Enhancing the Performance and Recyclability of Polyaniline/TiO₂ Hybrid Nanocomposite by Immobilizing with Zein/Hydroxyethyl cellulose Composites for Removal of Anionic dyes

Tadesse Bassie Gelaw 1,2 and Balladka Kunhanna Sarojini 2*

1 Industrial Chemistry, Mangalore University, Mangalagangothri-574199, Karnataka, India; Email: bksaroj35@gmail.com
2 Department of Chemistry, Debre Tabor University, Amhara regional state, Ethiopia; Email: tadesse.bassie892@gmail.com

Abstract

Fabricating a stable, recyclable, and eco-friendly photocatalyst for dye treatment is vital in sustaining a clean ecosystem. In this regard, polyaniline/TiO₂ (PANI/TiO₂) photocatalyst was immobilized by zein/hydroxyethyl cellulose (zein/HEC) adhesive to enhance recyclability and catalytic activity. The blending of zein/HEC/PANI/TiO₂ photocatalyst involves in situ oxidative polymerization, followed by immobilization with zein/HEC functionalized composites. The PANI/TiO₂ composite was successfully grafted with the adhesive through physicochemical interaction, as evidenced by field emission scanning electron microscope (FESEM), Fourier transform infrared spectroscopy (FTIR), and Powder X-ray diffractometer (XRD). The simultaneous thermal analysis (STA) results show that the photocatalyst has the best thermal stability relative to PANI and PANI/TiO₂ in the recommended range of dye degradation temperature. The effect of external factors like TiO₂ nanoparticle proportion, pH of the solution, and catalyst dosage was studied in response to dye degradation capacity. The synthesized catalyst is efficient to degrade methyl orange in a wide range of pH. The kinetics of the catalysis reaction obeys first order kinetics. The maximum degradation efficiency achieved was 97.9 and 84.3% in the presence and absence of light, respectively. The catalyst was easily recovered by decantation, and its catalytic efficacy was more than 94% after five cycles. Hence, it is a promising alternative for decolorizing anionic dyes from wastewater.

Keyword:
zein/HEC, PANI/TiO₂, Photocatalyst, recyclability, TiO₂ nanoparticle

1. Introduction

The worldwide development of industries contributes to an increase in the release of different hazardous wastes to the environment. Among the harmful wastes, dyes are the primary toxic and
persistent organic chemicals released from textile, pharmaceutical, food, paper, and cosmetic industries. From the overall quantity of dyes produced globally, over 10% are released to the water body as waste [1]. This reduces dissolved oxygen levels [2] and photosynthesis rate in the aquatic system [3]. In addition, they are also poisonous and carcinogenic agents to living organisms [4]. Different approaches like adsorption [5], coagulation [6], filtration [7], ozonation [8], biodegradation [9], photocatalytic degradation [10], etc., have been developed to address these problems. Most of these methods have drawbacks, such as low-performance capacity, producing secondary pollutants, low stability, require huge investment, and complex separation processes [11]. Many studies showed that photocatalytic degradation had become the most preferred choice in the removal of dyes. Because it is economical [12], and the final degradation products have no negative impact on the ecosystem [13]. Thus, it is essential to develop a recyclable, efficient, and stable photocatalyst to remove wastewater dyes.

