Carbohydrate Polymers 88 (2012) 1002–1008

Contents lists available at SciVerse ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Application of bacterial extracellular polysaccharides/polyaniline composite for the treatment of Remazol effluent

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ARTICLE INFO

Article history:
Received 3 December 2011
Received in revised form 13 January 2012
Accepted 17 January 2012
Available online 24 January 2012

Keywords:
Dye effluent
Extracellular polymeric substance
Polyaniline
Reactive dyes
Wastewater treatment

ABSTRACT

A complex Remazol dye effluent, comprised of Remazol Brilliant Blue R, Remazol Black, Remazol Violet, Remazol Orange, sodium chloride, sodium carbonate, sodium hydroxide, and acetic acid, was decolorized using polyaniline/extracellular polymeric substance (Pn/EPS) composite. Scanning electron micrograph showed that the surface of the composite was rough with granular appearance, providing a good possibility for dyes adsorption. X-ray diffractogram (XRD) of the composite showed the main reflections of both Pn and EPSs ($2\theta = 6.0$, 20.1 and 26.2, 30.4, and 40.8). Experiments were carried out as a function of contact time, pH, and adsorbent dose. Under optimized conditions, the maximum percentage removal was found to be 99.8% for the complex Remazol effluent. The Freundlich isotherm model and pseudo first-order rate expression showed satisfactory fit to the equilibrium biosorption data of Pn/EPS composite. Fourier transform infrared spectroscopy, XRD, and desorption studies confirmed the involvement of aromatic, amino, hydroxyl, and carboxylic groups in dye adsorption. The results indicate that composite is suitable as an adsorbent material for the enhanced removal of dyes from complex Remazol effluent.

1. Introduction

Reactive dyes are commonly used in textile industries to dye cellulose fibers. These dyes are characterized by nitrogen to nitrogen double bonds (N=N azo bonds), and the color of the dyes is due to the azo bond and associated chromophores. The chromophore and functional group bind the dye stuff to the cellulose fiber. The reaction occurs by the formation of covalent bond, which is much more resistant to unusual conditions of use than the physicochemical bond between other classes of dyes and cellulose fiber. The reactive systems of these dyes react with ionized hydroxyl groups on the cellulose fiber. However, hydroxyl ions present in the dye bath can compete with the cellulose substrate, resulting in a percentage of hydrolyzed dyes which can no longer react with the cellulose fiber. Thus, 10–50% of the initial dye load will be present in the dye bath, giving rise to a highly colored effluent (Al-Degs, El-Barghouthi, El-Sheikh, & Walter, 2008; Vijayaraghavan, Won, & Yun, 2009). Moreover, some of the reactive dyes are toxic and pose a serious threat to aquatic biota and human beings. Therefore, there is a considerable need to treat reactive dye effluents before their discharge into receiving waters (Robinson, Chandran, & Nigam, 2002).

Numerous studies proposed a variety of adsorbent materials for the removal of reactive dyes from effluents (Elkady, Ibrahim, & El-Latif, 2011; Gu, Song, Li, & Sui, 2011; Vijayaraghavan et al., 2009; Xie, Zhao, & He, 2011). Among these, extracellular polymeric substances (EPSs), a biopolymer excreted by the microorganisms, have been recently investigated as adsorbent for the removal of organic and inorganic pollutants from aqueous solution (Jia et al., 2011; Ozturk, Aslim, & Suludere, 2010; Zhang et al., 2009). The presence of multiple functional groups such as carboxyl, phosphoric, sulfhydryl, phenolic, and hydroxyl groups have increased the application of EPS in biosorption process (Sheng, Yu, & Li, 2010). Proteins, lipids, carbohydrates, and nucleic acids in EPS all have the ability to complex with the organic and inorganic pollutants (Zhang, Wang, & Pan, 2006). Zhang et al. (2009) reported that the high-molecular weight of EPS with more binding sites and van der Waals forces together with its specific construct lead to excellent adsorption of Basic Blue 54. EPS have higher binding capacity for toluidine blue adsorption than fly ash because it has plenty of functional groups (Sheng, Zhang, & Yu, 2008). Yin, Hu, and Xiong (2011) reported that

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doi:10.1016/j.carbpol.2012.01.045

the EPS of *Aspergillus fumigatus* has effectively adsorbed Cu(II) and Cd(II) ions from aqueous solution. However, high solubility nature of the EPS has reduced the application of EPS in industrial scale (Sheng et al., 2008). Hence, a new approach is highly desirable to explore the EPS for adsorption process.

Polyaniline (Pn) is a conducting, semi-flexible rod polymer. The unique electrical and electrochemical properties, ease to synthesis, environmental stability, and simple doping/dedoping chemistry have increased the application of polymers in different scientific fields (Clark & Maher, 2009; Huang, Ball, & Kaner, 1998). Recently, Pn-based composites are used for the removal of organic and inorganic pollutants from aqueous solution. Alkyl-substituted polyaniline/chitosan (Pn/Ch) composite had effectively adsorbed Cr (VI) from aqueous solution (Yavuz, Dincturk-Atalay, Uygun, Gode, & Aslan, 2011). Polyaniline/iron oxide composite showed considerable potential for the removal of anionic dye Amido Black 10B from aqueous solution (Ahmad & Kumar, 2010). Hence, it is noteworthy to make the composites of the two polymers EPS and Pn. However, to our knowledge polyaniline/extracellular polymeric substance (Pn/EPS) has never been synthesized and used as an adsorbent for dye removal. Hence, the objectives of the present study were to (i) synthesize and characterize Pn/EPS composite, (ii) assess the potential of the composite for the treatment of reactive dye effluents, (iii) evaluate the experimental variables affecting optimal adsorption of dyes, and (iv) explore adsorption isotherms and kinetic models to identify the possible mechanism of the adsorption process.

