Research Article

Photocatalytic Degradation of Eosin Yellow Using Poly(pyrrole-co-aniline)-Coated TiO_2 /Nanocellulose Composite under Solar Light Irradiation

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The present study describes the feasibility of a novel adsorbent cum photocatalyst, poly(pyrrole-co-aniline)-coated TiO_2 /nanocellulose composite (P(Py-co-An)- TiO_2 /NCC), to remove eosin yellow (EY) from aqueous solutions. The removal of EY was investigated by batch adsorption followed by photocatalysis. The effect of various adsorption parameters like adsorbent dose, pH, contact time, initial concentration, and ionic strength has been optimized for treating effluents from the dye industry. Adsorption of EY reached maximum at pH 4.5 and complete removal of dye was achieved using 3.5 g/L of P(Py-co-An)- TiO_2 /NCC. Adsorption equilibrium data were fitted with Langmuir and Fritz-Schlunder isotherm models and the kinetics of adsorption follows a second-order mechanism. The adsorption capacity of P(Py-co-An)- TiO_2 /NCC was found to be 3.39×10^{-5} mol/g and reached equilibrium within 90 min. The photocatalytic degradation of adsorbed dye under sunlight was possible and about 92.3% of dye was degraded within 90 min. The reusability of P(Py-co-An)- TiO_2 /NCC was also investigated. The results indicate that P(Py-co-An)- TiO_2 /NCC is the best material for the wiping out of EY from aqueous solutions.

1. Introduction

Textile dyes are the largest group of chemicals being produced all over the world. The effluents from manufacturing and textile industries are discarded in large quantities into rivers and lakes causing water pollution and affect the ecosystem seriously [1]. So, the dye removal has been considered as a challenging problem for environmental scientists [2]. The developed dye removal strategies include biological treatment, coagulation, flotation, adsorption, oxidation, and electrochemical techniques [3]. Adsorption is a preferred method due to its high efficiency, ease of handling, and the availability of low cost adsorbents [4]. However, it has been reported that the majority of dyes are only adsorbed and are not degraded and are also ineffective that they simply transfer the pollutants to another phase rather than destroying them [5]. Photocatalysis for the purification of wastewater from industries and households has attracted much attention in recent years. Photocatalytic degradation

relies on the technology of advanced oxidation processes (AOPs) in which electron-hole pair radicals able to undergo secondary reactions are created [6].

TiO_2 has been extensively used as a photocatalyst, owing to its inexpensive, nontoxic, and photoelectric properties [7]. It can also be used in harsh conditions for its high chemical and thermal stability. However, lack of recyclability and low adsorption ability for the pollutants, especially for the nonpolar organic compounds, are the disadvantages faced while using bare TiO_2 . Organic molecules which can effectively adsorb to the surface of the photocatalyst will be more susceptible to direct oxidation [8]. Nano- TiO_2 is an active material which has advantages such as innocuity, resisting and decomposing bacteria, UV resistance, and superhydrophilicity [9].

Anchoring of TiO_2 on various supports including carbon, glass fibers, montmorillonite, organic materials, and zeolites may increase their photochemical stability. Organic materials with UV light resistance have been widely used as supports

for TiO_2 photocatalyst, since they have the advantages such as low cost and easy separation from reaction solution. Cellulose, obtained from wood pulp and cotton, is such a material used for this purpose due to its low cost and easy availability. Cellulose has been explored as a substrate for composite materials because of the presence of functional groups that may be employed in various activation processes. Additionally, it was suggested that the holes' scavenging ability increases with the increasing number and spatial distribution of the hydroxyl groups in the polyhydroxyl compounds [10]. When cellulose is converting to their nanocrystals, the holes' scavenging ability increases due to the large number of hydroxyl groups exposed to the surface. The nanocellulose is mechanically strong and produced a strength of 25% that of carbon nanotubes [11].

Conducting polymers such as polypyrrole, polyaniline, and polythiophene have functioned as dopants which shift the border of the TiO_2 particles to longer wavelengths, thereby improving the optical absorption in the visible region. These hybrid conducting polymer/ TiO_2 composites exhibit excellent properties unlike those of the individual materials, such as controlled conductivity and thermal or mechanical stability, and these properties have made them potentially applicable as anode materials for lithium-ion batteries [12], anode electrodes for dye solar cells [13], or photocatalytic materials [14]. The conjugated polymers could be separated from the aqueous phase by using simple gravity settling and could be recycled easily. The conjugated polymers have an extended conjugation system and behave like semiconducting materials with low charge carrier mobility. Polyaniline (PAn) has been deposited on various materials to perform desired applications [15]. Polypyrrole (PPy) has a potential application in the field of composite materials due to their appreciable environmental stability, higher electrical conductivity, easier synthesis, and solubility in different solvents [16].

As we know, eosin yellow (EY) is widely used for staining purposes; however, it is listed as a carcinogen. The present work is aimed at wiping out the textile dye, EY, from the environment for the well-being of the organisms. In the present work, a novel polymer composite, poly(pyrrole-co-aniline)-coated TiO_2 /nanocellulose composite [P(Py-co-An)- TiO_2 /NCC] was prepared for the adsorptive removal of EY from aqueous solutions, followed by photocatalytic degradation under sunlight. For the preparation of this polymeric hydrogel, glutaraldehyde, the agent widely used for industrial water treatment and a preservative, was selected as a crosslinker.

