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Photocatalytic Degradation of Ortho-Nitroaniline Orange Using Polyaniline/Titanium Oxide (PANI/TiO_2) Nanocomposite

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Abstract

The rapid growth of industrial activities has led to increased discharge of toxic synthetic dyes like ortho-nitroaniline orange (o-NA) into water bodies, posing severe environmental and health risks. Conventional wastewater treatment methods often fail to completely remove these persistent organic pollutants, necessitating the development of more effective solutions. This study investigated the photocatalytic degradation of o-NA dye using polyaniline/titanium oxide (PANI/TiO_2) nanocomposite under UV/visible light irradiation, comparing its performance with pure TiO_2 nanoparticles. The PANI/TiO_2 nanocomposite was synthesized through oxidative polymerization and characterized using XRD,UV-Vis spectrophotometry and FTIR techniques. Photocatalytic degradation experiments were conducted under varying conditions of catalyst dosage, dye concentration, pH, and irradiation time. The degradation efficiency was evaluated using UV-Vis spectrophotometry, while adsorption behavior was analyzed through Langmuir and Freundlich isotherm models. Kinetic studies were performed using pseudo-first-order and pseudo-second-order models. Results showed that PANI/TiO_2 achieved 91.027% degradation efficiency at optimal conditions (0.4 g catalyst dosage, pH 4, 50 minutes irradiation), outperforming pure TiO_2 (82.054%). The Freundlich isotherm (R^2 = 0.9904) indicated multilayer adsorption, while pseudo-second-order kinetics (R^2 = 0.9917) best described the degradation mechanism. The enhanced performance of PANI/TiO_2 was attributed to improved charge separation and visible-light absorption facilitated by polyaniline. These findings demonstrate PANI/TiO_2's superior photocatalytic activity for dye degradation compared to TiO_2 alone. The study recommends further exploration of PANI/TiO_2 composites for real wastewater treatment applications, with focus on optimizing synthesis for cost-effectiveness and scalability. Future research should investigate the long-term stability and reusability of these nanocomposites under continuous flow conditions to assess their practical implementation potential.

Keywords: Photocatalysis, PANI/TiO_2 nanocomposite, ortho-nitroaniline orange, dye degradation, adsorption isotherms, reaction kinetics

1. Introduction

The rapid growth of industrialization has led to the increased discharge of synthetic organic dyes into water bodies, posing severe environmental and health risks (Singh et al., 2014). Among these pollutants, ortho-nitroaniline orange (ONAO), a toxic azo dye, is widely used in textile, printing, and dyeing industries, contributing to water pollution due to its non-biodegradability and potential carcinogenicity (Nallal et al., 2022). Conventional wastewater treatment methods, such as adsorption, coagulation, and biological degradation, often fail to completely remove such persistent organic pollutants. Consequently, advanced oxidation processes (AOPs), particularly photocatalysis,

have emerged as a promising solution for the efficient degradation of organic dyes into harmless byproducts (Cirpan et al., 2014).

Photocatalytic degradation leverages semiconductor materials to generate reactive oxygen species (ROS) under light irradiation, facilitating the breakdown of complex organic molecules (Williams et al., 2005). Titanium dioxide (TiO_2) has been extensively studied as a photocatalyst due to its chemical stability, non-toxicity, high photoelectric conversion efficiency, and strong oxidative capability (Nicolas et al., 2003). However, TiO_2 suffers from limitations such as a wide bandgap (~3.2 eV), restricting its activation to ultraviolet (UV) light, and rapid electron-hole recombination, which diminishes its photocatalytic efficiency (Gowrishankar et al., 2006). To overcome these drawbacks, researchers have explored doping TiO_2 with metals, non-metals, and coupling it with conductive polymers to enhance visible-light absorption and charge separation (Baksi et al., 2014).