2. Materials and methods

2.1. Materials

Aniline was procured from Sigma–Aldrich (St. Louis, MO) and it was distilled before use. Ammonium peroxydisulfate (initiator), Reactive Blue, Reactive Orange, Reactive Violet, Reactive Black, and all the auxiliary chemicals were also purchased from Sigma–Aldrich.

2.2. EPS preparation

The EPS was prepared according to Celik, Aslim, and Beyatli (2008). In brief, *Bacillus* sp. was cultured in 3 L of Luria Bertani broth for 2 days at 37 °C. After incubation, the cells were separated by centrifugation at 10,000 rpm for 20 min. The resulting supernatants were precipitated overnight at 4 °C with six volumes of 95% ethanol. Precipitated EPS were recovered by centrifugation (12,000 rpm for 20 min at 4 °C) and vacuum dried at −80 °C.

2.3. Synthesis of Pn/EPS composites

One gram of EPS was dissolved in 30 mL of water and the solution was stirred for 5 min. To this, about 0.01 M of aniline monomer in 1 M HCl was added, and the mixture was stirred thoroughly using a magnetic stirrer to form a homogenous solution. Ammonium peroxydisulfate in 1 M HCl was added drop wise to the above solution with constant stirring at ice. The molar ratio of oxidant to monomer was 1:2. After complete addition of oxidant, the reaction mixture was stirred for 5 h and then kept in a refrigerator overnight. After completion of the polymerization, the resulting greenish-black product was collected by centrifuging and washing with deionized water and methanol until the polymerization solution became colorless. The final precipitate was freeze-dried under vacuum at −80 °C for 24 h and used for adsorption studies. Fig. 1 shows the general polymerization mechanism of Pn/EPS composite.

2.4. Characterization of Pn/EPS composite

Morphological features and surface characteristics of Pn/EPS composite were obtained from scanning electron microscopy (SEM) using a JEOL JSM-6400 microscope (Tokyo, Japan). The Fourier transform infrared spectroscopy (FTIR) spectra of the Pn/EPS composite before and after adsorption of dyes were obtained on a Perkin-Elmer FTIR spectrophotometer (CA, USA) in the diffuse reflectance mode at a resolution of 4 cm^{-1} in KBr pellets. X-ray diffractograms (XRDs) were obtained using a Cu Kα incident beam (λ = 0.1546 nm), monochromated by a nickel filtering wave at a tube voltage of 40 kV and tube current of 30 mA. Scanning was done in the region of 2θ from 3° to 80° at 0.04°/min with a time constant of 2 s.

2.5. Reactive dye effluent preparation

Synthetic dyeing effluent was prepared according to cotton dyeing procedure used at an integrated textile manufacturing plant (Alaton, Balcioglu, & Bahnemann, 2002). The composition for the effluents was considered according to the reactive dye stuff content and colors applied to the cotton fabrics in the dyeing stage. The chemical components present in the dyeing effluent comprises of Remazol Brilliant Blue R (RBBR) (0.5 mM), Remazol Black (RB) (0.5 mM), Remazol Violet (RV) (0.5 mM), Remazol Orange (RO) (0.5 mM), sodium chloride (710 mM), sodium carbonate (122 mM), sodium hydroxide (13 mM), and acetic acid (13 mM). The selected reactive dyestuff had vinylsulfone anchor groups. In the presence of alkali, the anchor vinylsulfone groups react with cellulosate anions through the nucleophilic addition. Thus to ensure that all the chemicals in the dye stuffs were 100% hydrolyzed; the mixture was boiled

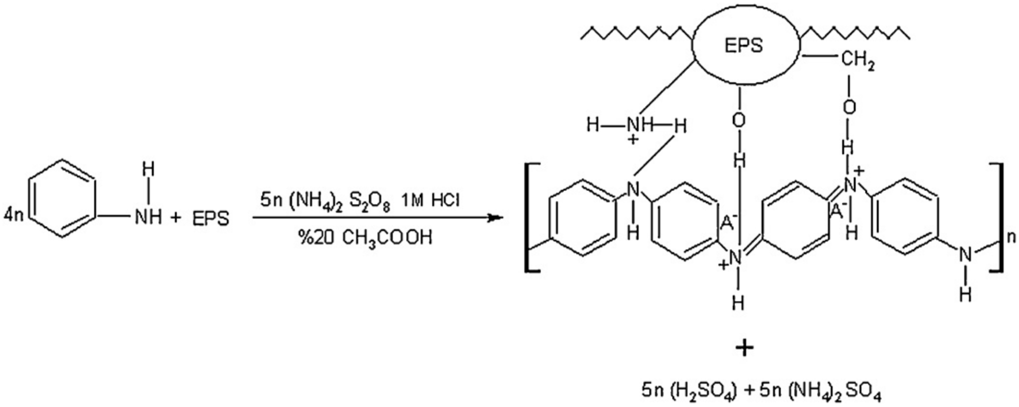

Fig. 1. Polymerization mechanism of Pn/EPS composite.

with all the auxiliary chemicals for 3 h, and 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.