2. Materials and Methods

2.1. Materials. Sawdust of *Mangifera indica* was a kind gift from Local Saw mill, Trivandrum. Titanium(IV) isopropoxide (97%), eosin yellow (EY), pyrrole (Py), aniline (An), and glutaraldehyde were purchased from Sigma Aldrich. $\text{H}_2\text{S}_2\text{O}_4$, NaOH, HNO_3 , FeCl_3 , H_2O_2 , ethanol, HCl, and ammonium persulfate (APS) were received from E. Merck, India. All the chemicals were used without further purification. Deionized

water was used in preparing the aqueous stock solutions for the adsorption-photocatalytic experiments.

2.2. Preparation of P(Py-co-An)- TiO_2 /NCC

2.2.1. Extraction of Nanocellulose (NC) from Sawdust. Cellulose has been extracted from sawdust and was converted to nanocrystals following the procedure reported earlier [17]. Briefly, sawdust was pretreated with 10% H_2SO_4 solution (120°C , 10 min) and centrifuged to remove rich pentosans solution. Delignification was achieved by the subsequent treatment with 1% NaOH (100°C , 1 h). The obtained brown mass upon bleaching with 5% H_2O_2 (80°C , 1 h) yielded white cellulose. About 5 g of cellulose was dispersed in 250 mL distilled water under magnetic stirring (20 min). 140 mL 98% sulfuric acid was dropped to the homogenized mixture, without causing heating. After complete addition, the mixture was heated at 50°C for 2 h. The hot mixture was diluted ten times with ice cooled distilled water. The obtained white colloid was centrifuged, washed many times with water, and freeze-dried.

2.2.2. Preparation of TiO_2 /NC Composite (TiO_2 /NCC). NC (0.2 g), HNO_3 (5 mL, 0.1 M), and absolute ethanol (100 mL) were mixed with each other and the mixture was ultrasonically dispersed for 1 h. After dispersion, 1 mL of titanium(IV) isopropoxide was added to this mixture slowly with a constant pressure funnel under magnetic stirring. The reaction temperature was kept at 40°C for 4 h. Finally, the suspension was diluted fivefold with water, centrifuged, and then washed with water repeatedly. The precipitate was dialyzed against deionized water for 2 days and then freeze-dried.

2.2.3. Preparation of P(Py-co-An)- TiO_2 /NCC. P(Py-co-An)- TiO_2 /NCC was synthesized by chemical oxidation of its respective monomers, Py and An, by keeping their molar ratios constant at 1:1. The aqueous solution of TiO_2 /NCC (240 mg in 100 mL) was mixed with a solution of pyrrole (3 mL), aniline (3 mL), and HCl (37%, 0.16 mL) for 30 min where after APS (0.46 g) and of FeCl_3 (8.0 g) was added, respectively, in the solution for polymerization initiation, and stirred for 3 h. The obtained product with a layer of poly(pyrrole-co-aniline) was filtered, washed with ethanol, and dried at 50°C . The dried product, designated as P(Py-co-An)- TiO_2 /NCC, was sieved to get an average particle size of 0.096 mm and used for adsorption followed by photocatalytic experiments.

2.3. Characterization of P(Py-co-An)- TiO_2 /NCC. Surface morphology of the adsorbents was investigated by SEM micrographs recorded with a JEOL JSM 6390 LA scanning electron microscope. The Brunauer-Emmett-Teller (BET) surface area was determined using a model Q7/S surface area analyzer (Quantasorb, USA). The XRD patterns were recorded using X'Pert Pro X-ray diffractometer. Patterns were recorded in the 2θ range of $10-70^\circ$ at a scan rate of 2 counts/s. The FTIR spectra of adsorbents were recorded on KBr pellets with FTIR spectrophotometer in the wavelength

range of 550–4000 cm^{-1} (Shimadzu, Japan). Dried sample weighing 10 mg was dispersed in 200 mg of spectroscopic grade KBr to record the spectra at a resolution of 4 cm^{-1} . JASCO UV-visible (model V-550) spectrophotometer was used for the estimation of dye concentration in the solution and gel.

2.4. Adsorption of EY. Adsorption experiments were conducted to evaluate adsorption capacities of P(Py-co-An)-TiO₂/NCC. A stock solution of EY (10^{-2} M) was prepared in 1 L of double distilled water. The desired concentrations of the dye solution were obtained by proper dilution of the stock solution. 0.1 g of P(Py-co-An)-TiO₂/NCC was added into a stoppered bottle containing 50 mL of EY solution (10^{-5} M). pH of the solution was adjusted to the desired value with dilute HCl or NaOH. The mixture was shaken at 30°C for 90 min for adsorption, and then the mixture was filtered. The concentration of the dye solution before and after adsorption was estimated using UV-visible spectroscopic method. The adsorption (%) and the amount adsorbed (mol/g) were calculated as follows:

$$\text{Adsorption (\%)} = \frac{(C_0 - C_e)}{C_0} \times 100, \quad (1)$$

$$q_e = (C_0 - C_e) \times \frac{V}{m},$$

where C_0 and C_e (mol/L) are the concentrations of EY solution before and after adsorption, respectively, q_e is the adsorption capacity of the adsorbent, V (mL) is the volume of the EY solution, and m (g) is the mass of the adsorbent. Adsorbent dose experiments were conducted by shaking 10^{-5} M dye solution with 0.1–1.0 g of P(Py-co-An)-TiO₂/NCC. Adsorption kinetics was obtained by determining the adsorption capacity at different time intervals from 5 to 240 min. Adsorption isotherm was studied by changing the concentrations of the dye solution from 10^{-5} to 10^{-4} M.

