-66-NH_2$  (0.989) further confirms its strong agreement with this model, suggesting multilayer adsorption on a heterogeneous surface, complementing the findings of the Langmuir model.

The Temkin model, which incorporates adsorbateadsorbent interactions, revealed a higher adsorption energy (b<sub>T</sub>) and equilibrium binding constant ( $K_T$ ) for TiO<sub>2</sub>@UiO-66-NH<sub>2</sub> (25.665 J/mol and 81.077 L/mg), demonstrating stronger interactions and better performance compared to TiO<sub>2</sub>. However, the moderate R<sup>2</sup> value for TiO<sub>2</sub>@UiO-66-NH<sub>2</sub> (0.898) suggests that additional mechanisms may contribute to the adsorption process.

The Dubinin-Radushkevich model provided further insights into the adsorption mechanism. The significantly higher saturation capacity (Qs) of TiO<sub>2</sub>@UiO-66-NH<sub>2</sub> (148.324 mg/g) compared to TiO<sub>2</sub> (58.291 mg/g) confirms its enhanced adsorption potential. The mean adsorption energy (E) for TiO<sub>2</sub> (26.919 kJ/mol) suggests chemisorption, while the lower E value for TiO<sub>2</sub>@UiO-66-NH<sub>2</sub> (3.835 kJ/mol) indicates the dominance of physisorption. This distinction highlights the different adsorption behaviors of the two materials (J. Wang & Guo, 2020a).

The interconnected findings from these models reveal that the adsorption of NH<sub>3</sub>-N on TiO<sub>2</sub>@UiO-66-NH<sub>2</sub> involves a combination of monolayer, multilayer, and physisorption mechanisms, while TiO<sub>2</sub> primarily exhibits monolayer adsorption dominated by chemisorption. The enhanced performance of TiO<sub>2</sub>@UiO-66-NH<sub>2</sub> is attributed to its heterogeneous surface and the synergistic properties

conferred by UiO-66-NH<sub>2</sub>. Overall, the adsorption of NH<sub>3</sub>-N on  $TiO_2@UiO-66-NH_2$  is best described by the Freundlich and Langmuir models, as evidenced by higher R<sup>2</sup> values, indicating the occurrence of both monolayer and multilayer adsorption on heterogeneous surfaces.

Table 2. Parameters of the isotherm models for NH <sub>3</sub> -N					
Isotherm models	Parameters	TiO <sub>2</sub>	TiO <sub>2</sub> @UiO-66-NH <sub>2</sub>		
	Qm (mg/g)	68.823	68.729		
Langmuir	K <sub>L</sub> (L/mg)	0.009	0.0011		
Langinun	$R_L$	0.134	0.6637		
	R <sup>2</sup>	0.831	0.987		
	Kf	1.405	3.383		
Freundlich	n-1	0.339	1.218		
	R <sup>2</sup>	0.847	0.989		
	bт(J/mol)	19.888	25.665		
Temkin	$K_T(L/mg)$	0.056	81.077		
	R <sup>2</sup>	0.775	0.898		
	Qs	58.291	148.324		
Dubinin	$\beta$ (mol <sup>2</sup> /kJ <sup>2</sup> )	0.0006	0.261		
Radushkevich	E (kJ/mol)	26.919	3.835		
	R <sup>2</sup>	0.535	0.817		

# 3.4 Adsorption kinetics

The adsorption kinetics of NH<sub>3</sub>-N on TiO<sub>2</sub> and TiO<sub>2</sub>@UiO-66-NH<sub>2</sub> were evaluated using various kinetic models to understand the mechanism and rate-limiting steps involved in the process. These models included pseudo-first order, pseudo-second order, intraparticle diffusion, Elovich, mass transfer, and Bangham's models. The pseudo-first order model, which assumes that the adsorption rate is proportional to the difference between the current amount of adsorbate and its equilibrium concentration, did not fit the data well for either material, with TiO<sub>2</sub> showing an R<sup>2</sup> value of 0.757 and TiO<sub>2</sub>@UiO-66- $NH_2$  showing an even lower  $R^2$  of 0.411 (Revellame et al., 2020). This suggests that the adsorption on both materials does not follow a simple first-order process, possibly due to the presence of heterogeneous adsorption sites or other factors influencing the adsorption rate. The pseudo-second order model, which is based on chemisorption, where adsorption involves electron sharing or valency forces between the adsorbate and adsorbent, provided a much better fit for both materials, with high R<sup>2</sup> values (0.989 for  $TiO_2$  and 0.997 for  $TiO_2@UiO-66-NH_2$ ). This indicates that the adsorption of NH<sub>3</sub>-N on both TiO<sub>2</sub> and TiO<sub>2</sub>@UiO-66-NH<sub>2</sub> is mainly governed by chemisorption. The higher rate constant (K<sub>2</sub>) for TiO<sub>2</sub>@UiO-66-NH<sub>2</sub> (0.074) compared to TiO<sub>2</sub> (0.0131) suggests that NH<sub>3</sub>-N adsorption is faster on the composite material, highlighting the enhanced adsorption capacity of TiO<sub>2</sub>@UiO-66-NH<sub>2</sub> (J. Wang & Guo, 2020b)

