Removal of color and COD from actual textile effluent by hybrid biosorption and ultrafiltration processes

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ABSTRACT

The present study was investigated to find the efficiency of a hybrid process of an ecofriendly dehydrated Moringa oleifera biosorbent beads (DMB) and ultrafiltration (UF) membrane to remove organic pollutants from actual textile effluents. Experiments were conducted with a packed bed column (PBC) for the removal of dyes using various parameters such as flow rate, material mass and size of the biosorbent. The optimized biosorption process was then combined with a dead-end UF process for the removal of chemical oxygen demand/biochemical oxygen demand (COD/BOD) and turbidity. Three strategies were adopted by varying the sequences of UF and PBC. PBC followed by the UF process appears to be more effective for the removal of color (>99%), COD (90–93%) and turbidity (>95%), when compared to UF followed by the PBC process and the UF membrane alone. The results suggested that the treated effluent could be reused in industries for various purposes such as floor cleaning, gardening, etc.

Key words | biosorption, Moringa oleifera, textile effluent, ultrafiltration

INTRODUCTION

Textile industries, the backbone of the export market in India, are a water intensive industry concentrated in small clusters in different areas. Being a labor intensive process, the population also lives near the industrial conglomeration. The spent streams, with a variety of pollutants, including dyes, contaminate the nearby water sources. Most of the industries are small scale in nature, and cannot afford to treat the effluents individually. Being a critical industry for export earning, the government of India has implemented common effluent treatment plants (CETP), whereby all the local industries send the effluent to a common platform and the problem is addressed through the establishment of CETP. However, to ensure both safety and acceptability to the local community, there is a need to develop simple systems that are easy to operate and where the spent material does not burden the environment.

Various technologies have been studied and demonstrated for the treatment of textile wastewater, such as biological treatment, advanced oxidation methods, membrane filtration and adsorption. However, adsorption and nanofiltration techniques appear to be an effective method for the removal of dyes and pigments from industrial effluents. An extensive variety of adsorbents, such as activated carbon (Goel et al. 2003), pith carbon (Namasivayam & Kavitha 2002), bagasse fly ash (Gupta et al. 2000), rice husk (Chowdhry et al. 2009), soy bean hull (Marshall et al. 1999), activated clay (Hsu et al. 1997), sepiolite (Tabak et al. 2009) as well as chitosan beads (Chiou et al. 2005), have been studied for the removal of dyes. Most of these adsorbents had limited success owing to their ability to remove color and not all the other organic contaminants. Therefore it is necessary to investigate both adsorption and membrane techniques, separately or in combination. Further, toward a sustainable solution for purifying the contaminated source, it is desirable to identify natural materials that are biodegradable, inexpensive and easily available.

Currently, natural sorbents are economically and environmentally more acceptable for wastewater treatment. Among
these is *Moringa oleifera* (MO) seed, a biosorbent, which contains cellulose, lignin and crude fiber, and its matrix network, which contains both carboxylic and amino functional groups. These functional groups may be dissociated and consequently play a part in the biosorption process (Araujo et al. 2010; Vieira et al. 2010). Earlier studies have confirmed that MO has polypeptides of a molecular weight ranging from 6 to 16 kDa, and its isoelectric pH value of 10 shows high zeta potential, cationic and anionic properties, which can be used for dye decolorization in industrial effluent treatments (Agrawal et al. 2011; Kwaambwa & Rennie 2011). Considering the above properties, MO can act as a good biosorbent when it is encapsulated and these results were recently published by our research group (Radhakrishnan et al. 2014).

Normally, nanofiltration is a preferred technique for the treatment effluents because of the pollutants’ higher sizes. However, this technique does not lead to absolute separation as a fraction of feed solution commonly designated as a reject stream, which is rich in contaminant species, has to be discarded into the environment. Ultrafiltration (UF) may not be as efficient as nanofiltration, but its low pressure operation, high recovery of the feed, 100% backwash facility, and its ability to remove most of the organic and bio-species make it a candidate to compliment adsorption techniques to achieve the objectives.

In this study, MO in bead form was used as a biosorbent for the removal of color from the textile effluent using a packed bed column (PBC), and to investigate the efficiency using a hybrid technique with a UF membrane for the purification of effluents such as chemical oxygen demand (COD), biochemical oxygen demand (BOD) and turbidity. Further, using an UF process is more advantageous for the removal of total suspended solids (TSS) and heavy metals. To address the real time effluent, it is necessary to use a PBC system combined with an UF unit.