2.5. Photocatalytic Degradation of EY and the Regeneration of the Photocatalyst. Photocatalytic degradation of the dye was studied using P(Py-co-An)-TiO₂/NCC after adsorption experiment. The dye loaded swollen hydrogels were exposed to sunlight (at noon) and withdrawn at different time intervals from 5 to 120 min. Each sample is then analyzed spectrophotometrically at a wavelength of 515 nm. Degradation rate was calculated from the amount of the dye in the swollen gels as follows:

$$\text{Degradation ratio (\%)} = \frac{(C_0 - C_e)}{C_0} \times 100, \quad (2)$$

where C_0 and C_e are the initial and equilibrated concentrations of the dye (mol/L).

The samples obtained after photocatalytic degradation were washed thoroughly and adsorption-photocatalytic degradation experiments were repeated for four cycles in order to perform their regeneration capacity.

3. Results and Discussion

3.1. Preparation of the Photocatalyst, P(Py-co-An)-TiO₂/NCC. The photocatalyst, P(Py-co-An)-TiO₂/NCC, was prepared from TiO₂/NCC via chemical oxidation polymerization technique. Firstly, Cellulose was extracted from the value added product, sawdust, by acid-alkali treatment followed by bleaching with H₂O₂. The cellulose was made into nanocrystals via acid hydrolysis which improves its crystallinity and hydrophilicity. TiO₂/NCC was prepared from NC and the precursor Ti(OiPr)₄ using chemical precipitation method. PPy and PAN were coated onto TiO₂/NCC by chemical oxidation polymerization of pyrrole and aniline with FeCl₃. APS will generate TiO[•] free radicals and the polymer chain gets attached to it. The presence of the crosslinker, glutaraldehyde, will create a three-dimensional network structure, thereby increasing the water or solute holding capacity of the material.

3.2. Characterization Studies

3.2.1. Surface Morphology Analysis. The surface morphology of the samples is clearly displayed in Figure 1. The SEM image of the cellulose was observed to be smooth and fibrous and to have a layered structure, which provided a good condition for the adsorption of the dye pollutants. NC seems to be hydrophilic and behaves as gel structure. It may increase the swelling and diffusion of solute molecules from aqueous phase. TiO₂/NCC composite showed TiO₂ particles to be well dispersed and so reside equally on all regions on the surface. The polymerization onto TiO₂/NCC (Figure 1(d)) led to a heterogeneous rough surface, and this surface roughness leads to different prominent adsorption phases during the adsorption process [18].

3.2.2. XRD Analysis. Figure 2 shows the XRD patterns of cellulose, NC, TiO₂/NCC, and P(Py-co-An)-TiO₂/NCC. The XRD pattern of cellulose shows peaks at 2θ values of 22.1 and 34.2° correspond to crystalline domain of cellulose structure, whereas the broad hump at 15.8° indicates the amorphous nature of cellulose. The small shift and the increase in broadness of the characteristic peaks of NC may be due to the small particle size of NC. The sharper diffraction peaks of NC were aroused due to the partial removal of the amorphous regions during the acid hydrolysis treatment of cellulose [19]. The identified XRD patterns of TiO₂/NCC gave distinctive peaks at ~25.6, 38.2, 48.2, 54.6, and 63.4° (JCPDS card number 21-1272), which resemble the characteristic peaks of TiO₂, as given in earlier reports [7]. From Figure 2, it is observed that the crystalline peaks are relatively broad compared to those normally obtained for bulk material, indicating that the crystal sizes are smaller. The Debye-Scherrer equation [20] is used to determine the average crystal size of the NC and it is found to be in the range of 21.6 nm. The appearance of new peaks and the shifting of the characteristic peaks of TiO₂ in P(Py-co-An)-TiO₂/NCC clearly indicate that proper grafting had been occurring on the surface of TiO₂/NCC.

3.2.3. FTIR Analysis. The FTIR patterns of cellulose, NC, TiO₂/NCC, and P(Py-co-An)-TiO₂/NCC are presented in

FIGURE 1: SEM photographs of (a) cellulose, (b) NC, (c) TiO_2/NCC , and (d) $\text{P(Py-co-An)-TiO}_2/\text{NCC}$.

FIGURE 2: XRD patterns of cellulose, NC, TiO_2/NCC , and $\text{P(Py-co-An)-TiO}_2/\text{NCC}$.

FIGURE 3: FTIR spectra of cellulose, NC, TiO_2/NCC , and $\text{P(Py-co-An)-TiO}_2/\text{NCC}$.

Figure 3. The peaks observed at ~ 3441 and 3417 cm^{-1} are derived from hydroxyl groups in cellulose and water. The bands at ~ 2922 and 2899 cm^{-1} (C-H stretching of CH_2) and 1426 cm^{-1} (CH_2 symmetric bending) can be assigned to the stretching and bending modes of hydrocarbons in cellulose backbone [21]. The characteristic peaks of cellulosic material also appeared at 1112 and $\sim 1033\text{ cm}^{-1}$ (skeletal vibrations involving C-O stretching) [22]. The peak at $\sim 539\text{ cm}^{-1}$ clearly shows the presence of discrete anatase particles in TiO_2/NCC structure [23]. The two characteristic peaks at 1554 and 1492 cm^{-1} in $\text{P(Py-co-An)-TiO}_2/\text{NCC}$ correspond to the frequencies of aromatic ring in PAn, which are stretching of quinone ring and benzene rings, respectively [24]. Peaks attributed to out-of-plane bending vibration of C-H band of parasubstituted benzene ring were observed near 755 cm^{-1} and the stretching of C-N band of benzene ring was confirmed by the peak of 1267 cm^{-1} [25]. The band at 1457 cm^{-1} may be attributed to C-N stretching modes of vibration in pyrrole ring. The peak nearer to $\sim 3318\text{ cm}^{-1}$ found in TiO_2/NCC was not observed after polymerization which suggests that polymerization had occurred due to the breakage of intermolecular hydrogen bond present in TiO_2/NCC .