In the current study, TiO$_2$ nanoparticle is selected for the photocatalytic agent due to its chemical stability, non-toxicity, compatibility, and conductivity [14]. However, it was reported that the agglomeration of nanoparticles and recombination of excited electrons due to strong coulombic interaction strongly affect its catalytic activity during the reaction [15-16]. Hybridizing it with conductive polymers can reduce the instability of charge separation between the valence and conduction band and agglomeration of nanoparticles [17]. Polyaniline is the one that was exclusively used to boost the photocatalytic function of TiO$_2$. Because it possesses lower bandgap energy, and can easily excite electrons by absorbing light. Thus, TiO$_2$ nanoparticles in the hybrid composite trapped excited electrons from polyaniline to its conduction band, and hence the catalytic reaction is enhanced due to electron-hole stabilization [18]. In addition, polyaniline is commonly used for these purposes due to its biocompatibility, high electrical conductivity, chemical stability, and ease of synthesis [19]. However, it is not easy to recover the slurry of polyaniline/TiO$_2$ from the final product, particularly in large scale treatment [20-21]. Furthermore, these suspensions from the reaction medium prevent the incoming light from penetrating the entire part of the reaction system [22]. This effect limits the performance capacity of the photocatalyst in addition to the challenge of separation. Accordingly, it is essential to enhance the photocatalytic efficiency and recyclability of polyaniline/TiO$_2$ (PANI/TiO$_2$) photocatalyst. Thus, this study deals with improving and immobilizing PANI/TiO$_2$ photocatalyst by zein/hydroxyethyl cellulose (zein/HEC) functionalized composites.
Zein is composed of prolamine containing more than 50% hydrophobic residues of amino acids. Its hydrophilic nature can be enhanced by blending with water-soluble polymers due to hydrogen bonding between constituent species [23]. Composites of zein with hydrophilic polymer also possess a rough structure with high surface area microholes due to the self-aggregation of hydrophobic amide groups favored by hydrophilic group repulsion [24]. Besides, many active groups disclosed and positively charged functionalized networked porous structure of zein formed in acidic condition [25-26]. The microholes, functionalized porous structures, and different functional groups produce synergetic properties towards absorption [23, 27]. This property is essential to support the adsorption of dye pollutants to the heterogeneous catalyst surface. Furthermore, the strong interaction between zein and polyaniline makes the photocatalyst immobilization effective [28].

Hydroxyethyl cellulose is a well-known non-ionic stabilizer, binder, and water retainer in various composite products due to its high viscosity and stability in all pH ranges [29-30]. Hence, the composite of zein and hydroxyethyl cellulose is therefore suggested to be a stable and absorbing composite. Based on these facts, blending PANI/TiO$_2$ with zein/HEC composite immobilizes and increases adsortive-assisted catalytic function due to the combined effects of factionalized structures and various active groups.

In the past, materials like polyacrylonitrile [31], polystyrene cubes [32], Poly (vinyl alcohol) [33], diazonium salt [34], polyvinyl chloride (PVC), and epoxidized natural rubber (ENR-50) [35], etc., were used to immobilize and increase the recyclability of polyaniline/TiO$_2$ composite. But some of the immobilizers lower the efficiency of the catalyst [32], and others are toxic, such as polyvinyl chloride and epoxides [36]. Thus, it is reasonable to immobilize PANI/TiO$_2$ photocatalyst with nontoxic adhesive materials without affecting its catalytic activity. In this regard, glutaraldehyde crosslinked zein/HEC composite was used for anchoring PANI/TiO$_2$ and enhancing the photocatalytic activity. So far, there was no report on polyaniline/TiO$_2$ photocatalyst immobilized by zein/HEC composite polymer. Therefore, the objective of this work was to study the combined effect of zein and hydroxyethyl cellulose composite on PANI/TiO$_2$ adsortive assisted photocatalytic property for the degradation of anionic dye wastes. The newly synthesized zein/HEC/PANI/TiO$_2$ photocatalyst was characterized by FESEM connected with energy dispersive X-ray (EDX), STA, XRD, and FTIR instruments. The TiO$_2$ nanoparticles proportion,
catalyst dosage, and pH on the photocatalytic degradation reaction were optimized. The kinetics of the reaction was also evaluated using first order kinetic models. Furthermore, the photocatalyst's feasibility study was assessed by recycling and comparing it with previous reports.