2.6. Batch sorption study for dye removal

Batch adsorption experiments were carried out typically by adding 0.3 g Pn/EPS composite with 100 mL of dye effluent. If necessary, the pH of the solution was initially adjusted and controlled using 0.1 M NaOH or HCl. The flasks were stirred at a constant speed of 150 rpm at 25 ± 2 °C in a rotary incubated shaker. After the attainment of equilibrium, the supernatant was separated by centrifugation at 9000 rpm for 10 min, and the total dye concentration was analyzed using a UV–vis spectrophotometer (UV-1800 Shimadzu, Japan) at the wavelength maxima of 575 nm, after appropriate dilution.

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

$$\text{Removal}\,(\%) = \frac{(\text{Abs}_i - \text{Abs}_f)_{\text{at } 575\,\text{nm}}}{(\text{Abs}_i)_{\text{at } 575\,\text{nm}}} \times 100 \qquad (1)$$

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

$$Q = \frac{V(\text{Abs}_i - \text{Abs}_f)}{M} \qquad (2)$$

where V is the effluent volume (L) and M is the mass of the Pn/EPS 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:

$$Q = K_F(\text{Abs}_f)^{1/n} \qquad (3)$$

where K_F is the Freundlich isotherm constant (L/g) and n is 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:

$$Q_t = Q_e(1 - \exp(-k_1 t)) \qquad (4)$$

where Q_e is the extent of decolorization at equilibrium (L/g), Q_t is the extent of decolorization at time t (L/g), and k_1 is 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. Duplicate experiments were carried out for all the operating variables studied and only the average values were considered. Blank experiments were carried out with dye effluent solution (no adsorbent) concurrently to ensure that the sorption of dye on the walls of flasks was negligible.

2.7. Desorption study

The Pn/EPS composite, which were exposed to the dye effluent [RBBR (0.25 mM), RB (0.25 mM), RV (0.25 mM), RO (0.25 mM), sodium chloride (355 mM), sodium carbonate (61 mM), sodium hydroxide (6.5 mM), and acetic acid (6.5 mM)] at 25 ± 2 °C, was separated from the solution by centrifugation (6000 rpm for 10 min) and washed several times with nanopure purified water (conductivity = 18 μΩ/m, TOC < 3 ppb, Barnstead, Waltham, MA, USA). Later, Pn/EPS composite was dried completely and used for desorption experiments. The dye-loaded composites (0.3 g) were then brought into contact with 0.01 M NaOH. The mixture was agitated on a rotary shaker (150 rpm) at 25 °C for 1 h. After desorption, the supernatant was centrifuged, with the remaining procedure being the same as for the sorption experiments.

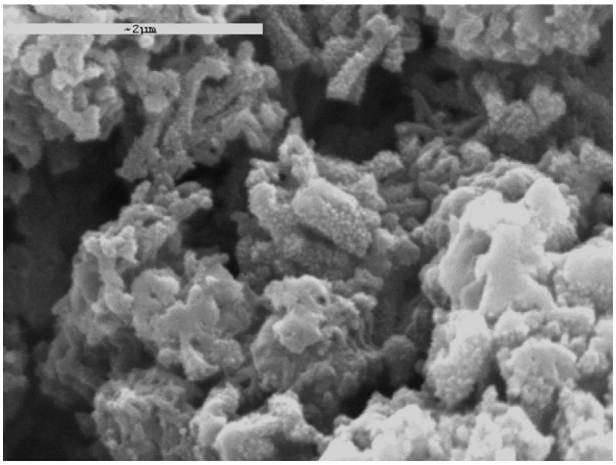

Fig. 2. SEM micrograph of Pn/EPS composite. The surface of the composite was rough and granular appearance.

3. Results and discussion

3.1. Characterization of Pn/EPS composite

Typical SEM micrograph of Pn/EPS composite is presented in Fig. 2, which shows that the particles are either circular or oval in shape. The size of the particles varied from 90 to 120 nm and mostly present in aggregates. The surface of the composite was rough with granular appearance, providing a good possibility for dyes to be trapped and adsorbed. FTIR analysis permits spectrophotometric observation of the Pn/EPS composite surface in the range of 400–4000 cm^{-1} and possibly provides the information regarding the functional groups present in the adsorbent. Thus, to investigate the functional groups involved in the adsorption of dyes in Pn/EPS composite, FT-IR analysis was carried out, and the results are presented in Fig. 3. The broad peak (3200–3231 cm^{-1}) was assigned to the stretching of the O—H group because of inter- and intra-molecular hydrogen bonding of polymeric compounds (Naumann, Helm, & Labischinski, 1991). Peaks observed at 2933, 2571, and 1560 cm^{-1} are attributed to N—H bending, while the band at 1487 cm^{-1} is attributed to the C—C aromatic ring stretching of the benzenoid unit (Karthikeyan, Kumar, & Elango, 2011). Furthermore, the spectrum showed the presence of prominent carboxyl (1297, 1242, and 1138 cm^{-1}), aromatic (878 and 796 cm^{-1}), and alkane (743, 686, 593, and 504 cm^{-1}) groups, which mostly come from the sugars and amino acids present in the bacterial EPS (Xu et al., 2011). X-ray powder diffraction is a rapid analytical technique to analyze the nature of materials. The XRD profile of the Pn/EPS composite is presented in Fig. 4. The composite exhibited characteristics peaks for Pn (2θ = 20.1 and 26.2) and EPS (2θ = 6.0, 30.4, and 40.8), and the intensity of the peaks indicate that the composite was partly crystalline and partly amorphous (Mishra, Kavita, & Jha, 2011; Pouget, Jozefowicz, Epstein, Tang, & Macdiarmid, 1991).