3.3. Adsorption Studies

3.3.1. Effect of Adsorbent Dose. The amount of the spent adsorbent determines the economic value of the adsorption process. The performances of the adsorbent $\text{P(Py-co-An)-TiO}_2/\text{NCC}$ and the precursor material cellulose were

FIGURE 4: Effect of adsorbent dose on EY adsorption onto $\text{P(Py-co-An)-TiO}_2/\text{NCC}$.

evaluated by varying their amounts from 0.5 to 5.0 g/L . As seen in Figure 4, the adsorption percentage of the sorbents increases with increase in amount because of the increased available surface sites for adsorption [26]. The complete removal of EY was achieved with an amount of TiO_2/NCC , 9.0 g/L , and $\text{P(Py-co-An)-TiO}_2/\text{NCC}$, 3.5 g/L , respectively. It means that the sorption efficiency of $\text{P(Py-co-An)-TiO}_2/\text{NCC}$ is 2.6 times more than the untreated cellulose at pH 4.5. The variation in the adsorption capacity between the various adsorbents could be related to the nature and concentration of surface groups responsible for the interaction with the dyes.

3.3.2. Effect of Solution pH. pH value of the solution is an important controlling parameter in the adsorption process, since it affects the surface charge of the adsorbent and the degree of speciation of adsorbate. As depicted in Figure 5, adsorption of EY on $\text{P(Py-co-An)-TiO}_2/\text{NCC}$ was strongly affected by the solution pH. As pH of the solution was increased from 2.0 to 9.0 , the percentage adsorption increases and reaches maximum at pH 4.5 and thereafter decreases. The maximum dye removal (%) at pH 4.5 was found to be 91.7% for an initial EY concentration of $1.0 \times 10^{-5}\text{ M}$. The increased uptake at much higher acidic solution can be attributed to the increasing electropositive charge of the adsorbent which favored the adsorption of dye anions through electrostatic attraction (Figure 6). At $\text{pH} < 4.5$, the aniline surfaces were positively charged and, at $\text{pH} > 4.5$, the surfaces were negatively charged. Aniline can exist as nondissociated and/or dissociated species in aqueous solutions. Aniline is an ionizable organic compound and is a weak base that can protonate to form anilinium ion. Thus, the high efficient removal of EY by $\text{P(Py-co-An)-TiO}_2/\text{NCC}$ is due to its high porosity, great surface area, and intrinsic positive charge of $\text{P(Py-co-An)-TiO}_2/\text{NCC}$ as a type of n-doping polymer in which the anionic dopant (Cl^-) is exchanged by the anionic dye.

TABLE 1: Kinetic parameters for the adsorption of EY onto P(Py-co-An)-TiO₂/NCC ($\pm$ standard deviation; $n = 3$).

$C_0 \times 10^{-5}$ (mol L ⁻¹)	$q_e, \text{exp} \times 10^{-5}$ (mol g ⁻¹)	Pseudo-first-order				Pseudo-second-order				
		k_1 (min ⁻¹)	$q_e, \text{cal} \times 10^{-5}$ (mol g ⁻¹)	R^2	χ^2	k^2 (g mol ⁻¹ min ⁻¹)	$q_e, \text{cal} \times 10^{-5}$ (mol g ⁻¹)	$h_0 \times 10^{-6}$	R^2	χ^2
1	0.458	0.270	0.447	0.974	0.0003	1.234	0.461	0.262	0.995	7×10^{-5}
5	2.202	0.279	2.157	0.977	0.007	0.003	2.218	0.015	0.996	0.0014

FIGURE 5: Effect of solution pH on EY adsorption onto P(Py-co-An)-TiO₂/NCC.

3.3.3. Effect of Adsorption Time. Figure 7 shows the effect of contact time on the batch adsorption of EY at 30°C and pH 4.5. It is obvious that the increase in contact time from 5 to 90 min increased the percentage removal of EY. This is due to the large number of active binding sites for adsorption during the initial stage and gradual occupancy of them makes the sorption less efficient in the later stages [27]. A further increase in contact time had a negligible effect on the percentage removal of EY. It implies that the sorption process is considerably fast and more than 91.7% and 88.1% of dye solution with initial concentrations of 1.0×10^{-5} and 5.0×10^{-5} M, respectively, were adsorbed within 90 min.

Adsorption Kinetics. To perform the adsorption process on a larger scale, the elucidation of kinetic parameters and the sorption characteristics of the adsorbent are required. With that purpose, we analyzed the experimental kinetic data with pseudo-first-order and pseudo-second-order equations (see (3)). The first-order kinetics model assumes mass transport as the rate limiting mechanism, whereas the second-order one assumes chemical adsorption as the rate limiting mechanism. Consider

$$\text{Pseudo-first-order: } q_t = q_e (1 - e^{-k_1 t}), \quad (3)$$

$$\text{Pseudo-second-order: } q_t = \frac{k_2 q_e^2 t}{1 + t k_2 q_e},$$

where q_e and q_t (mg/g) are the amount of dye adsorbed on P(Py-co-An)-TiO₂/NCC at equilibrium and time t (min),

respectively. k_1 (min⁻¹) is the rate constant for the pseudo-first-order adsorption process. k_2 (g mol⁻¹ min⁻¹) is the rate constant for the pseudo-second-order kinetics.

