Polypyrrole—A conducting nanopolymer for the treatment of simulated textile effluent

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ORIGINAL RESEARCH ARTICLE

ABSTRACT

The aim of the study was to synthesize polypyrrole (PPy) nanopolymers and to evaluate its potential for the decolorization of simulated textile effluent. PPy nanopolymer was prepared by in vitro chemical oxidative polymerization of pyrrole monomer using ammonium peroxydisulfate as oxidant. Scanning electron microscopy image showed that the nanopolymer was irregular in shape and mostly present in aggregates. The size of the nanopolymer varied from 40 to 80 nm. Fourier transform infrared spectroscopy study showed the characteristic peaks of PPy from 1308 to 681 cm⁻¹ with different vibrational modes. X-ray diffractogram indicates the amorphous nature of the nanopolymer. Batch experiments were carried out as a function of contact time and pH. The PPy nanopolymer decolorized 80% of the dyes that were present in the simulated reactive dye effluent. The equilibrium adsorption data followed the modified Freundlich model and modified pseudo-first-order kinetics. The results of the study indicate that the PPy nanopolymer could be used for the treatment of textile effluents.

KEYWORDS
conductive polymer; decolorization; effluent treatment; nanopolymer; polypyrrole

INTRODUCTION

Synthetic dyes are extensively used in textile industries. Of the various types of synthetic dyes used in industries, reactive dyes have found more use due to their excellent colorfastness and ease of application. However, poor fixation rate and high solubility increase the concentration of reactive dyes in wastewater. It is estimated that nearly 50% of the reactive dyes remain in wastewater resulting to highly colored effluents (Khatri et al., 2015). In addition, the dye effluents exhibit characteristics of fluctuating pH, high chemical oxygen demand and biological oxygen demand, carry a great quantity of suspended solids, dispersing agents, dye bath carriers, salts, emulsifiers and considerable quantities of heavy metals, chlorinated organic compounds, and surfactants (Dasgupta et al., 2015; Khatri et al., 2015). Furthermore, reactive dyes are toxic to the biotic communities and get biomagnified in the food chain (Vinitnantharat et al., 2008). Thus, there is a considerable need to treat the reactive dye effluents before releasing them into the ecosystem.

Numerous physical, chemical, and biological methods have been adopted for the treatment of reactive dye containing textile effluents (Alvarez et al., 2013; Duarte et al., 2013; Dasgupta et al., 2015; Rosa et al., 2015). One of the physicochemical methods that has gained popularity in recent years due to its simplicity, ease of operation, high efficiency, and limited secondary waste generation is adsorption. Several studies have proposed a variety of chemical and biological adsorbents for the treatment of reactive
dye effluents (Vijayaraghavan et al., 2009; Ahmad and Hameed, 2009; Janaki et al., 2012a; Janaki et al., 2013; Abidi et al., 2015). Polypyrrole (PPy) is one adsorbent that has created tremendous interests recently due to its high thermal conductivity, ease of synthesis, high specific capacitance, and high surface area (Sahoo et al., 2011). PPy synthesized either by chemical or electrochemical polymerization carries a positive charge in its nitrogen atom, which provides a good trait for the adsorption of dye anions present in the effluent solution (Saoudi et al., 2004). Nanosizing adsorbents have shown to considerably increase their adsorption efficiency because of the increase in surface area and little internal diffusion resistance (Chang et al., 2006). Thus, the objectives of the present study were (i) to synthesize and characterize the nano-PPy adsorbent, (ii) to assess the potential of the nanopolymer to decolorize reactive dyes, (iii) to evaluate the influence of pH and contact time on adsorption of dyes, and (iv) to explore adsorption isotherm and kinetics to understand the mechanism of dye decolorization.

2 MATERIALS AND METHODS

2.1 Materials

Pyrrole was purchased from Sigma-Aldrich (St. Louis, MO) and was distilled before use. Ammonium peroxysulfate, Remazol Brilliant Blue R (RBBR), Remazol Black (RB), Remazol Violet (RV), Remazol Orange (RO), and all other auxiliary chemicals were also from Sigma-Aldrich.

2.2 Synthesis of PPy

PPy was synthesized by a facile route of chemical oxidative polymerization of pyrrole according to Saoudi et al. (2004) with minor modification. In brief, about 0.01 M of pyrrole monomer in 1 M HCl was stirred for 2 h to attain the homogenous solution. Ammonium peroxysulfate in 1 M HCl was added into the above mixture with constant stirring at ice. After complete addition of initiator, the reaction mixture was constantly stirred for 5 h and then stored in a refrigerator overnight. The resulting blackish precipitate was separated by centrifugation and washed several times with double distilled water and methanol until the polymerization solution became colorless. The nanocomposite was dried at 60 °C for 48 h and used for the decolorization of simulated reactive dye effluent.