2. Materials and Methods

2.1 Materials

Aniline with purity 99% was procured from SPECTROCHEM (Mumbai, India). α-Zein (Analytical reagent) and a mixture of 20% rutile and 80% of anatase TiO₂ (<100 nm size) were obtained from Sigma Aldrich (China). Ammonium persulphate (purity,98%) was purchased from Sisco research laboratory Pvt. Ltd. (Taloja, Maharashtra, India), and HCL (purity, 35-37%) was obtained from Alpha Chemika (Mumbai, India). Glutaraldehyde (purity, 25%) and High viscosity HEC (viscosity, 250-450 mPas at 2% H₂O & 20 °C) were purchased from LOBA Chemie (Kochi, Kerala, India)

2.2 Synthesis of zein/HEC/PANI/TiO₂ composite

PANI/TiO₂ hybrid nanocomposites were fabricated by oxidative in-situ polymerization. An equimolar concentrations of ammonium persulphate and aniline were prepared using 1M HCl. Both solutions were stirred in a separate container until a clear, transparent solution was formed. Presonicated aqueous solution of TiO₂ nanoparticles was added to the polyaniline solution and stirred for half an hour. This solution temperature was adjusted to 0 –5 °C in an ice bath. With continuous stirring, ammonium persulphate solution was added, and stirring continued for five hours. This green acidic solution pH was adjusted to three to prevent zein breakdown during mixing [37].

Zein functionalization was performed by dissolving zein powder in dilute hydrochloric acid using the previous standard method with a slight modification [25]. Typically, HCl (0.4M) was prepared in 70% ethanol solution. Then zein powder was transferred to this solution. The reaction mixture was stirred for 12 hours at 70 °C to convert hydrophobic amine groups of zein to hydrophilic ones. Hydroxyethyl cellulose solutions were also dissolved separately in 50% ethanol solution. The hydroxyethyl cellulose and zein solution were mixed with a glutaraldehyde crosslinker and stirred overnight. The green polyaniline/TiO₂ composite solution was added to the zein/HEC gel solution
and stirred for 12 hours to immobilize photocatalyst. Then it was neutralized by adding NaOH until the pH becomes above six and precipitated by adding excess water. It was allowed to settle all the precipitates. After decanting the supernatant, it was washed with water, followed by acetone. Zein/HEC/PANI/TiO₂ composite obtained was transferred to an oven set at 60 °C for drying in 12 hrs. Finally, it was crushed into small size. In the same procedure, the hybrid composite with different proportions of TiO₂ was prepared for further characterization.

2.3 Characterization

The elemental composition and morphology of the hybrid composite were determined by FESEM connected with the EDX analyzer (CARL ZE155, OXFORD instruments EDX, USA). The possible interactions and functional groups present in the composite were confirmed by FTIR (IRPrestige-20, Shimadzu, Japan) in the wave ranging from 400 to 2000 cm⁻¹. XRD (PANALYTICAL, XPERT PRO, Cu-Kα radiation) was used to determine composite (crystal structure or amorphous) patterns. The thermal stability of the hybrid nanocomposite was described by STA (STA 6000, PerkinElmer, Waltham, USA) with a heating rate of 10 °C per minute at a temperature range of 25 °C to 800 °C under normal condition.

2.4 Adsorptive assisted photocatalytic study

The adsorptive assisted photocatalytic study was performed using batch photoreactors. In this experiment, 0.03 g of the photocatalyst was immersed in a catalytic bath containing 100 ml of 125 μM of methyl orange (MO) and stirred continuously. After 30 minutes of adsorption in the dark environment, it was irradiated with an 18 W UV light source with a wavelength of 395 nm. In a predetermined interval, 4 ml of the sample was withdrawn, and the analyte concentration was determined by UV-Vis spectrophotometer (UV-1800, Shimadzu, Japan). For recycling, zein/HEC/PANI/TiO₂ composite was allowed to settle for half an hour and then isolated from the first phase by decantation. After that, it was washed with acidic water followed by distilled water repeatedly and rinsed with acetone. Finally, it was dried in an oven set at 60 °C before using for the second cycle with a freshly prepared MO solution. A similar procedure was used for the rest of the cycles. The catalytic efficiency (η) of the hybrid composite was calculated from equation 1.

\[ \eta = \frac{(C_o - C_e) \times 100}{C_o} \]
where $C_0$ and $C_e$ are the initial and equilibrium dye concentrations of the solution respectively.