Additionally, the initial adsorption rate h_0 (mol g⁻¹ min⁻¹) can be calculated from pseudo-second-order kinetic model as follows:

$$h_0 = k_2 q_e^2. \quad (4)$$

Kinetic parameters for different concentrations were calculated by a nonlinear curve fitting method using ORIGIN program (version 7.5) and are listed in Table 1. The computed values of correlation coefficient (R^2) and chi-square (χ^2) values measure the degree of fitness of the model with the experimental kinetic data. Higher R^2 (>0.99) and lower χ^2 values obtained for the pseudo-second-order model indicate that this model could define the experimental results more precisely than pseudo-first-order model which indicates that the rate-limiting step may be a chemical sorption involving valence forces through exchange of ions between the adsorbent and adsorbate. As the initial dye concentration increases, the initial adsorption rate (h_0) increases. The values of k_2 were found to be decreased with increase of initial concentration and may be due to lowering the probability of collision between the dye molecules which faster the movement of dye towards the adsorbent surface at lower concentrations.

3.3.4. Effect of Solute Concentration. Adsorption isotherm measures the adsorption efficiency of a polymer over a range of analyte concentrations. It describes the interactive behavior between adsorbate and adsorbent and is important for predicting the adsorption capacity of adsorbent, which is the main parameter required for design of an adsorption system. The increase in concentration of dye solution caused an increase in adsorption capacity (Figure 8), since the increase in initial dye concentration facilitates the dye movement from bulk to the surface of the adsorbent.

For evaluating the maximum adsorption capacity and adsorption mechanism, the experimental isotherm data were interpreted using the equilibrium isotherm models, such as Langmuir, Freundlich, and Fritz-Schlunder isotherm equations, as follows:

$$\begin{aligned} q_e &= \frac{Q^0 b C_e}{1 + b C_e}, \\ q_e &= K_F C_e^{1/n}, \\ q_e &= \frac{q_{FS} K_{FS} C_e}{1 + q_{FS} C_e^\alpha}, \end{aligned} \quad (5)$$

FIGURE 6: Possible interactions between EY and P(Py-co-An)-TiO₂/NCC. FIGURE 7: Kinetic modeling for the EY adsorption onto P(Py-co-An)-TiO₂/NCC.

where q_e (mol/L) is the amount adsorbed at equilibrium, C_e (mol/L) is the equilibrium concentration of the dye on adsorption, Q^0 (mol/g) is the maximum adsorption capacity at complete monolayer, and b (L/mol) is the Langmuir constant related to the affinity of binding sites and is a measure

of the energy of adsorption. K_F (mol^{1-1/n} L^{1/n}/g) and $1/n$ are the Freundlich constants related to adsorption capacity and intensity of adsorption, respectively. q_{FS} is the Fritz-Schlunder maximum adsorption capacity (mol/g), K_{FS} is the Fritz-Schlunder equilibrium constant (L/mol), and α is the Fritz-Schlunder exponent.

The Langmuir isotherm [28] is based on assumption of structurally homogeneous adsorbent and monolayer coverage with no interaction between the sorbate molecules. According to this model, once a dye molecule occupies a site, no further adsorption can take place at that site [29]. The Langmuir parameters can be used to predict the affinity between the sorbate and sorbent using dimensionless separation factor (R_L):

$$R_L = \frac{1}{1 + bC_0}, \quad (6)$$

where b is the Langmuir isotherm constant relating to binding energy and C_0 is the initial solute concentration. The values of R_L at 30°C were determined and were found to be 0.2874, 0.1678, 0.1185, 0.0916, 0.0746, 0.0629, 0.0545, 0.0479, 0.0429, and 0.0387 at an initial dye concentration of 1, 2, 3, 4, 5, 6, 7, 8, 9, and 10 × 10⁻⁵ mg/L, respectively. R_L values for the present experimental data fell between 0 and 1, which is indicative of favorable adsorption of EY onto P(Py-co-An)-TiO₂/NCC. The maximum monolayer adsorption capacity, based on Langmuir model, was 3.397 mol/g. The adsorption capacity of the adsorbent P(Py-co-An)-TiO₂/NCC towards EY was

TABLE 2: Isotherm parameters for the adsorption of EY onto P(Py-co-An)-TiO₂/NCC at 30°C (±standard deviation; $n = 3$).

$Q^0 \times 10^{-5}$ (mol g ⁻¹)	Langmuir			Freundlich				Fritz-Schlunder				
	b (L mol ⁻¹)	R^2	χ^2	K_F (mol ^{1-1/n} L ^{1/n} g ⁻¹)	$1/n$	R^2	χ^2	q_{FS} (mol g ⁻¹)	K_{FS} (L mol ⁻¹)	α	R^2	χ^2
3.397	2.480	0.996	0.005	2.160	0.326	0.949	0.062	2.504	3.385	0.997	0.996	0.005

FIGURE 8: Isotherm modeling for the EY adsorption onto P(Py-co-An)-TiO₂/NCC.

found to be much higher as compared to the conjugated polymer-grafted sawdust [30].