3.2. Effect of adsorbent dosage

The effect of Pn/EPS composite concentration on the decolorization of the Remazol effluent at a contact time of 2 h was studied by varying the adsorbent dosage from 0.2 to 0.5 g L^{-1} in effluent solution containing RBBR (0.25 mM), RB (0.25 mM), RV (0.25 mM), RO (0.25 mM), sodium chloride (355 mM), sodium carbonate (61 mM), sodium hydroxide (6.5 mM), and acetic acid

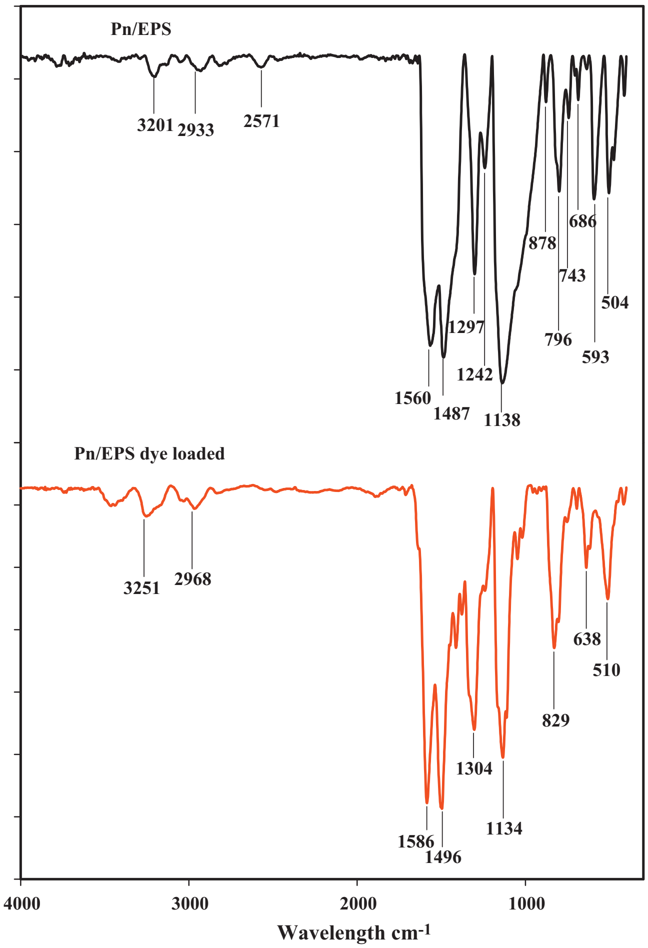

Fig. 3. FTIR spectra of Pn/EPS composite before and after treatment with complex Remazol effluent.

(6.5 mM). Dye decolorization efficiency increased with increasing Pn/EPS composite content (Fig. 5). Increased adsorbent concentration implies a greater surface area of Pn/EPS composite and, consequently, a greater number of binding sites. However, the adsorbent doses 0.4 and 0.5 g L^{-1} had not significantly increased the decolorization efficiency and adsorption equilibrium rate. The limited removal rate at high adsorbent dosage could be due to the concentration gradient between the Pn/EPS composite and dye effluent. The optimum adsorbent dosage was found to be 0.3 g L^{-1} and used for the successive experiments. Similar results have been reported for the adsorption of cationic dyes by kaolin (Nandi, Goswami, & Purkait, 2009).

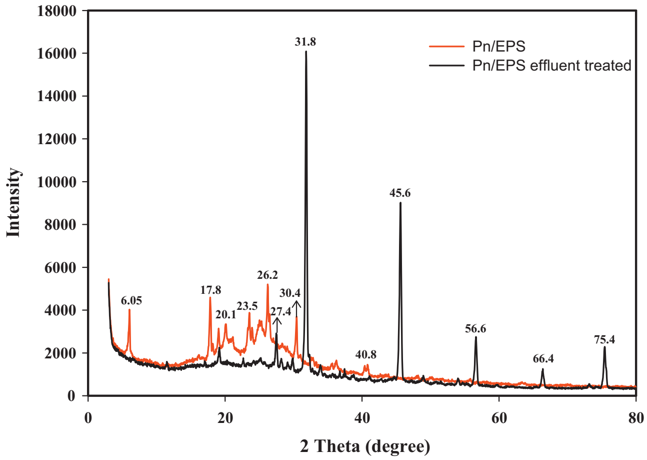

Fig. 4. XRD pattern of the Pn/EPS composite before and after treatment with complex Remazol effluent.