**EXPERIMENTAL**

**Biosorbent DMB preparation and characterization**

Dried MO seeds were purchased from Genius seeds, Coimbatore, India. The seeds were de-shelled and the fresh white kernels were washed with de-ionized water and air dried. Then, a pulverization process was carried out to convert it into a fine powder, which was encapsulated by mixing with sodium alginate in the ratio 1:5 and then cross-linked by a phase inversion technique using 3% calcium chloride solution. This was done by extruding the alginate suspension drop by drop into pre-chilled CaCl₂ using a peristaltic pump, which converted them into *M. oleifera* beads instantaneously (Dominguez et al. 2005). The flow rate of the pump was adjusted to produce 250 spherical beads per hour. After encapsulation, the beads in the salt solution were allowed to dry at room temperature and harden. Eventually, the DMB were washed with 99% ethanol for sterilization and then used for the treatment process. The physical appearances and properties of the DMB have been characterized, such as porosity, bulk density and stability using standard procedure, as shown in Table 1.

**Adsorbate-textile effluent source and characterization**

The textile effluent sample was collected from the clarifier unit in an effluent treatment plant at Erode, Tamil Nadu (India). It is a complex effluent obtained from two different dyeing processes. The physico-chemical parameters of the wastewater were characterized immediately after collection in terms of pH, BOD, COD (Merckmillipore kit) and turbidity. The characterizations of raw samples were in accordance with the standard methods of the American Public Health Association as shown in Table 2.

**Biosorption in PBC studies**

The schematic diagram of the PBC is shown in Figure 1.

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**Table 1 | Characterization of dehydrated MO bead**

<table>
<thead>
<tr>
<th>S. no.</th>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Porosity (%)</td>
<td>40–45</td>
</tr>
<tr>
<td>2.</td>
<td>Bulk density (g cc⁻¹)</td>
<td>1.5</td>
</tr>
<tr>
<td>3.</td>
<td>Stability</td>
<td>Stable and rigid</td>
</tr>
<tr>
<td>4.</td>
<td>Mean diameter (mm)</td>
<td>1.75–2.25</td>
</tr>
<tr>
<td>5.</td>
<td>BET surface area (m² g⁻¹)</td>
<td>14.5</td>
</tr>
<tr>
<td>6.</td>
<td>Q max (cm³ g⁻¹)</td>
<td>0.0167</td>
</tr>
<tr>
<td>7.</td>
<td>Pore volume (cm³ g⁻¹)</td>
<td>0.05</td>
</tr>
</tbody>
</table>
The column was made of Pyrex glass with an inner diameter of 2.5 cm and a height of 35 cm. A sieve made up of stainless steel was placed at the bottom of the column. Over the sieve, a layer of glass beads was placed to prevent loss of biosorbent. The DMB was packed above the glass beads to the required bed height (BH). A peristaltic pump (Model Masterflex, Cole-Parmer Instrument Co., USA) was used to pump the feed stream (influent) through the column and to control the desired flow rate. The treated effluent samples were collected at regular time intervals from the outlet of the column, and the dye concentrations were periodically analyzed by UV-Spectrophotometer. Further, the effluent was characterized immediately after collection in terms of pH, BOD, COD and turbidity. All the biosorption experiments were carried out at room temperature (30 ± 2°C).

Parametric studies were carried out using different BHs (Z) varying from 5 to 15 cm, feed flow rates (F/R) (Qf) varying from 1 to 5 mL min⁻¹ and bead sizes varying from 1.5 to 2.5 mm of the adsorbent mass. Further, Thomas (1948), Yoon & Nelson (1984) models and Bohart & Adams (1920) model were formulated from the prediction of the breakthrough curve.

Table 2  | Characterization of textile effluent and CPCB-textile industrial discharge limit