3. Result and Discussion

3.1 Morphology Analysis

Zein/HEC/PANI/TiO$_2$ composite morphology was described in comparison with pure polyaniline and PANI/TiO$_2$ composite, as shown in fig. 1. Most of the polyaniline molecules had long road-like fibers, as shown in fig. 1 (a). The addition of TiO$_2$ nanoparticles changed this structure and formed short length fibers as evidenced by fig.1(b). This shows that TiO$_2$ nanoparticles interacted with polyaniline molecules and preventing long chain road-like structure formation. In fig.1(c), a porous crosslinked networked structure with some fibers was also observed, indicating that PANI/TiO$_2$ was partially grafted in the polymer matrix of the Zein/HEC composite network. The average particle size was computed by counting more than 150 particles from the FESEM image using Image J software. Based on this calculation, the average dimensions of polyaniline, PANI/TiO$_2$, and zein/HEC/Pani/TiO$_2$ nanoparticles were 53.21 nm, 46.13 nm, and 61.64 nm, respectively. In addition to morphological changes, it is also essential to describe major constituent species present in the composite using EDX. The elements, O, C, N, and Ti were expected components in the composite. From the EDX spectrum shown in fig.1(a), there were no spectral peaks related to Ti, while Ti peaks were observed in fig. 1(b) and (c) confirming that TiO$_2$ nanoparticles were involved in the hybrid composite. Both the weight and atomic percent of nitrogen were also negative in pure polyaniline and PANI/TiO$_2$ composite, confirming that nitrogen content was less and could not be detectable. However, as shown in fig. 1(c) of EDX graph, nitrogen appeared due to zein/HEC composite addition. This was the indication for nitrogen-containing groups (zein) in the composite [28]. As shown in fig.1(b) and (c), the percentage composition of components in polyaniline and PANI/TiO$_2$ changed with the addition of TiO$_2$ nanoparticle and zein/HEC composite, respectively. This also confirmed that TiO$_2$ nanoparticles and zein/HEC composites took part in the hybrid composite formation.
Fig.1 FESEM-EDX graphs of a) PANI, b) PANI/TiO\textsubscript{2} and C) zein/HEC/PANI/TiO\textsubscript{2} 

### 3.2 X-ray diffraction Analysis

The XRD patterns of glutaraldehyde crosslinked zein/HEC composite, pure PANI, PANI/TiO\textsubscript{2}, and zein/HEC/PANI/TiO\textsubscript{2} were compared. Hydroxyethyl cellulose has no XRD diffraction peaks [38]. Hence, the two broad peaks observed in fig.2 (a) were due to zein, indicating that the composite was structurally amorphous [39]. In fig.2(b), the peaks at $\theta = 8.9$ and 14.96 were the distinct doping diffraction of low crystalline polyaniline. The peaks at $\theta = 21.04$ and 25.34 confirmed the presence of polyaniline emeraldine chain with repeated units [40-42]. The peaks observed in fig.2(c) at $\theta = 25.35^\circ$, 37.85$^\circ$, 48.04$^\circ$,54.13$^\circ$, 55.13$^\circ$ and 62.87$^\circ$ were due to anatase TiO\textsubscript{2} nanoparticles in the hybrid nanocomposite [14, 18, 43]. In fig.2(c) and (d), there were similar peaks of TiO\textsubscript{2} nanoparticle with a slight variation in intensity, indicating that the crystal structure of TiO\textsubscript{2} present in the hybrid nanocomposite was not affected by either the polyaniline or the zein/HEC composite, similar with the previous report [43]. The average crystal size was estimated from the Debye–Scherrer's equation.