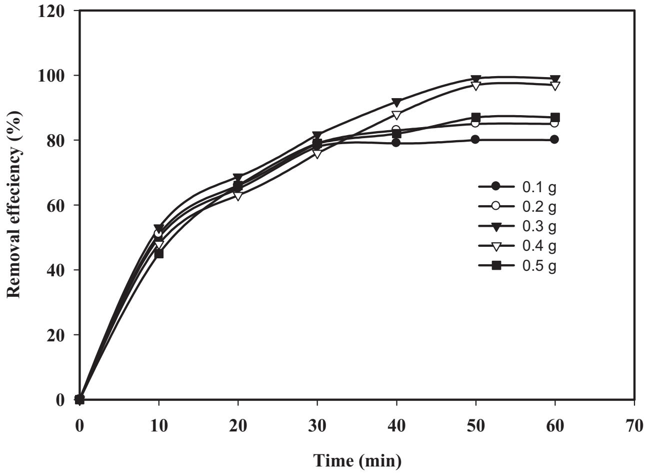

Fig. 5. Effect of adsorbent dosage on removal of dyes from complex Remazol effluent.

3.3. *Effect of pH*

The pH of the aqueous solution is recognized as one of the most important parameter which affects the adsorption process. The solution pH influences the surface charge of adsorbent material, the degree of ionization processes of the dye molecules, and also the effluent chemistry. In addition, it is directly related to competition ability of hydrogen ions with adsorbate ions to active sites on the adsorbent surface. Thus, the effect of pH on the decolorization of dye bath effluent was evaluated at different pH conditions ranging from 2 to 8, and the results are depicted in Fig. 6. It is evident from the graph that the decolorization efficiency of Pn/EPS composite was strongly pH dependent. The decolorization efficiency increased notably with increasing the pH from 2 to 3 and reached a maximum at pH 3. A further increase in the pH (4–8) had significantly decreased the decolorization potential of Pn/EPS composite. Higher adsorption rate at lower pH (2 and 3) was due to the protonation of functional groups such as amino groups, which increases the electrostatic interaction between the positively charged adsorbent surface and the negatively charged dye molecules. However, limited adsorption at higher pH (4–8) was due to the presence of

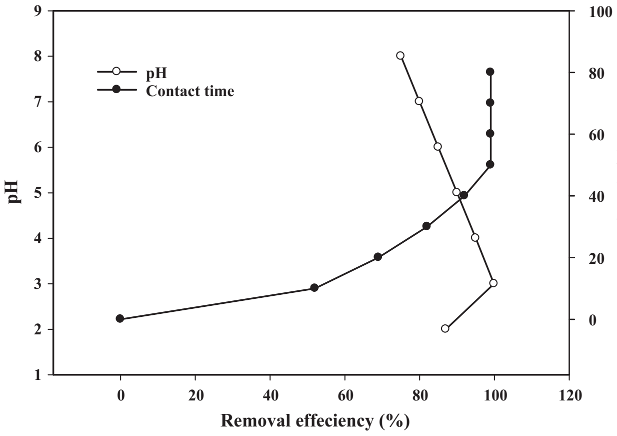

Fig. 6. Influence of pH and contact time on removal of dyes from complex Remazol effluent.

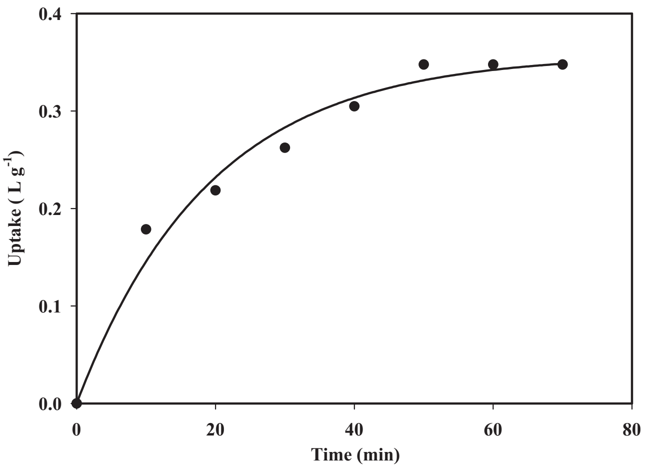

Fig. 7. Pseudo first-order kinetics plots for Remazol dyes on Pn/EPS composite.

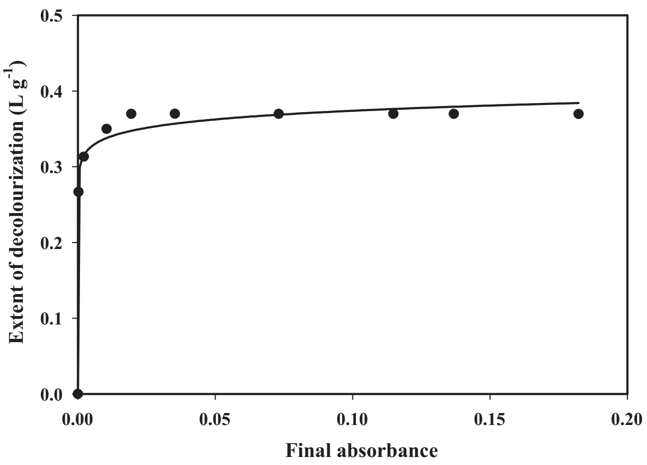

Fig. 8. Freundlich isotherm for the sorption of Remazol dyes on Pn/EPS composite.

excess OH^- ions and deprotonation of functional groups, which reduces the interactions between the adsorbent and adsorbate. The limited adsorption at pH 4–8 could be due to the formation of hydrogen bond, by Van der Waals forces and ion exchange with other groups present in the Pn/EPS composite. Similar observation has been reported for sorption of Malachite green onto degreased coffee bean (Baek, Ijagbemi, Se-Jin, & Kim, 2010).