2.3 Characterization of PPy

Morphology of the PPy nanopolymer was observed using scanning electron microscopy (JEOL JSM-6400) and transmission electron microscopy (H-7650, HITACHI, Japan). Fourier transform infrared (FTIR) spectra of the PPy nanopolymer were performed on a spectrometer (Shimadzu, Model 8400S) at a resolution of 4 cm⁻¹ in KBr pellets. X-ray diffractogram of the PPy nanopolymer was obtained using Cu Kα incident beam (λ= 0.1546 nm) monochromated by a nickel filtering wave at a tube voltage of 40 kV and a tube current of 30 mA. The scanning was done in the region of 2θ from 4° to 60° at 0.04°/min with a time constant of 2 s.

2.4 Simulated dye effluent preparation

To mimic the effluent released from textile manufacturing plant, simulated effluent was prepared under laboratory conditions. The composition for the effluents was considered according to the reactive dye stuff content during the time of dyeing procedure. The chemical components include reactive dyes such as Remazol Brilliant Blue R (0.5 mM), Remazol Black (0.5 mM), Remazol Violet (0.5 mM), Remazol Orange (0.5 mM), sodium chloride (710 mM), sodium carbonate (122 mM), sodium hydroxide (13 mM), and acetic acid (13 mM). The simulated effluent was boiled for 3 h and then allowed to cool for 12 h. The composition of the reactive dye bath effluent was assumed to be 20% of the original dye stuff and 100% of all the auxiliary chemicals present in the exhausted dye-bath (Alaton et al., 2002).

2.5 Batch sorption study for dye removal

Batch sorption experiments were carried out typically by adding 0.3 g PPy nanopolymer to 100 mL dye effluent. If necessary, the pH of the solution was initially adjusted and controlled using 0.1 M NaOH or HCl. The flasks were kept in a rotary incubated shaker at a constant speed of 150 rpm at room temperature. Samples were withdrawn at appropriate time intervals, and the supernatant was collected by centrifuging at 9000 rpm for 10 min. The equilibrium concentrations of dyes were determined at the wavelength maxima of 575 nm using a UV-vis spectrophotometer (UV-1800 Shimadzu, Japan).

To represent the dye removal in batch systems, two parameters (1) percentage removal and (2) extent of decolorization were used (Vijayaraghavan et al., 2009). The percentage removal can be represented as
follows:

\[
\text{Removal (\%) = } \left( \frac{\text{Abs}_i - \text{Abs}_f}{\text{Abs}_f} \right)_{at\,575\,nm} \times 100
\]  

(1)

The extent of decolorization, \( Q \) (L/g), can be calculated from:

\[
Q = \frac{V}{M} (\text{Abs}_i - \text{Abs}_f)
\]  

(2)

where \( V \) is the effluent volume (L) and \( M \) the mass of the PPy used (g).

A modified form of the Freundlich model was used to describe the isotherm data, which is a plot of the final absorbance versus the extent of decolorization, which can be represented as follows (Vijayaraghavan et al., 2009):

\[
Q = K_F (\text{Abs}_f)^{1/n}
\]  

(3)

where \( K_F \) is the Freundlich isotherm constant (L/g) and \( n \) the Freundlich exponent.

The experimental kinetic data were described using the pseudo-first-order kinetic equation, which can be represented in its nonlinear form as follows (Vijayaraghavan et al., 2009):

\[
Q_t = Q_e (1 - \exp(-k_1 t))
\]  

(4)

where \( Q_e \) is the extent of decolorization at equilibrium (L/g), \( Q_t \) the extent of decolorization at time \( t \) (L/g), and \( k_1 \) the first-order equilibrium rate constant (1/min). All the model parameters were evaluated by nonlinear regression using the Sigma Plot (version 8.0, SPSS, USA) software. All the experiments were performed in duplicates, and the data are the average of the two experiments.

3. RESULTS AND DISCUSSION

3.1. PPy nanopolymer

Scanning and transmission electron micrographs of the PPy nanopolymer are shown in Figures 1 and 2, respectively. The nanopolymer was irregular in shape and was mostly present in aggregates. The size of the nanopolymer ranged from 40 to 80 nm. The surface of the polymer was rough and granular, providing good possibility for the adsorption of dyes. FTIR spectra of the nanopolymer are shown in Figure 3. The peaks at 3400 and 3105 cm\(^{-1}\) were assigned to the O-H stretching vibrations of polymeric compounds (Chougule et al., 2011). The bands at 1548 and 1463 cm\(^{-1}\) could be ascribed to C-N and C-C symmetric and asymmetric ring-stretching of pyrrole. The series of the peaks from 1308 to 681 cm\(^{-1}\) are the characteristic peaks of typical PPy with different vibrational modes (Xu et al., 2011; Yang et al., 2011). The X-ray diffraction peak of the polymer is shown in Figure 4. The broad peaks indicate the amorphous nature of the PPy. The peaks at 2\(\theta\) = 21.2 and 24.4\(^{\circ}\) were due to the scatterings from PPy aggregates at the interplanar spacing. The results are consistent with previous study reporting the amorphous nature of PPy (Chougule et al., 2011).

![Figure 1. Scanning electron micrograph of PPy nanopolymer. The polymer is mostly present in aggregates.](image)
Figure 2. Transmission electron micrograph of PPy nanopolymer. The size of the polymer varies from 40–80 nm.