Freundlich isotherm equation can be applied to nonideal sorption on heterogeneous surfaces as well as to multilayer sorption. The value of Freundlich exponent $1/n$ (0.326) is in the range of 0 to 1, indicating a favorable adsorption. Fritz-Schlunder isotherm model [31] is a widely accepted isotherm model in which Fritz and Schlunder the equations of Langmuir and Freundlich were developed empirically. The isotherm plots and the isotherm parameters are represented in Figure 8 and Table 2, respectively.

As suggested by Figure 8 and Table 2, the equilibrium sorption data were best presented by Fritz-Schlunder isotherm. According to R^2 and χ^2 values, the adsorption isotherm data follow the order: Fritz-Schlunder > Langmuir > Freundlich.

3.4. Photocatalytic Studies

3.4.1. Photocatalytic Degradation of EY and Its Mechanism. The photocatalytic activities of P(Py-co-An)-TiO₂/NCC were evaluated by the degradation of EY in an aqueous solution under sunlight irradiation. No degradation of EY was

FIGURE 9: Kinetic data for the photodegradation of EY onto P(Py-co-An)-TiO₂/NCC.

observed in the absence of a photocatalyst under visible light illumination. It was observed that photocatalytic degradation of EY increases with increase in irradiation time and 92.3% of the dye was degraded within 90 min. Photocatalytic degradation was found to follow first-order rate equation, for lower concentrations, as follows:

$$\ln\left(\frac{C_0}{C}\right) = kt, \quad (7)$$

where C is the concentration of the dye at time t (mol/L), t is the illumination time in minutes, k is the reaction rate constant (min⁻¹), and C_0 is the concentration of the dye before irradiation (mol/L). Figure 9 shows the relationship between $\ln(C/C_0)$ of EY and photodegradation time in the presence of P(Py-co-An)-TiO₂/NCC for 90 min under visible light irradiation. The plot of $\ln(C_0/C)$ versus time represents a straight line, the slope of which upon linear regression equals the apparent first-order rate constant “ k ” and was calculated to be 0.00575 min⁻¹ in the present study.

3.4.2. Mechanism of Photocatalysis. TiO₂ particles can absorb UV light from the sunlight to create electrons (e^-) in the conduction band and holes (h^+) in the valence band, respectively. If the electrons and holes cannot be captured in time, they will recombine with each other within a few nanoseconds, which will reduce the photocatalytic efficiency of TiO₂. However, due to the existence of the interface between polymer and TiO₂, separated electrons and holes have little possibility to recombine again in the case of composites. This ensures

higher charge separation efficiency and better photooxidation capacity for the nanocomposite. In addition, the conjugated polymer can absorb the visible light and produces an electron (e^-) that transfers to the conduction band of TiO_2 [32, 33] and then to an adsorbed electron acceptor like dye, yielding oxygen radicals to degrade pollutants into mineral end products [34].

Thus, the heterogeneous photocatalytic degradation of an azo compound can be summarized by the following reactions [35]:

Several authors make use of these types of conjugated polymers in the photodegradation of dye under visible light. The conjugated polymers (CPs) with extended p-conjugated electron systems showed the relatively high photoelectric conversion efficiency and charge transfer due to their high absorption coefficients in the visible part of the spectrum, high mobility of charge carriers, and good stability [36]. pH adjustments using acid (H^+) or alkali (OH^-) during adsorption processes may increase the photocatalytic reaction rate, in accordance with (v) and (vi). According to previous literature, the hydroxyl radical will oxidize eosin yellow to its leuco form, which may ultimately degrade to environmentally benign products such as water, carbon dioxide, and inorganic salts like bromides. It was confirmed that $\text{OH}^\bullet$ radical participates as an active oxidizing species in the degradation of eosin yellow as the rate of degradation was appreciably reduced in presence of hydroxyl radical scavenger [37].

3.4.3. Photorecyclability of $\text{P(Py-co-An)-TiO}_2/\text{NCC}$. To examine the photocatalytic stability, adsorption of EY onto $\text{P(Py-co-An)-TiO}_2/\text{NCC}$ hydrogel was carried out at optimum conditions and the adsorbed dye material was exposed to sunlight for degradation. This process was repeated for four cycles and the results obtained were depicted in Figure 10. It can be found that the adsorption capacity and photodegradation efficiency of EY slightly decrease with the recycling runs up to four successive cycles. The above results indicate

FIGURE 10: Adsorption-photocatalytic degradation cycle of EY on $\text{P(Py-co-An)-TiO}_2/\text{NCC}$.

that $\text{P(Py-co-An)-TiO}_2/\text{NCC}$ shows excellent photocatalytic stability.