$$d_{DRX} = \frac{k\lambda}{B\cos\theta}$$

Where $d$ is the diameter of the crystal, $\lambda$ is the wave length of X-ray radiation, $k$ is a constant = 0.15418, $B$ is the line width at the half maximum intensity, and $\theta$ is the Bragg diffraction angle.
The proximate average crystal size calculated from equation (2) were 4.86, 11.73 and 11.36 nm for PANI, PANI/TiO₂ and zein/HEC/PANI/TiO₂ respectively. The proximate average crystal size between PANI/TiO₂ and zein/HEC/PANI/TiO₂ also confirmed that TiO₂ nanoparticle was not affected by the composite material.

![Fig.2 XRD peaks of a) zein/HEC, b) Pure PANI, c) PANI/TiO₂ and d) zein/HEC/PANI/TiO₂ hybrid nanocomposites](image)

### 3.3 FTIR Analysis

The characteristics FTIR peaks of PANI, PANI/TiO₂, zein/HEC/PANI/TiO₂, and glutaraldehyde crosslinked zein/HEC/PANI/TiO₂ were elucidated in fig.3. The quinoid (C=N) and benzoid (C=C) unit ring stretching vibrations were observed in the wave number of 1557 cm⁻¹ and 1462 cm⁻¹ respectively, as shown in fig.3(a) [44]. These two units confirmed the formation of emeraldine polyaniline. The peak corresponding to C-N stretching in the benzenoid unit was observed at the wave number of 1285 cm⁻¹ [45]. At 1230 cm⁻¹, protonated conductive polyaniline emeraldine salt characteristic was also observed due to C-N⁺ stretching vibration [46]. The peaks around 791 and 1020 cm⁻¹ were due to out plane and in-plane bending vibrations of =C-H, respectively [47]. In fig. 3(b), the features polyaniline peaks of C=C and C-N (1462 cm⁻¹ and 1285 cm⁻¹) were transformed to higher wave numbers (1472 cm⁻¹ and 1291 cm⁻¹) due to Ti-N interaction in the composite [48] while the peak corresponding to quinone remains unchanged. All the
characteristics peaks of pristine polyaniline observed between 450 cm\(^{-1}\) and 2000 cm\(^{-1}\) were also present in PANI/TiO\(_2\) composite, and new peaks appeared at 501 and 572 cm\(^{-1}\) due to TiO\(_2\) nanoparticles as shown in fig. 3(b) [49]. But some spectra shifted to higher wave number and decrease in intensity in PANI/TiO\(_2\) composite due to the surface interactions of TiO\(_2\) nanoparticles with hydrogen bonds and N-H groups in polyaniline [50]. In fig.3(c), almost all the spectral peaks appeared in polyaniline, and PANI/TiO\(_2\) were also observed with additional spectrum in 1652 cm\(^{-1}\) due to amide I. More peaks around 1557 & 1285 cm\(^{-1}\) due to amide II and III were also expected but overlapped with the peaks of quinone and benzene ring stretching vibrations, respectively. The strong and sharp spectral peaks observed in fig.3(c) became diminished, as shown in fig. 3(d) revealing that zein/HEC crosslinked with PANI/TiO\(_2\) through glutaraldehyde crosslinker.

![FTIR spectra](image)

**Fig.3** FTIR spectra of a) Pristine PANI, b) PANI/TiO\(_2\), c) zein/HEC/PANI/TiO\(_2\) and d) glutaraldehyde crosslinked zein/HEC/PANI/TiO\(_2\)

### 3.4 Thermal Analysis

As shown in fig.4(a), in the decomposition of polyaniline emeraldine salt, two nonlinear weight losses were observed from 25 to 100 °C and from 100 to 310 °C. The first weight loss was due to the evaporation of water and a small amount of HCl. In the second case, from 100 to 310 °C, the primary weight change was due to the dopant (HCl) removal. Additionally, some water molecules firmly attached to the polymer surface were also released [51-52]. Similar to the previous report, the weight loss from 300 to 800 °C showed a linear degradation curve [50]. Most of the molecules
removed from 300 to 700 °C were ammonia and aniline molecules. Above 700 °C temperature, ammonia and acetylene were the possible degradation products [53].