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Initial textile effluent</th>
<th>CPCB-textile industrial discharge limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH @ 25°C</td>
<td>9.4</td>
<td>6.0–8.5</td>
</tr>
<tr>
<td>Conductivity (mS/cm)</td>
<td>6.9 ± 0.05</td>
<td>NA</td>
</tr>
<tr>
<td>Color (visual method)</td>
<td>Dark green</td>
<td>Colorless</td>
</tr>
<tr>
<td>BOD (mg L⁻¹)</td>
<td>425</td>
<td>50</td>
</tr>
<tr>
<td>COD (mg L⁻¹)</td>
<td>1,255</td>
<td>250</td>
</tr>
<tr>
<td>TDS (mg L⁻¹)</td>
<td>9,552</td>
<td>450</td>
</tr>
<tr>
<td>TSS (mg L⁻¹)</td>
<td>28</td>
<td>10–50</td>
</tr>
<tr>
<td>TOC (mg L⁻¹)</td>
<td>218</td>
<td>20</td>
</tr>
<tr>
<td>Chloride as Cl⁻ (mg L⁻¹)</td>
<td>528</td>
<td>1,000</td>
</tr>
<tr>
<td>Sulphate as SO₄ (mg L⁻¹)</td>
<td>80</td>
<td>1,000</td>
</tr>
<tr>
<td>Oil and grease (mg L⁻¹)</td>
<td>15</td>
<td>10</td>
</tr>
<tr>
<td>Turbidity (NTU)</td>
<td>15</td>
<td>5–10</td>
</tr>
<tr>
<td>Zinc (mg L⁻¹)</td>
<td>BDL</td>
<td>5</td>
</tr>
<tr>
<td>Copper (mg L⁻¹)</td>
<td>BDL</td>
<td>2</td>
</tr>
<tr>
<td>Manganese (mg L⁻¹)</td>
<td>1.08 ± 0.5</td>
<td>2</td>
</tr>
<tr>
<td>Cobalt (mg L⁻¹)</td>
<td>0.288 ± 0.05</td>
<td>0.5</td>
</tr>
<tr>
<td>Nickel (mg L⁻¹)</td>
<td>1.704 ± 0.5</td>
<td>3</td>
</tr>
<tr>
<td>Cadmium (mg L⁻¹)</td>
<td>BDL</td>
<td>2</td>
</tr>
<tr>
<td>Chromium (mg L⁻¹)</td>
<td>Trace amount</td>
<td>2</td>
</tr>
</tbody>
</table>

TDS: total dissolved solids; TOC: total organic carbon; BDL: below detection limit.
Theory-breakthrough analysis

For the determination of breakthrough curves, the column was randomly packed with DMB and there was a continuous flow of the influent into the column until the effluent concentration at the outlet stream became equivalent to the inlet stream. In a PBC, the biosorbent located at the entry point of the influent, which is known as the mass transfer zone (MTZ), comes into contact with the solution at its highest concentration level ($C_o$). As time proceeds, this MTZ saturates rapidly and the zone starts moving downwards through the column of the next zone. When the biosorption zone reaches the exit of the bed, the concentration of the biosorbent in the effluent becomes equal to the influent concentration. The biosorption performance of the column was calculated by plotting the outlet concentration $C_{out}/C_o$ as a function of time or volume throughout the curve known as the breakthrough curve (Malkoc et al. 2006). The time taken for the effluent concentration to reach a specific breakthrough concentration of interest is called the breakthrough time ($t_b$). The breakthrough time for each of the column operations was defined as the time when the effluent concentration ($C_t$) reach 50% of the initial concentration ($C_o$). The capacity of the bed at the breakthrough point is calculated from Equation (1), which is given as:

$$q_b = \frac{C_o}{m} \int_0^{V_b} \left(1 - \frac{C_t}{C_o}\right) dV$$

where $q_b$ is the bed capacity at the breakthrough point (mg g⁻¹), $C_o$ is the initial dye concentration (mg L⁻¹), $m$ is the biosorbent mass, $C_t$ is the exit dye concentration (mg L⁻¹), and $V_b$ is the volume processed at the breakthrough point. Further, the numbers of bed volumes (BV) were established before the breakthrough point was reached, to find the performance of the packed bed adsorber, which is directly related to the BV. Subsequently, the bed exhaustion rate (BER) and the empty bed resistance time (EBRT) were investigated to check the rate of exhaustion of beds. The BV is expressed as Equation (2):

$$BV = \frac{Volume \ of \ effluent \ treated \ at \ breakthrough \ point(L)}{Volume \ of \ adsorbent \ bed(L)}$$

The BER and EBRT are expressed in Equations (3) and (4):

$$BER = \frac{Mass \ of \ beds \ in \ packed \ bed \ column}{Volume \ of \ effluent \ treated \ at \ breakthrough \ point(L)}$$

$$EBRT = \frac{Fixed \ bed \ volume}{Volumetric \ flow \ rate \ of \ the \ effluent}$$

The design of the column depends on the effect of operational parameters such as the inlet feed flow rate and various BHs for the biosorption performance.