4. Conclusions

Eosin yellow (EY) is a carcinogenic dye and its exposure may cause adverse effects. Here we prepared a conductive conjugated polymer/semiconductor system, poly(pyrrole-co-aniline)-coated $\text{TiO}_2/\text{nanocellulose}$ composite ($\text{P(Py-co-An)-TiO}_2/\text{NCC}$), for the removal of EY from aqueous solutions. The samples under preparation stage were characterized by SEM, XRD, and FTIR analyses. The systematic adsorption cum photocatalytic studies were carried out to explore the optimum conditions for the dye removal. Adsorption of dye was highly dependent on pH and 91.7% of the dye was adsorbed at pH of 4.5 within 90 min. An adsorbent dose of 3.5 g/L was needed for the complete adsorption of EY from aqueous solutions. Adsorption follows both Langmuir and Fritz-Schlunder isotherm models and pseudo-second-order kinetics, suggesting that chemisorption may be the mechanism behind the adsorption process. Photocatalytic degradation of EY under sunlight produced reliable results. $\text{P(Py-co-An)-TiO}_2/\text{NCC}$ shows excellent photocatalytic stability and recyclability. Thus, the present investigation shows that the photocatalyst, $\text{P(Py-co-An)-TiO}_2/\text{NCC}$, is a valuable material for the adsorption and photocatalytic degradation of EY dye from aqueous solutions and can be developed as a support for the removal of EY dye from industrial effluents.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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References

- [1] G. M. Walker, L. Hansen, J.-A. Hanna, and S. J. Allen, "Kinetics of a reactive dye adsorption onto dolomitic sorbents," *Water Research*, vol. 37, no. 9, pp. 2081–2089, 2003.
- [2] Y.-Y. Xu, M. Zhou, H.-J. Geng et al., "A simplified method for synthesis of Fe_3O_4 @PAA nanoparticles and its application for the removal of basic dyes," *Applied Surface Science*, vol. 258, no. 8, pp. 3897–3902, 2012.
- [3] B. Y. Shi, G. H. Li, D. S. Wang, C. H. Feng, and H. X. Tang, "Removal of direct dyes by coagulation: the performance of preformed polymeric aluminum species," *Journal of Hazardous Materials*, vol. 143, no. 1-2, pp. 567–574, 2007.
- [4] R. Ansari, M. S. Tehrani, and E. Alizadeh, "Application of poly(3-methyl thiophene)-saw dust nanocomposite for removal of anionic carmoisine dye from aqueous solutions," *Journal of Advanced Scientific Research*, vol. 3, pp. 86–92, 2012.
- [5] F. Al-Momani, E. Touraud, J. R. Degorce-Dumas, J. Roussy, and O. Thomas, "Biodegradability enhancement of textile dyes and textile wastewater by VUV photolysis," *Journal of Photochemistry and Photobiology A: Chemistry*, vol. 153, no. 1-3, pp. 191–197, 2002.
- [6] S. Banerjee, J. Gopal, P. Muraleedharan, A. K. Tyagi, and B. Raj, "Physics and chemistry of photocatalytic titanium dioxide: visualization of bactericidal activity using atomic force microscopy," *Current Science*, vol. 90, no. 10, pp. 1378–1383, 2006.
- [7] F. Deng, Y. Li, X. Luo, L. Yang, and X. Tu, "Preparation of conductive polypyrrole/ TiO_2 nanocomposite via surface molecular imprinting technique and its photocatalytic activity under simulated solar light irradiation," *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, vol. 395, pp. 183–189, 2012.
- [8] M. A. Tariq, M. Faisal, M. Muneer, and D. Bahnemann, "Photochemical reactions of a few selected pesticide derivatives and other priority organic pollutants in aqueous suspensions of titanium dioxide," *Journal of Molecular Catalysis A: Chemical*, vol. 265, no. 1-2, pp. 231–236, 2007.
- [9] Y. Yang, H. Zhang, P. Wang, Q. Zheng, and J. Li, "The influence of nano-sized TiO_2 fillers on the morphologies and properties of PSF UF membrane," *Journal of Membrane Science*, vol. 288, no. 1-2, pp. 231–238, 2007.
- [10] I. A. Shkrob, M. C. Sauer Jr., and D. Gosztola, "Efficient, rapid photooxidation of chemisorbed polyhydroxyl alcohols and carbohydrates by TiO_2 nanoparticles in an aqueous solution," *The Journal of Physical Chemistry B*, vol. 108, no. 33, pp. 12512–12517, 2004.
- [11] S. Kamel, "Nanotechnology and its applications in lignocellulosic composites, a mini review," *eXPRESS Polymer Letters*, vol. 1, no. 9, pp. 546–575, 2007.
- [12] C. Lai, G. R. Li, Y. Y. Dou, and X. P. Gao, "Mesoporous polyaniline or polypyrrole/anatase TiO_2 nanocomposite as anode materials for lithium-ion batteries," *Electrochimica Acta*, vol. 55, no. 15, pp. 4567–4572, 2010.
- [13] J.-D. Kwon, P.-H. Kim, J.-H. Keum, and J. S. Kim, "Polypyrrole/titania hybrids: synthetic variation and test for the photo-voltaic materials," *Solar Energy Materials and Solar Cells*, vol. 83, no. 2-3, pp. 311–321, 2004.
- [14] H.-C. Liang and X.-Z. Li, "Visible-induced photocatalytic reactivity of polymer-sensitized titania nanotube films," *Applied Catalysis B: Environmental*, vol. 86, no. 1-2, pp. 8–17, 2009.
- [15] D. Shao, J. Hu, C. Chen, G. Sheng, X. Ren, and X. Wang, "Polyaniline multiwalled carbon nanotube magnetic composite prepared by plasma-induced graft technique and its application for removal of aniline and phenol," *The Journal of Physical Chemistry C*, vol. 114, no. 49, pp. 21524–21530, 2010.
- [16] G. Chakraborty, K. Gupta, A. K. Meikap, R. Babu, and W. J. Blau, "Synthesis, electrical and magnetotransport properties of polypyrrole-MWCNT nanocomposite," *Solid State Communications*, vol. 152, no. 1, pp. 13–18, 2012.
- [17] T. S. Anirudhan and S. R. Rejeena, "Adsorption and hydrolytic activity of trypsin on a carboxylate-functionalized cation exchanger prepared from nanocellulose," *Journal of Colloid and Interface Science*, vol. 381, no. 1, pp. 125–136, 2012.
- [18] A. Dolatshahi-Pirouz, K. Rechendorff, M. B. Hovgaard, M. Foss, J. Chevallier, and F. Besenbacher, "Bovine serum albumin adsorption on nano-rough platinum surfaces studied by QCM-D," *Colloids and Surfaces B: Biointerfaces*, vol. 66, no. 1, pp. 53–59, 2008.
- [19] A. Alemdar and M. Sain, "Isolation and characterization of nanofibers from agricultural residues—wheat straw and soy hulls," *Bioresource Technology*, vol. 99, no. 6, pp. 1664–1671, 2008.
- [20] P. Scherrer, "Bestimmung der Grösse und der inneren Struktur von Kolloidteilchen mittels Röntgenstrahlen," *Nachrichten von der Gesellschaft der Wissenschaften zu Göttingen*, vol. 26, pp. 98–100, 1918.
- [21] H.-J. Lee, T.-J. Chung, H.-J. Kwon, H.-J. Kim, and W. T. Y. Tze, "Fabrication and evaluation of bacterial cellulose-polyaniline composites by interfacial polymerization," *Cellulose*, vol. 19, no. 4, pp. 1251–1258, 2012.
- [22] H. S. Barud, R. M. N. Assunção, M. A. U. Martinez et al., "Bacterial cellulose-silica organic-inorganic hybrids," *Journal of Sol-Gel Science and Technology*, vol. 46, no. 3, pp. 363–367, 2008.
- [23] L. M. Daniel, R. L. Frost, and H. Y. Zhu, "Synthesis and characterisation of clay-supported titania photocatalysts," *Journal of Colloid and Interface Science*, vol. 316, no. 1, pp. 72–79, 2007.
- [24] A. Kapil, M. Taunk, and S. Chand, "Preparation and charge transport studies of chemically synthesized polyaniline," *Journal of Materials Science: Materials in Electronics*, vol. 21, no. 4, pp. 399–404, 2010.
- [25] A. Gök, B. Sari, and M. Talu, "Synthesis and characterization of conducting substituted polyanilines," *Synthetic Metals*, vol. 142, no. 1-3, pp. 41–48, 2004.
- [26] R. Ansari, A. Mohammad-Khah, and Z. Mosayebzadeh, "Application of unripe grape juice waste as an efficient low cost biosorbent for dye removal," *Annals of Biological Research*, vol. 2, pp. 323–328, 2011.
- [27] R. Ansari and M. B. Keivani, "polyaniline conducting electroactive polymers thermal and environmental stability studies," *E-Journal of Chemistry*, vol. 3, no. 4, pp. 202–217, 2006.
- [28] I. Langmuir, "The adsorption of gases on plane surfaces of glass, mica and platinum," *Journal of the American Chemical Society*, vol. 40, no. 9, pp. 1361–1403, 1918.