TiO₂ nanoparticles cannot decompose under the temperature range of 25 to 800 °C [54]. Thus, the decomposition of PANI/TiO₂ under this temperature range was due to polyaniline degradation. But, under similar temperature change, the decay of PANI/TiO₂ was less than pure polyaniline, as shown in fig. 4(b). This proved that PANI/TiO₂ thermogravimetric stability was higher than pure PANI due to TiO₂ nanoparticle strong interaction with polyaniline [50].

In the thermal degradation of zein/HEC/PANI/TiO₂, three major weight loss changes were observed; as shown in fig.4(c), the first weight change from 25 to 120 °C was due to the removal of water from the hybrid nanocomposite surface. In the second phase, around 23% weight loss was due to the composite degradation from 220 to 375 °C temperature ranges [55-56]. In the third stage, the degradation continued from 390 to 600 °C due to pyrolysis reactions of HEC [56] and degradation of polyaniline. Above 600 °C, a linear degradation curve similar to fig. 4(a) was observed due to further degradation of polyaniline [53]. The weight loss of zein/HEC/PANI/TiO₂ corresponding to 25 to 310 °C was lower than pure polyaniline and PANI/TiO₂, as depicted in fig.4(c), proving that its highest thermal stability in this region. The photocatalytic dye degradation reaction favored between 25 and 80 °C reaction temperature [57]. Hence, the newly synthesized photocatalyst has better thermal stability for degrading dye molecules.

![Fig.4 STA thermograms of a) pure polyaniline, b) PANI/TiO₂, and c) zein/HEC/PANI/TiO₂](image-url)
4. **Photocatalytic activity of zein/HEC/Pani/TiO$_2$ composites**

4.1 **Effect of TiO$_2$ on zein/HEC/PANI/TiO$_2$ hybrid composite**

The hybrid composite catalytic efficiency was evaluated by changing the proportions of TiO$_2$ nanoparticles under fixed methyl orange concentration, catalyst dosage, pH, and reaction time. The degradation efficiency of zein/HEC/PANI/TiO$_2$ hybrid nanocomposite with TiO$_2$ proportions of 0%, 5%, 10%, 15% and 20% relative to aniline is shown in fig.5. The catalytic reaction efficiency increased with increasing TiO$_2$ nanoparticles, and the highest dye degradation efficiency was achieved at 10% load of TiO$_2$. Further increasing the nanoparticle decreases catalytic degradation. This is because the catalyst's surface area decreased due to nanoparticles' spontaneous agglomeration at higher proportions of TiO$_2$ [16]. In addition, a high proportion of TiO$_2$ prevents the UV light source from striking to polyaniline surface; thus, polyaniline was unable to sensitize the reaction, which leads to decreased degradation [33]. Thus, the amount of TiO$_2$ nanoparticles in the composite should be lower than polyaniline. Because a high concentration of polyaniline is not only sensitizing the reaction but also effectively stabilizing the nanoparticles of TiO$_2$ by preventing nanoparticle aggregation [58].

![Fig.5 Effects of TiO$_2$ proportion on photocatalytic degradation efficiency of Zein/HEC/PANI/TiO$_2$ catalyst](image)