Among conductive polymers, polyaniline (PANI) has garnered significant attention due to its tunable electrical conductivity, environmental stability, and unique redox properties (MacDiarmid et al., 2012). PANI can exist in multiple oxidation states, with the emeraldine salt form exhibiting high electrical conductivity upon protonation (Babel et al., 2021). When combined with TiO_2, PANI forms a heterostructured nanocomposite that improves charge carrier separation, extends light absorption into the visible region, and enhances photocatalytic activity (Luo et al., 2013). The PANI/TiO_2 nanocomposite has demonstrated superior performance in degrading organic pollutants, owing to synergistic effects such as improved electron transfer and reduced recombination rates (Zhang et al., 2018).

Despite the promising potential of PANI/TiO_2 nanocomposites, studies on their application in the degradation of ortho-nitroaniline orange remain limited. This work focuses on synthesizing PANI/TiO_2 nanocomposites via in-situ oxidative polymerization and evaluating their photocatalytic efficiency in degrading ONAO under UV and visible light irradiation. The nanocomposites will be characterized using X-ray diffraction (XRD), UV-Vis spectroscopy, scanning electron microscopy (SEM), and transmission electron microscopy (TEM) to elucidate their structural, optical, and morphological properties. Additionally, kinetic studies will be conducted to determine the degradation mechanism and reaction rates. This study contributes to the development of efficient photocatalysts for wastewater treatment, addressing the critical need for sustainable solutions to mitigate dye pollution. The findings will provide insights into optimizing PANI/TiO_2 nanocomposites for environmental remediation, paving the way for their large-scale application in industrial wastewater treatment.

2. Materials and Equipment

The study utilized high-purity chemicals, including t ortho-nitroaniline orange dye. Analytical-grade nitric acid (HNO_3) and sodium hydroxide (NaOH) solutions were prepared for pH adjustment. The equipment employed for characterization and analysis included a X-ray diffractometer (Rigaku Mini Flex 600), dynamic light scattering (DLS, CILAS Nano DS), Fourier-transform infrared spectroscopy (FTIR, PerkinElmer Frontier), and UV-Vis spectrophotometer.

Preparation of Dye Solutions and PANI/TiO_2 Nanocomposite

A stock solution (1000 ppm) of ortho-nitroaniline orange dye was prepared by dissolving 1.0 g of the dye in distilled water and diluting to 1000 mL. Intermediate and working solutions (10–50 ppm) were obtained via serial dilution using the dilution formula C1V1=C2V2. The PANI/TiO_2 nanocomposite was synthesized through an oxidative polymerization method, where aniline was polymerized in the presence of TiO_2 nanoparticles, followed by characterization using XRD, and FTIR to confirm structural properties.

Photocatalytic Degradation Experiments

The degradation studies were conducted in a photo-reactor under controlled conditions. A fixed amount of PANI/TiO_2 nanocomposite (0.4 g) was added to 50 mL of dye solution in 250 mL conical flasks, which were then agitated at 150 rpm under UV irradiation. Aliquots were withdrawn at predetermined intervals, and residual dye concentration was measured using a UV-Vis spectrophotometer at the dye's maximum absorbance wavelength. The degradation efficiency (%) was calculated using the equation:

$$\text{Degradation Efficiency (\%)} = D.E(\%) = \frac{C_0 - C_1}{C_0} X100 \quad (1)$$

Adsorption Isotherms and Kinetics

The experimental data were fitted into Langmuir and Freundlich isotherm models to understand the adsorption mechanism. The Langmuir isotherm, indicating monolayer adsorption, was expressed as:

$$\theta \frac{q_a}{q_m} = \frac{bC_e}{1+bC_e} \quad (2)$$

Thermodynamic Analysis

The feasibility and spontaneity of the adsorption process were assessed using thermodynamic parameters, including Gibbs free energy (ΔG∘), enthalpy (ΔH∘), and entropy (ΔS∘), derived from the equations:

The free energy of adsorption (ΔG°) can be related with Langmuir adsorption constant by the following equations;

$$\Delta G^{\circ} = -RT\ln K_L \quad (3)$$

$$\ln K = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (4)$$

3. Results and Discussion

The study investigated the photocatalytic degradation of ortho-nitroaniline (o-NA) dye using TiO_2/PANI composites and TiO_2 nanoparticles by varying catalyst dosage, initial dye concentration, irradiation time, and pH. The adsorption behavior was analyzed using Langmuir and Freundlich isotherm models, and the degradation kinetics were evaluated using first-order and second-order kinetic models.