UF set-up

After the column studies, the textile effluent was treated by a dead-end UF process at constant pressure as shown in Figure 2. A filtration cell with a UV membrane made from polysulfone material was used for the purpose of research, which was originally developed by the Bhabha Atomic Research Centre (Prabhakar et al. 2001) with the following characteristics: membrane type: hollow fiber; Size of pores, μm: 0.01; Molecules cut off, KDa: 50; Type and direction of filtration: dead end, ‘outward and inside’; Working temperature °C: 0-40; Working range of pH: 2-11.

A feed tank with a 5 L capacity and a membrane module of 190 mm length and 50 mm outer diameter was used. The module was horizontally fitted and the wastewater was passed through the membrane tangentially via a peristaltic pump, and the permeate samples were collected from the outlet of the module. After each experimental cycle, the
membrane was washed with distilled water for 15 min to remove the dye particles from the surface of the membrane. Further, it was cleaned chemically by soaking it in 0.5% HNO₃ (v/v) for 2 h and the system was recycled by deionized water at higher flow rate for several times. For the quantitative analysis of fouling, the percentage reduction in permeate flux (J) was calculated according to Equation (5):

\[ J(\%) = \left(\frac{J_f - J_i}{J_i}\right) \times 100 \tag{5} \]

where \( J_i \) and \( J_f \) are the initial and final permeation flux measured at the steady state condition for 1 h (Keerthi et al. 2013).

**Sophisticated analysis**

The Fourier transform infra-red (FTIR) was performed in order to give qualitative and preliminary analysis of the functional groups that might be involved in dye uptake. For FTIR analysis, the effluent was dried and mixed with 1:10 ratio of KBr pellet form and it was determined by FTIR reflection measurements using an ALPHA FT–IR spectrometer. The surface morphology of DMB was identified by a scanning electron microscope (SEM) and the images were recorded using an Agilent Technology scanning probe microscope. The amount of dye decolorization was analyzed by UV-Spectrophotometer using the ELICO-SL210.

**Statistical and error analysis**

Column experiments were conducted in triplicate (\( n = 3 \)) and all the data revealed are the mean value represented by the error bar. Regression coefficients and standard deviations were calculated using the SPSS PC + TM statistical package (1983). Multiple mean comparisons were computed using least significant difference (LSD), and the significance level is \( p < 0.05 \). To consider the best fit model to describe the performance of the breakthrough curves, regression coefficients and average absolute percentage deviation (\( \varepsilon \) %) were analyzed. The regression coefficients (\( R^2 \)) can be fitted between the experimental and theoretical values of the Thomas, Yoon–Nelson and Adam–Bohart equations. The average percentage deviation (\( \varepsilon \)%) was calculated according to Equation (6), and showed fit between the experimental and theoretical values of \( C_o/C_i \) used for plotting the breakthrough curves.

\[ \varepsilon \% = \frac{1}{N} \sum_{i=0}^{\infty} \left| \frac{(C_o/C_i)_{exp} - \left(\frac{C_o}{C_i}\right)_{th}}{C_o/C_i}_{exp} \right| \times 100 \tag{6} \]

**RESULTS AND DISCUSSION**

**Characterization of textile effluent and DMB**

The FTIR spectra of real textile effluent (RE), after column (AC) and after ultrafiltration (AF) studies are represented in Figure 3. From Figure 3(a), the peak which is dominated by a broad and stretch absorption at 3,465–3,300 cm\(^{-1}\), is assigned to the O–H stretching mode of the large prevailing intra molecular H-bonded groups. In addition, the 3,755–3,700 cm\(^{-1}\) region was mostly attributed to free OH–groups. However, in Figure 3(b) there is no intra molecular H-bond stretch band, which might be due to adsorption. In real effluent spectra, the peak observed at 1,464 cm\(^{-1}\) can be assigned to C–C groups of aromatics. However, in the case of biosorption and UF spectra it was greatly reduced, which emphasizes that the aromatic ring in real effluent would likely participate in dye biosorption. In adsorption spectra, the peaks observed at 1,627 cm\(^{-1}\) may be attributed to the N–H (amine) groups of the MO beads, whereas it was found, but greatly reduced, in AF spectra. Further, the SEM micrographs of DMB before and after adsorption are shown in Figure 4. This shows the presence of asymmetric pores...
and open pore structure (Figure 4(a)) which provides the high internal surface area on the surface of the DMB which was favorable for the biosorption. From Figure 4(b), the SEM after biosorption image, there is a clear demarcation in the surface morphology, and the pores are completely packed by the binding of dye molecules.