3.4. Effect of contact time

Contact time is an important factor which must be carefully optimized during effluent treatment. The influence of contact time on the uptake of dyes from the effluent was investigated, and the results are presented in Fig. 6. The rapid decolorization rate was observed during the first 10 min, which gradually decreased with lapse of time until equilibrium (50 min). Further increase in contact time did not enhance the decolorization rate. The initial rapid adsorption was due to the presence of large number of binding sites onto the exterior surface of the Pn/EPS composite, and gradual occupancy of these sites reduced the adsorption rate and the reaction becomes less efficient. At this point, the amount of dye being adsorbed onto the composite was in a state of dynamic equilibrium with the amount of dye desorbed from the composite. The time required to attain this state of equilibrium was termed as equilibrium time, and the amount of dye adsorbed at the equilibrium time reflected the maximum adsorption capacity of the adsorbent under these particular conditions. Similar conclusions have been proposed by Chowdhury, Mishra, Saha, and Kushwaha (2011) for adsorption of Malachite Green by chemically modified rice husk.

3.5. Adsorption models

In order to investigate the mechanism of adsorption process and its potential rate-controlling steps such as mass transfer and chemical reaction, kinetic models were used for the experimental data. The kinetics of Remazol dye effluent onto Pn/EPS was analyzed using the pseudo first-order kinetic equation. The curve as predicted by pseudo first-order plot is shown in Fig. 7. Values of Q_e, k_1, and R^2 were calculated as 0.3577 L/g, 0.0522 min^{-1}, and 0.9794, respectively. The correlation coefficient was closer to unity, and the difference between the experimental Q_e and calculated Q_e were very less, indicating the better fit of pseudo first-order kinetic model.

Equilibrium data, commonly known as the adsorption isotherm, are the fundamental requirements for the design of adsorption systems. The isotherm expresses the relation between the mass of the dye adsorbed at a particular temperature, the pH, particle size, and liquid phase on the dye concentration. The shape and parameters of the isotherm provide the important information about the sorption mechanisms, the surface properties of adsorbate, and affinity of the dye molecules for adsorption (Annadurai, Ling, & Lee, 2008). Fig. 8 shows the adsorption isotherm, i.e., the extent of decolorization (Q) against the final absorbance (Abs_f), at pH 3. To obtain the isotherm points, the Remazol effluent was diluted to different strengths. The experimental isotherm followed the traditional trend, which was an increased extent of decolorization with increasing effluent strength, reaching saturation at the higher effluent strength.

In order to investigate the biosorption isotherms, a modified form of the Freundlich model was used. The Freundlich equation is an empirical equation which suggests that adsorption energy exponentially decreases on completion of the sorptional centers of an adsorbent. 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. Very high correlation coefficient ($R^2 > 0.988$) was obtained, indicating that the isotherm obtained for the complex Remazol effluent followed the Freundlich model. Fig. 8 shows the isotherm curve predicted by the Freundlich model, which was in good accord with the experimental data. The K_F and n_F values were 0.4147 L/g and 0.0449, respectively.

3.6. FTIR and XRD studies

The FTIR spectra of dye-loaded Pn/EPS composite are shown in Fig. 3. The differences in the spectra of the loaded Pn/EPS composite are based on the changes in the nature of the surface like participation of specific functional groups in adsorption interaction and the ensuing chemical changes thereon. The peak observed at 3251 cm^{-1} and disappearance of peak at 3200 cm^{-1} indicates the participation of hydroxyl groups in adsorption reaction. The major shift at peaks 2968, and 1586 cm^{-1}, and disappearance of peak at 2571 cm^{-1} indicates the involvement of amino groups in adsorption reaction. Similarly, the disappearance of peaks at 1242, 796, 743, and 593 cm^{-1} and major shift at 638 cm^{-1} confirmed the involvement of carboxylic, alkane, and aromatic groups in dye removal. The results are consistent with previous studies reporting the involvement of different functional groups for the adsorption of dyes (Zhang et al., 2009). The XRD pattern of the dyes laden Pn/EPS composite is presented in Fig. 4. The disappearance of several hallow peaks ($2\theta = 6.05$, 17.8, 20.1, 23.5, 26.2, 30.4, and 40.8) and presence of new well-defined peaks ($2\theta = 27.4$, 31.8, 45.6, 56.6, 66.4 and 75.4) indicate that the amorphous nature of the polymer have changed into crystalline nature. The results have further confirmed the chemisorption of dye molecules on the adsorbent. Similar conclusions have been proposed by Namasivayam and Kavitha (2006) for dyes and phenol loaded coir pith carbon.

3.7. Mechanism of dye adsorption

The major challenge in adsorption study is the elucidation of adsorption mechanism. However, it depends on the chemical composition of the adsorbent, the nature of the adsorbate, the solution environment, and type of interactions between the adsorbent and adsorbate (Salem, 2011). In the present study, the adsorption of reactive dye molecules on the polymeric material was discussed in the following steps:

- In aqueous solution, the dye molecule dissolves and the sulfonate group of the dye is dissociated and converted into dye anions:

  $$\mathrm{DSO_3Na} \xrightarrow{\text{water}} \mathrm{DSO_3}^- + \mathrm{Na}^+ \qquad (5)$$

  Simultaneously, in the presence of H^+, the amino groups present in the cross-linked polymer were protonated as (NH_3^+).
- Migration of these reactive dye anions from solution to the surface of the Pn/EPS matrix.
- Dye anions are electrostatically attracted by the nitrogen moiety present in the constituent polymer:

  $$\mathrm{RNH_3}^+ + \text{Dye-}\mathrm{SO_3}^- \rightarrow \text{R-}\mathrm{NH_3}^+\text{—}\mathrm{O_3}^-\text{S-Dye} \qquad (6)$$

- Adsorption of the dye molecules on the free polymeric surface occurs by chemisorption.