4.2 **Effect of pH**

The catalyst surface and dye solution's charges are affected by the variation of pH in the reaction path. Therefore, it is vital to optimize the pH of the reaction condition to obtain maximum
degradation products. Thus, the photocatalytic degradation reaction was performed with different pH values ranging from 2 to 12. The degradation efficiency was decreased when pH goes towards a lower acidic pH below four and higher basic pH above ten. But in the mild acidic and basic pH degradation, efficacies were higher, as shown in fig. 6. This is because the zein surface in a mild acidic condition is positively charged due to side amine groups' protonation on glutamine residues [59]. Hence the anionic methyl orange adsorption on the surface of the catalyst was enhanced, supporting catalytic reaction. But in a strongly acidic solution, it decreased due to the loss of positively charged groups by the change of glutamine into glutamic acid. Similarly, a dramatic decrease in higher basic pH was caused by the generation of negatively charged groups due to deprotonation of carboxylic groups on glutamate. This creates strong electrostatic interaction with anionic dyes, which caused a decrease in the reaction [60]. Different amino acid groups were disclosed in a mildly alkaline solution, and thus, catalytic degradation was enhanced. Also, PANI/TiO₂ is positively charged in acidic media and negatively charged in higher pH. Hence, the electrostatic force of attraction between the catalyst and dye molecules favored an acidic environment but diminished in a strong alkaline condition [32]. The neutral and mild alkaline conditions were more efficient than mild acidic conditions, as shown in fig. 6. Sedghi et al.; also reported similar results using polyaniline modified TiO₂/polyacrylonitrile nanocomposite [31].

With a 95% confidence level, the photocatalytic degradation of methyl orange was strongly affected by acidic (pH<4) and basic (pH>10) conditions. However, there were no significant changes in the photocatalytic degradation of methyl orange with the pH ranging from 4 to 10, as shown in fig. 6. This result depicted that the newly synthesized photocatalyst was efficient in a wide range of pH, which is essential to treat anionic dye wastes without adjusting pH. Even though no substantial change, 97.5165% was the maximum degradation efficiency achieved at neutral pH. Hence, it was this pH used for all investigations carried out in this study.
Fig. 6 The effect of pH on photocatalytic degradation of methyl orange by zein/HEC/PANI/TiO$_2$

4.3 Effect of Catalyst dosage

The influence of catalyst dosage on the degradation of methyl orange has been investigated at a pH of 7, 100 ml of 125 µM dye concentration, and 110 minute degradation time. The quantity of catalysts used was 0.01g, 0.02g, 0.03 g, 0.04, 0.05, 0.06, 0.07 and 0.08 g. As depicted in fig.7, the efficacy increases with an increasing amount of zein/HEC/PANI/TiO$_2$ hybrid nanocomposite. With an increasing amount of catalyst, the number of photons adsorbed on it increased due to the increased number of available active sites. Hence the number of dye molecules adsorbed on the photoactivated surface increased, and thus the rate of degradation is enhanced [62]. However, the degradation dependency of dyes with the catalyst higher than 0.03 g was an insignificant increment, as shown in fig.7. When the amount of photocatalyst is beyond the optimum limit, the probability of dye molecules to bind on the photocatalyst surface becomes equal since there are sufficient active sites. Thus, the photocatalytic degradation rate becomes nearly constant, whatever the catalyst increased [63].
Fig. 7 Effects of zein/HEC/PANI/TiO$_2$ dosage on the degradation of methyl orange

4.4 Efficacy and kinetic study

The photocatalytic activity of zein/HEC/PANI/TiO$_2$ hybrid nanocomposite was evaluated with and without light. The degradation of MO by zein/HEC/PANI/TiO$_2$ in the presence of light was considerably higher than in the dark condition, as shown in fig. 8(a) and (b). In the dark environment, zein/HEC/PANI/TiO$_2$ hybrid nanocomposite decolorized about 80.1% dye molecules in 50 minutes. While more than 91% of dye molecules undergo degradation reaction in the same duration, except the light was irradiated. This confirmed that even though the adsorption is also high, the catalyst degradation efficacy was significantly enhanced with light. The highest removal efficiencies achieved in 110 minutes with and without light were 97.9% and 84.3%, respectively.
Fig. 8  Degradation of methyl orange by zein/HEC/PANI/TiO₂ a) without, and b) with light irradiation

The efficiency and overall degradation rate per gram of catalyst and minute of the current investigation were compared with previous reports, as shown in table 1.