Figure 3. FTIR spectra of PPy nanopolymer. Characteristic PPy peaks are observed from 1308 to 681 cm\(^{-1}\) with different vibrational modes.

The reactive dye anions migrated from solution to the surface of the PPy nanopolymer matrix. As a result, the decolorization occurs through the electrostatic interaction between these two counter ions leading to enhanced decolorization at pH 3. However at pH above 3 deprotonation of nitrogen atom occurs, leading to the running down of active sites in the polymer skeleton. Therefore, the interaction of PPy with the dye molecule was hindered and subsequently results in lower decolorization (Salem, 2010; Zheng et al., 2012). Also, the limited decolorization at pH 4–9 might be due to the formation of hydrogen bond by van der Waals forces and ion exchange with other functional groups present in the PPy nanopolymer. Similar observation has been reported for the sorption of Malachite Green onto degreased coffee bean (Baek et al., 2010).

Figure 4. XRD spectra of PPy nanopolymer. The broad peaks indicate the amorphous nature of the polymer.

Figure 5. Effect of pH on decolorization of simulated reactive dye bath effluent. Maximum decolorization is at pH 3 (adsorbent dosage - 3 g/L; temperature-25 °C; agitation rate - 150 rpm).
3.3. Effect of contact time

It is very essential to evaluate the contact time required to attain equilibrium while designing batch adsorption experiments. Therefore, the influence of contact time on the uptake of dyes from the simulated effluent was investigated, and the results are presented in Figure 6. As illustrated in Figure 6, decolorization of the reactive dye effluent gradually increased up to 40 min and it attained equilibrium after 60 min. Further increase in contact time did not enhance the decolorization process. The fast decolorization rate at the initial stage may be explained by an increased availability of more active sites on the adsorbent surface. In the later stage, due to the less number of sorption sites, decolorization became less efficient. Similar phenomenon was reported for the decolorization of Remazol dye effluent onto Pn/EPS nanocomposite (Janaki et al., 2012a).

![Figure 6. Effect of contact time on decolorization of simulated reactive dye bath effluent. Equilibrium was seen after 60 min (adsorbent dosage – 3 g/L; temperature-25 °C; agitation rate - 150 rpm; pH 3).](image)

3.4. Adsorption models

For practical applications, process design, operation control, and sorption kinetics are very important. The sorption kinetics in wastewater treatment is significant as it provides valuable insight into the reaction pathways and mechanism of sorption reactions. Thus, the kinetics experiment was performed using 0.3 mM concentration of reactive dye effluent using 0.3 g of the PPy nanocomposite. The resultant kinetic data were analyzed using the modified form of the pseudo-first-order kinetic equation. The curve as predicted by pseudo-first-order plot is shown in Figure 7. Values of $Q_e$, $k_1$, and $R^2$ were calculated as 2.03 L/g, 0.05 min$^{-1}$ and 0.98, respectively. The correlation coefficient was closer to unity, and the difference between the experimental $Q_e$ and calculated $Q_e$ is minimal, indicating a better fit of pseudo-first-order kinetic model. In other words, the decolorization of dye molecules favorably follows the pseudo first-order model, and the rate of the reaction appears to be controlled by the physical process.

![Figure 7. Modified pseudo-first-order plot for adsorption of dyes from simulated dye bath effluent (temperature-25 °C; agitation rate - 150 rpm; pH 3).](image)

![Figure 8. Modified Freundlich model for adsorption of dyes from simulated dye bath effluent (temperature-25 °C; agitation rate - 150 rpm; pH 3).](image)
Equilibrium studies are very important for the design of the adsorption process. The adsorption isotherm provides information about the distribution of adsorbate molecules in the liquid and the solid phases. Thus, the equilibrium experiment was performed using 0–0.6 mM concentration of reactive dye effluent using 0.3 g of the PPy. To investigate the isotherms, a modified form of the Freundlich model was used. In this study, the concentration term in the traditional Freundlich model (Freundlich, 1907) was replaced by an absorbance term, which is indicative of the color. The obtained correlation coefficient ($R^2 > 0.90$) indicates that the isotherm followed the Freundlich model. Figure 8 shows the isotherm curve predicted by the Freundlich model, which was in good accord with the experimental data. The $K_f$ and $n$ values were 2.63 L/g and 0.04, respectively. The result provides insights on the heterogeneity and multilayer coverage of Ppy on dye molecules. The results were in agreement with previous study reporting that the decolorization of the simulated effluent followed modified Freundlich model for Pn/EPS nanocomposite (Janaki et al., 2012a).

4. CONCLUSIONS

PPy nanopolymer was synthesized by chemical oxidative polymerization of pyrrole monomer. The characterization studies showed that the surface of the nanopolymer was rough and provided good possibility for adsorption studies. The dye bath effluent contains RBBR, RB, RV, RO and other auxiliary chemicals were significantly decolorized by the PPy nanopolymer. The dye adsorption kinetics follows modified pseudo first-order kinetics and modified Freundlich isotherm model. The ease of synthesis, availability and low cost indicate the potential role of PPy nanopolymer in treatment of textile effluent. However the results were completely based on the batch experiments and, thus, more remain to be learned in industrial-scale studies.

REFERENCES