Table 1: Effect of Varying Catalyst Dosage

Catalyst Dosage (g)	Degradation Efficiency of o-NA (%)
	TiO_2/PANI
0.2	Lower
0.4	91.027 (Maximum)
1	75.95

The photocatalytic degradation efficiency of o-NA was significantly influenced by the catalyst dosage for both TiO_2/PANI and TiO_2. An optimal dosage of 0.4 g was observed for both catalysts, yielding the highest degradation efficiencies (91.027% for TiO_2/PANI and 82.054% for TiO_2). Below this optimum, limited active sites and ROS generation hindered degradation. Beyond this point, increased turbidity and catalyst aggregation reduced light penetration and active surface area, leading to decreased efficiency. TiO_2/PANI consistently showed superior degradation compared to pure TiO_2 across all dosages, attributed to the enhanced charge transfer properties of polyaniline.

Table 2: Effect of Varying (o-NA) Concentration

Initial o-NA Concentration (ppm)	Degradation Efficiency of o-NA (%)
	TiO_2/PANI
10	92.99
20	85.78
30	69.801
40	59.077
50	56.842

An inverse relationship was observed between the initial o-NA dye concentration and degradation efficiency for both catalysts. Higher degradation efficiencies were achieved at lower dye concentrations (10 ppm), likely due to sufficient active sites and ROS availability relative to the dye molecules. As the dye concentration increased, competition for active sites and reduced light penetration led to lower degradation efficiencies. TiO_2/PANI exhibited superior degradation across all concentrations, attributed to enhanced visible light absorption and charge separation due to PANI.

Table 3: Effect of Varying Time

Irradiation Time (minutes)	Degradation Efficiency of o-NA (%)
	TiO_2/PANI
10	48.137
20	54.401
30	59.48
40	72.516
50	94.864 (Maximum)

4. Discussion

The photocatalytic degradation efficiency increased with increasing irradiation time for both catalysts. Longer irradiation times allowed for greater interaction between photons and the photocatalysts, leading to enhanced charge carrier generation and ROS production, resulting in higher dye degradation. TiO_2/PANI consistently showed higher degradation efficiencies than TiO_2 at all time points, again highlighting the benefits of PANI in improving photocatalytic activity.

Table 4: Effect of Varying pH

pH	Degradation Efficiency of o-NA (%)
	TiO_2/PANI
2	67.866
4	93.820 (Maximum)
6	65.986
8	51.477
10	42.074

The pH of the solution significantly affected the photocatalytic degradation efficiency. The highest degradation efficiencies for both TiO_2/PANI (93.820%) and TiO_2 (87.963%) were observed at pH 4. Acidic conditions favored dye adsorption onto the positively charged catalyst surface (below the pHpzc of TiO_2). Alkaline conditions led to reduced degradation due to electrostatic repulsion and potential scavenging of ROS by hydroxyl ions. TiO_2/PANI indicates superior performance across all pH values.

Table 5: Langmuir Isotherm

Catalyst	R^2
TiO_2/PANI	0.954
TiO_2	0.805

The Langmuir isotherm, assuming monolayer adsorption, provided a better fit for TiO_2/PANI ($R^2 = 0.954$) compared to TiO_2 ($R^2 = 0.805$). This suggests that the adsorption of o-NA onto TiO_2/PANI is more uniform with stronger dye-photocatalyst interactions, likely due to the enhanced surface area, active sites, and charge transfer facilitated by PANI. The poorer fit for TiO_2 indicates potential multilayer adsorption or surface heterogeneity.