| Initial MO concentration (C₀) (mg/L) | Catalyst dose (mg) | Efficiency (%) | Time (adsorption + illumination) (minute) | Degradation per g of catalyst (mg/g) | Rate per total time & catalyst (mg/min.g) | Reference |
|-------------------------------------|--------------------|----------------|------------------------------------------|-------------------------------------|------------------------------------------|-----------|
| 40.92                               | 30                 | 97.91          | 110                                      | 133.55                              | 1.214                                    | Current study |
| 100                                 | 10                 | 92             | 360                                      | 920                                 | 2.556                                    | [33]      |
| 20                                  | 80                 | 96             | 360                                      | 30                                  | 0.083                                    | [43]      |
| 10                                  | 100                | 100            | 50                                       | 10                                  | 0.2                                      | [63]      |
| 50                                  | 100                | 97.84          | 120                                      | 25                                  | 0.208                                    | [64]      |
| 3.2733                              | 5                  | 90.3           | 280                                      | 29.62                               | 0.106                                    | [65]      |
| 15                                  | 30                 | 81.4           | 100                                      | 12.21                               | 0.1221                                   | [66]      |

As shown in table 1, zein/HECPANI/TiO₂ is the best alternative for degrading a high amount of methyl orange per gram of catalyst in a short duration. The kinetics of the photocatalytic degradation reaction was investigated using the Langmuir-Hinshelwood model. In low concentration, the value $1 + K_2[A]_t$ is nearly equal to unity. The rate law expression becomes a multiple of the apparent rate constant and concentration.

$$Rate = \frac{-d[A]_t}{dt} = \frac{k_1K_2 [A]_t}{1 + K_2[A]_t} \approx K_{app}[A]_t^{3}$$
After integration, equation 3 can be written as

\[
\ln\left(\frac{[A]_t}{[A]_o}\right) = -k_{app}t
\]

where \( K_1 \) and \( k_2 \) are the reaction rate and the reactant adsorption constants respectively, \([A]_o\) is initial dye concentration, \([A]_t\) is the concentration of the reactant at any time \( t \) and \( K_{app} \) is the apparent rate constant. From fig. 9, the straight line or the correlation coefficient \( R^2 = 0.992 \) proved that the photocatalytic degradation of methyl orange by zein/HEC/PANI/TiO₂ obeys the kinetics of 1st order reaction.

**Fig. 9** Kinetic models of first order reaction for methyl orange photocatalytic degradation by zein/HEC/PANI/TiO₂ hybrid nanocomposite

### 4.5 Recyclability Evaluation

Recoverability and reusability are essential metrics used to assess the economic viability of the catalyst. Hence, after optimizing TiO₂ proportion, catalyst dose, and pH, the catalyst's recoverability was conducted for five cycles. The catalyst's performance corresponding to 1st, 2nd, 3rd, 4th, and 5th cycles was 97.91, 96.52, 96.09, 95.14, and 94.03% respectively. The result indicates that the performance difference between the 1st and the last cycle was small. This shows that glutaraldehyde crosslinked Zein/HEC composite effectively immobilized PANI/TiO₂ photocatalyst. The slight variation between degradation cycles also showed that
zein/HEC/PANI/TiO₂ hybrid nanocomposite is a promising photocatalyst in terms of stability and efficacy.

5. Conclusion

In this investigation, zein/HEC/PANI/TiO₂ hybrid nanocomposite was produced by insitu oxidative polymerization followed by immobilization with zein/HEC functionalized composite. The composite of zein/HEC paste effectively immobilized PANI/TiO₂ photocatalyst. More than 97.9% of methyl orange undergoes decolorization within 110 minutes. Zein/HEC/PANI/TiO₂ photocatalyst performance was 94% after five cycles, indicating its high stability and recyclability. In summary, the newly synthesized photocatalyst is an invaluable alternative for removing dyes (especially anionic dyes) from wastewater.

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