The results are consistent with the previous study by Karthikeyan et al. (2011) for the removal of fluoride ion from water using eco-friendly conducting biopolymer composites.

3.8. Cycles of sorption and desorption

To investigate the possibility of reuse of Pn/EPS composite as well as to further understand the mechanism of adsorption, batch sequential sorption–desorption experiments were conducted for five cycles. The sorption experimental data revealed the fact that strong acidic condition (pH 3) was necessary for binding the reactive dye molecules onto the polymeric substances. Thus, it would be logical that the adsorbed dyes could be recovered under reversely condition, i.e., strongly basic. Therefore, 0.01 M NaOH was used as eluant for unbinding the molecules. The performance of the eluant was satisfactory and the elution efficiency was greater than 94%. Under the more basic condition, the negatively charged sites increase on the polymeric surface, and it acts as a driving force for the elution of dye anions by electrostatic repulsion and is given by the following equation:

$$\text{R-}\mathrm{NH_3}^+\text{—}\mathrm{O_3}^-\text{S-Dye} + \mathrm{OH}^- \rightarrow \mathrm{RNH_2} + \text{Dye-}\mathrm{SO_3}^- + \mathrm{H_2O} \qquad (7)$$

In the series of sorption and desorption cycle, the loss in the sorption capacity was less than 5%. Hence, Pn/EPS composite can be easily regenerated and reused for the practical purposes. Desorption of the dye molecules under alkaline pH has further confirmed the ionic interactions between the dye molecules and Pn/EPS composite.

4. Conclusion

In this study, potential of the Pn/EPS composite for the treatment of complex Remazol effluent was evaluated, and the observations are summarized below:

- Characterization of Pn/EPS composite revealed that the polymer contains the characteristic features of both Pn and EPS. The XRD indicates that the composite was partly crystalline and amorphous.
- The Remazol effluent comprised of four reactive dyes, with excess auxiliary chemicals, was completely decolorized by Pn/EPS composite within 60 min (solution). The adsorption kinetics obeys the pseudo first-order model and follows the Freundlich isotherm model.
- The interaction between the dyes and the adsorbent was confirmed by FTIR spectroscopy. Amino, aromatic, hydroxyl, and carboxylic groups were the main functional groups involved in the ionic interaction between dye molecules and polymers. Desorption experiments have further confirmed the ionic interaction between the adsorbent and adsorbate.
- The availability and simple methods for synthesis, comparatively low cost, and relatively high dye removal capacity represent an attractive option for the treatment of Remazol dye bearing industrial effluents.

Acknowledgment

The authors (S. Kamala-Kannan and A.K. Ramasamy) are grateful to Prof. K. Muthuchelian, Vice Chancellor, Periyar University, Tamil Nadu, India, for his encouragement towards the collaborative research between Periyar University and Chonbuk National University.

References

Ahmad, R., & Kumar, R. (2010). Conducting polyaniline/iron oxide composite: A novel adsorbent for the removal of Amido Black 10B. *Journal of Chemical and Engineering Data*, *55*, 3489–3493.

Alaton, I. A., Balcioglu, I. A., & Bahnemann, D. W. (2002). Advance oxidation of a reactive dyebath effluent: Comparison of O_3, H_2O_2/UV-C and TiO_2/UV-A processes. *Water Research*, *36*, 1143–1154.

Al-Degs, Y. S., El-Barghouthi, M. I., El-Sheikh, A. H., & Walter, G. M. (2008). Effect of solution pH, ionic strength, and temperature on adsorption behavior of reactive dyes on activated carbon. *Dyes and Pigments*, *77*, 16–23.

Annadurai, G., Ling, L. Y., & Lee, J. F. (2008). Adsorption of reactive dye from an aqueous solution by chitosan: Isotherm, kinetic and thermodynamic analysis. *Journal of Hazardous Materials*, *152*, 337–346.

Baek, M. H., Ijagbemi, C. O., Se-Jin, O., & Kim, D. S. (2010). Removal of Malachite Green from aqueous solution using degreased coffee bean. *Journal of Hazardous Materials*, *176*, 820–828.

Celik, G. Y., Aslim, B., & Beyatli, Y. (2008). Characterization and production of the exopolysaccharide (EPS) from *Pseudomonas aeruginosa* G1 and *Pseudomonas putida* G12 strains. *Carbohydrate Polymers*, *73*, 178–182.

Chowdhury, S., Mishra, R., Saha, P., & Kushwaha, P. (2011). Adsorption thermodynamics, kinetics and isosteric heat of adsorption of malachite green onto chemically modified rice husk. *Desalination*, *265*, 159–168.

Clark, N. B., & Maher, L. J. (2009). Non-contact, radio frequency detection of ammonia with a printed polyaniline. *Reactive and Functional Polymers*, *69*, 594–600.