Table 6: Freundlich isotherm

Catalyst	R^2
TiO_2/PANI	0.9904
TiO_2	0.9757

The Freundlich isotherm, describing heterogeneous surfaces and multilayer adsorption, showed an excellent fit for both TiO_2/PANI (R^2 = 0.9904) and TiO_2 (R^2 = 0.9757). The better fit of the Freundlich model compared to Langmuir revealed that the adsorption process involves multilayer coverage and varying adsorption energies on heterogeneous surfaces. The slightly higher R^2 for TiO_2/PANI indicates a more heterogeneous surface due to the incorporation of PANI, leading to enhanced adsorption capacity and consequently better photocatalytic efficiency.

Kinetics

Table 7: First Order Kinetics

Catalyst	R^2	Rate Constant (min^{-1})
TiO_2/PANI	0.9911	0.0266
TiO_2	0.9757	-1.516

The photocatalytic degradation of o-NA for both catalysts showed a strong correlation with the first-order kinetic model. TiO_2/PANI exhibited a higher R^2 value (0.9911) and a positive rate constant (0.0266 min^{-1}), indicating that the degradation rate is directly proportional to the dye concentration and that PANI enhances the photocatalytic activity. The negative rate constant for TiO_2 suggests a different degradation mechanism, possibly limited by surface adsorption.

Table 8: Second Order Kinetics

Catalyst	R^2	Rate Constant (mg/L/min)
TiO_2/PANI	0.9917	7.403
TiO_2	0.995	8.124

The second-order kinetic model also showed a strong fit for both catalysts, with slightly higher R^2 values compared to the first-order model, suggesting it more accurately describes the degradation process. The second-order model indicates that the degradation rate depends on both the dye concentration and the availability of active sites. TiO_2 showed a slightly higher rate constant in the second-order model, suggesting it might be more effective at lower dye concentrations, while TiO_2/PANI's performance is likely enhanced by its better adsorption capacity, making it more efficient overall, especially at higher concentrations.

5. Conclusion

Based on the results and discussion, the study conclusively demonstrates the superior photocatalytic degradation efficiency of the TiO_2/PANI composite for the removal of o-NA dye compared to bare TiO_2 nanoparticles under UV/visible light irradiation. This enhancement was consistently observed across various experimental parameters, including optimal catalyst dosage (0.4 g), varying initial dye concentrations (with higher efficiency at lower concentrations), extended irradiation times (up to 50 minutes), and an acidic pH of 4 (Sharma et al., 2022; Li et al., 2021).

The improved performance of the TiO_2/PANI composite can be attributed to the synergistic effect of polyaniline (PANI). This validated the study that revealed PANI facilitates better charge separation, reducing electron-hole recombination, and extends light absorption into the visible range, thereby boosting the photocatalytic activity (Ghorbani et al., 2020; Akpan & Hameed, 2021). Furthermore, the adsorption studies, best described by the Freundlich isotherm for both catalysts (TiO_2/PANI R^2 = 0.9904, TiO_2 R^2 = 0.9757), this supports the findings that heterogeneous multilayer adsorption, with TiO_2/PANI exhibiting a more heterogeneous surface due to PANI incorporation (Wang et al., 2023).

Kinetic analysis using both first-order (TiO_2/PANI k = 0.0266 min^{-1}, R^2 = 0.9911) and second-order (TiO_2/PANI k = 7.403 mg/L/min, R^2 = 0.9917) models indicated a strong correlation with the experimental data. The higher rate constant observed for TiO_2/PANI in the first-order model further supports its enhanced degradation capability (Banerjee et al., 2023).

In summary, the TiO_2/PANI composite proves to be a more efficient photocatalyst for o-NA dye removal due to its enhanced adsorption properties and improved charge separation facilitated by PANI. These findings aligned with the study that highlights the potential of such composite materials in wastewater treatment applications for the effective degradation of organic pollutants (Chen et al., 2022; Gómez-González et al., 2021).

Based on the enhanced photocatalytic performance observed with the TiO_2/PANI composite for o-NA dye removal, further exploration of its application in real wastewater treatment scenarios is recommended. Future studies should consider optimizing the composite synthesis for cost-effectiveness and scalability. Studies on long-term stability and reusability of TiO_2/PANI under continuous flow conditions would also be beneficial for practical implementation.

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