**Continuous-PBC studies**

**Influence of material mass**

The influence of material mass (MM) on the biosorption of dyes from the textile effluent was investigated, corresponding to three different BHs viz. 12.25 g (5 cm), 24.50 g (10 cm) and 36.75 g (15 cm) at a constant flow rate (2 mL min\(^{-1}\)) with a constant dye concentration, which is shown by the breakthrough curve in Figure 5. As seen from the curve, both the breakthrough time, \(t_b\) and exhaustion time, \(t_e\) are found to increase when increasing the MM, whereas the shape of the breakthrough is slightly different with the variation of MM. From Figure 5, an earlier breakthrough and exhaustion time was attained in BH–5 cm, \((t_b = 17 \text{ min} \text{ and } t_e = 310 \text{ min})\) followed by BH–10 cm \((t_b = 20 \text{ min} \text{ and } t_e = 360 \text{ min})\) and BH–15 cm \((t_b = 35 \text{ min} \text{ and } t_e = 400 \text{ min})\), respectively. An increase in dye uptake was observed at elevated BH due to the increase in the amount of DMB. This provides more fixations of the cations with the active binding sites for the biosorption process, and the increase of biosorbent mass provides a larger surface area leading to an increase in the volume of the treated solution. As the MM increases, simultaneously the MTZ also increases in the column, moving downwards from the entrance of the bed to the exit. Hence, for the same influent concentration and fixed bed system, an increase in BH would create a longer distance for the MTZ to reach the exit, subsequently resulting in an extended breakthrough time (Chowdhury et al. 2013).

**Influence of flow rate**

The influence of feed flow rate on the biosorption of dyes on the DMB by varying the flow rate (1–5 mL min\(^{-1}\)) with a constant fixed BH of 15 cm was investigated and the results are shown in Figure 6. Breakthrough curves \(C_t/C_0\) against time (min) are shown in plots (Figure 6) for two flow rates, 1 mL min\(^{-1}\) and 5 mL min\(^{-1}\), respectively. In the case of a higher flow rate, the MTZ moves from the bottom to the top of the column; as a result, the column gets saturated early. At a higher flow rate, the breakthrough curve is steeper due to the low biosorption
equilibrium, which results in lower dye uptake. It was found that the biosorbent becomes saturated at 5 mL min⁻¹. This behavior suggests that the residence time of the effluent in the column is not sufficient for biosorption. From the curve, the breakthrough (tₜb) and exhaustion time (tₑ) were attained at 55 min and 430 min for 1 mL min⁻¹ and 5 mL min⁻¹, tₜb = 10 min and tₑ = 280 min, respectively (Lin et al. 2013).

Influence of particle size

The influence of different particle sizes was investigated for the biosorbent used during the PBC studies, which had an important effect on column performance. The influence of particle size on dye uptake was studied with the particles in the size ranges 1.5–1.75 and 2.0–2.25 mm. Figure 7 indicates that decreasing the size of the biosorbent leads to an increase in breakthrough time. The smaller particle size ranges provide more efficient breakthrough curves than larger particle size ranges. Moreover, the total external surface area per unit volume for smaller particles will be larger and provides more sorption sites, which leads to greater biosorption (Malkoc et al. 2006). From Figure 7, the breakthrough (tₜb) and exhaustion time (tₑ) was attained at 50 min and 480 min at 1 mL min⁻¹ (smaller particles), respectively, but at tₜb = 30 and tₑ = 430 min (larger particles), respectively.

Modeling of breakthrough curves

PBC data obtained were further analyzed for their breakthrough behaviors using three different mathematical equation models such as the Thomas, Yoon–Nelson, and Adams–Bohart models. The biosorption performance was assessed at an initial concentration ratio, Cᵢ/Cₒ > 0.05, consequently, 5% breakthrough until Cᵢ/Cₒ > 0.95, i.e. 95% breakthrough for dye decolorization by considering water quality and the operating limits of the MTZ of the packed column (Malkoc et al. 2006).