Elkady, M. F., Ibrahim, A. M., & El-Latif, M. M. A. (2011). Assessment of the adsorption kinetics, equilibrium and thermodynamic for the potential removal of reactive red dye using eggshell biocomposite beads. *Desalination*, *278*, 412–423.

Freundlich, H. (1907). Ueber die Adsorption in Loesungen. *Zeitschrift fr Physikalische Chemie*, *57*, 385–470.

Gu, Y., Song, P., Li, T., & Sui, W. (2011). Synthesis and characterization of carboxymethyl-polyaminate chitosan and its adsorption behavior toward a reactive dye. *Carbohydrate Research*, *346*, 769–774.

Huang, S. C., Ball, I. J., & Kaner, R. B. (1998). Polyaniline membrane for pervaporation of carboxylic acids and water. *Macromolecules*, *31*, 5456–5464.

Jia, C., Li, P., Li, X., Tai, P., Liu, W., & Gong, Z. (2011). Degradation of pyrene in soils by extracellular polymeric substances (EPS) extracted from liquid cultures. *Process Biochemistry*, *46*, 1627–1631.

Karthikeyan, M., Kumar, K. K. S., & Elango, K. P. (2011). Batch sorption studies on the removal of fluoride ions from water using eco-friendly conducting polymer/biopolymer composites. *Desalination*, *267*, 49–56.

Mishra, A., Kavita, K., & Jha, B. (2011). Characterization of extracellular polymeric substances produced by micro-algae *Dunaliella salina*. *Carbohydrate Polymers*, *83*, 852–857.

Namasivayam, C., & Kavitha, D. (2006). IR, XRD and SEM studies on the mechanism of adsorption of dyes and phenols by coir pith carbon from aqueous phase. *Microchemical Journal*, *82*, 43–48.

Nandi, B. K., Goswami, A., & Purkait, M. K. (2009). Removal of cationic dyes from aqueous solutions by kaolin: Kinetic and equilibrium studies. *Applied Clay Science*, *42*, 583–590.

Naumann, D., Helm, D., & Labischinski, H. (1991). Microbiological characterization by FT-IR spectroscopy. *Nature*, *351*, 81–82.

Ozturk, S., Aslim, B., & Suludere, Z. (2010). Cadmium(II) sequestration characteristics by two isolates of *Synechocystis* sp in terms of exopolysaccharide (EPS) production and monomer composition. *Bioresource Technology*, *101*, 9742–9748.

Pouget, J. P., Jozefowicz, M. E., Epstein, A. J., Tang, X., & Macdiarmid, A. G. (1991). X-ray structure of polyaniline. *Macromolecules*, *24*, 779–789.

Robinson, T., Chandran, B., & Nigam, P. (2002). Removal of dyes from a synthetic textile dye effluent by biosorption on apple pomace and wheat straw. *Water Research*, *36*, 2824–2830.

Salem, M. A. (2011). The role of polyaniline salts in the removal of direct blue 78 from aqueous solution: A kinetic study. *Reactive and Functional Polymers*, *70*, 707–714.

Sheng, G. P., Zhang, M. L., & Yu, H. Q. (2008). Characterization of adsorption properties of extracellular polymeric substances (EPS) extracted from sludge. *Colloids and Surfaces B: Biointerfaces*, *62*, 83–90.

Sheng, G. P., Yu, H. Q., & Li, X. Y. (2010). Extracellular polymeric substances (EPS) of microbial aggregates in biological wastewater treatment systems: A review. *Biotechnology Advances*, *28*, 882–894.

Vijayaraghavan, K., Won, S. W., & Yun, Y. S. (2009). Treatment of complex Remazol dye effluent using sawdust- and coal-based activated carbons. *Journal of Hazardous Materials*, *167*, 790–796.

Xie, K., Zhao, W., & He, X. (2011). Adsorption properties of nano-cellulose hybrid containing polyhedral oligomeric silsesquioxane and removal of reactive dyes from aqueous solution. *Carbohydrate Polymers*, *83*, 1516–1520.

Xu, C., Zhang, S., Chuang, C., Miller, E. J., Schwehr, K. A., & Santschi, P. H. (2011). Chemical composition and relative hydrophobicity of microbial exopolymeric substances (EPS) isolated by anion exchange chromatography and their actinide-binding affinities. *Marine Chemistry*, *126*, 27–36.

Yavuz, A. G., Dincturk-Atalay, E., Uygun, A., Gode, F., & Aslan, E. (2011). A comparison study of adsorption of Cr(VI) from aqueous solutions onto alkyl-substituted polyaniline/chitosan composites. *Desalination*, *279*, 325–331.

Yin, Y., Hu, Y., & Xiong, F. (2011). Sorption of Cu(II) and Cd(II) by extracellular polymeric substances (EPS) from *Aspergillus fumigatus*. *International Biodeterioration and Biodegradation*, *65*, 1012–1018.

Zhang, D., Wang, J., & Pan, X. (2006). Cadmium sorption by EPSs produced by anaerobic sludge under sulfate-reducing conditions. *Journal of Hazardous Materials*, *138*, 589–593.

Zhang, Z., Xia, S., Wang, X., Yang, A., Xu, B., Chen, L., et al. (2009). A novel biosorbent for dye removal: Extracellular polymeric substance (EPS) of *Proteus mirabilis* TJ-1. *Journal of Hazardous Materials*, *163*, 279–284.