- [29] V. Vimonses, S. Lei, B. Jin, C. W. K. Chow, and C. Saint, "Adsorption of congo red by three Australian kaolins," *Applied Clay Science*, vol. 43, no. 3-4, pp. 465-472, 2009.
- [30] R. Ansari and Z. Mosayebzadeh, "Removal of Eosin Y, an anionic dye, from aqueous solutions using conducting electroactive polymers," *Iranian Polymer Journal*, vol. 19, no. 7, pp. 541-551, 2010.
- [31] W. Fritz and E.-U. Schlunder, "Simultaneous adsorption equilibria of organic solutes in dilute aqueous solutions on activated carbon," *Chemical Engineering Science*, vol. 29, no. 5, pp. 1279-1282, 1974.
- [32] S. Zhu, W. Wei, X. Chen, M. Jiang, and Z. Zhou, "Hybrid structure of polyaniline/ZnO nanograft and its application in dye-sensitized solar cell with performance improvement," *Journal of Solid State Chemistry*, vol. 190, pp. 174-179, 2012.
- [33] R. Jamal, Y. Osman, A. Rahman, A. Ali, Y. Zhang, and T. Abdiryim, "Solid-state synthesis and photocatalytic activity of polyterthiophene derivatives/TiO₂ nanocomposites," *Materials*, vol. 7, no. 5, pp. 3786-3801, 2014.
- [34] X. Huang, G. Wang, M. Yang, W. Guo, and H. Gao, "Synthesis of polyaniline-modified Fe₃O₄/SiO₂/TiO₂ composite microspheres and their photocatalytic application," *Materials Letters*, vol. 65, no. 19-20, pp. 2887-2890, 2011.
- [35] J. Cunningham, G. Al-Sayyed, and S. Srijaranai, *Aquatic and Surface Photochemistry*, Lewis Publisher, CRC Press, 1994.
- [36] S. Min, F. Wang, and Y. Han, "An investigation on synthesis and photocatalytic activity of polyaniline sensitized nanocrystalline TiO₂ composites," *Journal of Materials Science*, vol. 42, no. 24, pp. 9966-9972, 2007.
- [37] S. Gupta, R. Diptisoni, and S. Benjamin, "Use of barium chromate in photocatalytic degradation of eosin yellow," *Chemical Science Transactions*, vol. 4, pp. 851-857, 2015.