Applications of the Thomas model

The experimental data were fitted to the Thomas model to determine the maximum dye biosorption capacity of the column (qₒ), and the Thomas rate constant (kₜh), which is shown in Table 3. Further, this model is based on the assumption that the process follows Langmuir isotherms of equilibrium with no axial dispersion, and the rate driving force which obeys second order reversible reaction kinetics (Bhaumik et al. 2013). The linearized form of the Thomas model Equation (7) can be expressed as follows:

\[
\ln \left( \frac{C_o}{C_t} - 1 \right) = \frac{k_{th} q_o m}{v} - \frac{k_{th} C_o}{vt}
\]

where kₜh (mL mg⁻¹ min⁻¹) is the Thomas rate constant, qₒ (mg g⁻¹) is the equilibrium adsorbate uptake per gram of the biosorbent, Cₒ and Cᵢ (mg L⁻¹) are the inlet and outlet concentration (g), m is the mass of adsorbent in the column, and v (mL min⁻¹) stands for flow rate. The value Cᵢ/Cₒ is the ratio of outlet to inlet effluent concentrations. By plotting the linear plots of ln [(Cₒ/Cᵢ) – 1] against time (t), the rate constant value (kₜh) was determined and the maximum capacity of biosorption (qₒ) was obtained from the slope and intercepts using values from the column experiments. The regression coefficient (R²), average percentage deviation (ε %) and relative constants such as qₒ (mg g⁻¹) and the kₜh value were calculated from the experimental data, which are shown in Table 3. The regression coefficients (R²) were in between 0.8 and 0.9, and it was observed that the values of average percentage deviation were nominal (i.e. ε% = 2.35–5.35), concluding that the experimental data fitted well with the Thomas model. From Table 3, in general it was observed that by increasing the flow rate, the maximum biosorption capacity (qₒ) decreased but the values of the rate constant (kₜh) increased.
Further, by extending the BH, the values of \( q_o \) are decreased and the \( k_{th} \) value increased significantly. In addition, from Table 3, it was found that at 10 cm of BH with 1 mL min\(^{-1} \) flow rate gives maximum adsorption values (\( q_o, 1,543 \text{ mg g}^{-1} \)).

**Application of the Yoon–Nelson model**

A theoretical model developed by Yoon–Nelson was useful to investigate the breakthrough behavior of textile effluent on DMB. In addition, this model was derived based on the assumption that the rate of decrease in the probability of biosorption for each adsorbate molecule is proportional to the probability of adsorbate biosorption and the probability of an adsorbate breakthrough on the biosorbent (Yoon & Nelson 1984; Chowdhury et al. 2015). The linearized model of a single component system is expressed as Equation (8):

\[
\ln \left( \frac{C_t}{C_o - C_t} \right) = k_{YN} t - \tau_{YN} \tag{8}
\]

where \( k_{YN} \) (min\(^{-1} \)) is the Yoon–Nelson rate constant and \( \tau \) (min) is the time required for 50% adsorbate breakthrough. The values of \( k_{YN} \) and \( \tau \) were estimated from the slope and intercepts of the linear graph between \( \ln \left( \frac{C_t}{C_o - C_t} \right) \) versus time \( t \) at different flow rates, BHs, different particle sizes and the values of \( k_{YN} \) and \( \tau \) are illustrated in Table 3. From Table 3, values of \( k_{YN} \) were found to increase with a higher flow rate with lower BH, whereas they decreased with a lower flow rate and higher BH. Nevertheless, \( \tau \) (the time required for 50% breakthrough) was higher at a lower flow rate and higher BH. In addition, from Table 3, it was found that \( \tau \) (min) values of 205 and 223 min were obtained at 10 BH with F/R 1 mL min\(^{-1} \) and 15 BH with F/R 2 mL min\(^{-1} \). The values of the regression coefficients (\( R^2 \)) are listed in Table 3, and it was found that most of the values of \( R^2 \) were between the range of 0.8–0.9. Furthermore, there was a good concurrence between predicted and experimental data which provide the best fit to the Yoon–Nelson model.