Intraparticle diffusion, which accounts for the diffusion of the adsorbate within the adsorbent material, did not emerge as the dominant rate-limiting step, as reflected by the relatively low  $R^2$  values for both TiO<sub>2</sub> (0.519) and  $TiO_2$ @UiO-66-NH<sub>2</sub> (0.386). The intraparticle diffusion rate constant ( $K_i$ )was higher for TiO<sub>2</sub> (0.075) than for TiO<sub>2</sub>@UiO-66-NH<sub>2</sub> (0.025), suggesting that diffusion within the  $TiO_2$ particles plays a more significant role in the adsorption

process (Pholosi et al., 2020). The Elovich model, which is often used for heterogeneous surfaces, also showed a good fit for both materials with  $R^2 \, values \, of \, 0.979$  for  $TiO_2$  and 0.935 for TiO<sub>2</sub>@UiO-66-NH<sub>2</sub>. The rate constant (K) for TiO<sub>2</sub> was significantly higher (1.723) than for TiO<sub>2</sub>@UiO-66-NH<sub>2</sub> (0.628), indicating that TiO<sub>2</sub> adsorbs NH<sub>3</sub>-N more effectively than the composite. The equilibrium adsorption capacities  $(Q_e)$  were 4.2 mg/g for TiO<sub>2</sub> and 1.217 mg/g for TiO<sub>2</sub>@UiO-66-NH<sub>2</sub>, further confirming the faster adsorption kinetics of TiO<sub>2</sub>. The mass transfer model, which describes the diffusion of NH<sub>3</sub>-N from the bulk solution to the adsorbent surface, provided valuable insights into the efficiency of adsorption. The mass transfer coefficient (K<sub>0</sub>) was much higher for  $TiO_2@UiO-66-NH_2$  (1.806 min<sup>-1</sup>) compared to  $TiO_2$  (0.152) min<sup>-1</sup>), indicating that mass transfer is more efficient for the composite material. Both materials showed high R<sup>2</sup> values  $(0.982 \text{ for TiO}_2 \text{ and } 0.977 \text{ for TiO}_2 @UiO-66-NH_2)$ , suggesting that mass transfer plays an important role in the adsorption process. Bangham's model, which focuses on surface diffusion, showed that  $TiO_2$  had a higher surface diffusion coefficient (k<sub>b</sub>) of 0.152 L/g compared to TiO<sub>2</sub>@UiO-66-NH<sub>2</sub> (0.071 L/g). This indicates that adsorption occurs more efficiently on TiO<sub>2</sub> in terms of surface diffusion, although the fit of the data was moderate with R<sup>2</sup> values of 0.943 for TiO<sub>2</sub> and 0.866 for TiO<sub>2</sub>@UiO-66-NH<sub>2</sub> (Largitte & Pasquier, 2016).

In conclusion, the pseudo-second order model provided the best fit for both  $TiO_2$  and  $TiO_2@UiO-66-NH_2$ , suggesting that chemisorption is the predominant mechanism governing  $NH_3$ -N adsorption.  $TiO_2$  exhibited faster adsorption kinetics, while  $TiO_2@UiO-66-NH_2$  demonstrated superior adsorption capacity, likely due to the enhanced properties of the composite material. These findings suggest that  $TiO_2@UiO-66-NH_2$  may be more suitable for applications where high adsorption capacity is critical, whereas  $TiO_2$  may be more effective in systems requiring rapid adsorption. Further studies on the stability and long-term performance of these materials will be important for their potential application in wastewater treatment.

Table 3. Parameters of the kinetic models for NH	3-N
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Kinetic Models	Parameter	TiO <sub>2</sub>	TiO <sub>2</sub> @UiO-66-NH <sub>2</sub>
Decudo first	K1 (min-1)	0.018	0.003
PSeudo-IIISt	$Q_e(mg/g)$	7.047	9.469
order	R <sup>2</sup>	0.757	0.411
Decudo cocond	K2	0.0131	0.074
r seuuo-seconu	$Q_e(mg/g)$	9.163	3.267
oruer	R <sup>2</sup>	0.989	0.997
Introporticlo	Ki	0.075	0.025
diffusion	Ci	3.560	1.494
uniusion	R <sup>2</sup>	0.519	0.386
	K	1.723	0.628
Elovich	$Q_t$	4.2	1.217
	R <sup>2</sup>	0.979	0.935
	K <sub>0</sub> (min <sup>-1</sup> )	0.152	1.806
Mass transfer	D (mg/L)	6.733	13.985
	R <sup>2</sup>	0.982	0.977
Pangham's	$k_b(L/g)$	0.152	0.071
Dalighaili S	R <sup>2</sup>	0.943	0.866

# 4. Conclusions

The TiO<sub>2</sub>/UiO-66-NH<sub>2</sub> composites demonstrate significant potential for effectively treating pollutants in produced water. The adsorption behavior aligns with both the Freundlich and Langmuir isotherms. The composites demonstrated impressive removal efficiencies, achieving 88.46% for NH<sub>3</sub>-N and 81.97% for TDS, underscoring their effectiveness in addressing common contaminants in produced water. UV-vis analysis revealed a reduced band gap of 2.28 eV for the  $TiO_2/UiO-66-NH_2$  composites, which enhances their ability to absorb visible light and improve photocatalytic performance. Furthermore, the pseudosecond-order kinetic model was the best fit for both  $TiO_2$  and TiO<sub>2</sub>@UiO-66-NH<sub>2</sub> composites, indicating that chemisorption is the dominant mechanism for NH<sub>3</sub>-N removal. This suggests that the composites exhibit a strong affinity for NH<sub>3</sub>-N. Overall, these findings highlight the TiO<sub>2</sub>/UiO-66-NH<sub>2</sub> composites as a highly efficient material for mitigating water contamination, with significant potential for applications in both environmental and industrial water treatment processes.

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