**Application of the Adams–Bohart model**

The Adams–Bohart model was established based on the surface reaction theory, which assumes that the equilibrium is
not instantaneous. Therefore, the rate of biosorption was proportional to the fraction of the biosorption capacity and the concentration of the adsorbing species. According to this model, Equation (9) predicts the performance of the biosorption of a packed column:

\[
\ln\left(\frac{C_t}{C_0}\right) = K_{AB}C_0 t - K_{AB}N_0(z/U_o)
\] (9)

where \(C_0\) and \(C_t\) are the inlet and outlet adsorbate concentrations, respectively, \(z\) (cm) is the BH; \(U_o\) (cm min\(^{-1}\)) is the superficial velocity. \(N_0\) (mg L\(^{-1}\)) is the situation concentration and \(K_{AB}\) (L mg min\(^{-1}\)) is the mass transfer coefficient (MTC). Linear plots of \(\ln\left(\frac{C_t}{C_0}\right)\) against time \(t\) (min) at different flow rates, BH and particle size were plotted. The MTC (\(K_{AB}\)) and saturation concentration (\(N_0\)) values were calculated from the slope and intercept of the curves, which is illustrated in Table 3.

From Table 3, it was observed that MTC increased with an increase in BH and flow rate, which shows that the system was dominated by the external mass transfer (Ahmad & Hameed 2010; Inthorn et al. 2010). The values of the regression coefficients (\(R^2\)) are listed in Table 3, and it was found that the values of \(R^2\) were not in range and do not fit to the Adams–Bohart model.

**UF-permeate characteristics and flux**

In this study, the textile effluent was passed through the UF membrane directly under a constant transmembrane pressure of 1.5 bar and the permeate flux was investigated with filtration time. Further, permeate characteristics such as color, COD/BOD and turbidity were analyzed and the removal of color and COD/BOD were 70% and 65%, respectively, as shown in Table 4. Similarly, turbidity is significantly reduced, but the values are not much lower than the permissible limit as specified by the CPCB (Central Pollution Control Board, India). Reasonably, there were no significant changes in the pH of the permeate samples, while the pore size of the PES membrane was in the UF range. The variation of permeate flux with time at a constant transmembrane pressure of deionized water and permeate effluent is shown in Figure 8. It was observed that the flux of the deionized water maintained linearly, but in the case of effluent, the rate of increase in flux decreases and consequently the flux profile became flat. The initial permeate flux was found to be 655 L m\(^{-2}\) h\(^{-1}\) and the percentage reduction in permeate flux was approximately 32.5%. This was due to the buildup of a solute layer across the membrane surface, which offered higher resistance and consequently lower permeate flux (Bhattacharya et al. 2011).

**Hybrid process of PCB and UF membrane**

The PBC combined with UF, as well as vice-versa, was experimentally studied as follows. The results of the treated samples are listed in Table 4.

**Process I: UF followed by PBC**

In this experimental phase, the UF received textile effluent directly without any pre-treatment. In addition, the permeate effluent was passed through the PBC (BH–15 cm) at a flow...
rate of 1 mL min\(^{-1}\) and the column outlet parameters were measured. In this UF-biosorption study, due to the higher concentrations of the effluent, the membrane was observed with intensive coloration due to the strong biosorption on the surface and pores of the membrane, as shown in Figure 9(a). In addition, the permeability flux profile of UF also greatly reduced which requires adequate cleaning. Further, in the case of column studies, it exhibits faster kinetics and takes a longer breakthrough curve. Nevertheless, some dye molecules of the effluent have permeated through the membrane and may require another stage treatment. It should be noted that the UF followed by biosorption treatment was not effective and can be ruled out. The process may have to be supported with one more stage of the treatment.

Process II: PBC followed by UF

In the experimental study, effluent was first passed through PCB under different conditions followed by UF units. The samples were collected and analyzed as shown in Table 4. The results were confirmed by active decolorization and layers of the membrane being observed visually clear, as shown in Figure 9(b). Also, the membrane unit was found to be capable of several subsequent cycles without any sharp decline in the degree of the permeate flux and maintained the capacity of the effluent treatment effectively constant. From this, the sequential running of the biosorption–UF was found to substantially decrease the maintenance cost. Finally, biosorption followed by UF gave promising results, such as removal of color, COD/BOD, turbidity and the values were much lower than the permissible limit as CPCB.

CONCLUSIONS

The integration process of biosorption and UF was an effective method for the treatment of textile effluents. Biosorption was optimized with the influence of MM, flow rate and size of the biosorbent. By varying the sequences of UF and biosorption process, biosorption followed by UF could be effective for the removal of color (>99%), COD (90–93%) and turbidity (>95%). In the case of the flux phenomenon, the reduction percentage of the permeate flux was found to be 32.5%. Hence, we conclude that the hybrid process could be efficient and considered for the treatment of textile effluents on a pilot scale level.

REFERENCES


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First received 19 February 2015; accepted in revised form 15 April 2015. Available online 20 May 2015