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New Type Biomembrane: Transport and Biodegradation of Reactive Textile Dye

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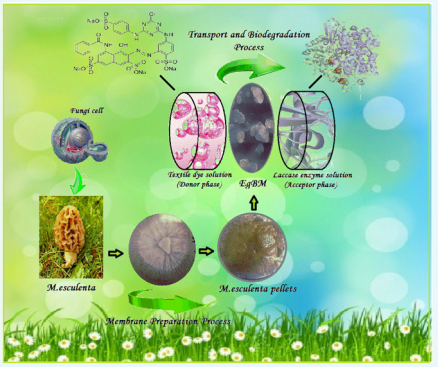
ABSTRACT: In traditional separation processes, there are environmental risks still because of the presence of toxic agents. Thus, a novel biomembrane microreactor named eco-green biomembrane (EgBM) was developed to perform the transport, biodegradation, and cleaning of a textile dye aqueous solution (3 mg/L) from the donor (*i.e.*, textile dye) to the acceptor (*i.e.*, laccase enzymes) phases. In the present work, *Morchella esculenta* pellets were used as carriers and degraders instead of using the traditional chemical carriers. The optimized EgBM was made of cellulose triacetate (16.1%) as a base polymer, 2-nitrophenyl octyl ether (25.2%) as a plasticizer, and *M. esculenta* fungus pellets (58.7%) as both carriers and degraders. A decoloration percentage of 98.6% ± 0.8 in 60 h was attained, which was due to two mechanisms: biosorption (15.4% ± 0.1) on fungal mycelium and biodegradation (83.2% ± 0.6) by laccase enzymes. The EgBM was achieved not only by the transport of reactive textile dyes used in the donor phase but also by the biodegradation and biosorption of the dyes.



1. INTRODUCTION

The textile industry ranks among the most polluting industries, given its large discharge volume of wastewater during dyeing characterized by an intense coloration and untreated or refractory material. Such wastewater is among the most problematic types of wastewater in the environment because its colorant material is highly resistant to degradation and bears a reactive complex structure.[1] In particular, the color parameters of the dyeing process create severe problems for environmental balance because dark wastewater blocks the passage of sunlight, which decelerates photosynthesis and, in turn, negatively affects organic life.

Reactive dyes with heavy metals cannot be removed from wastewater because they are stable against light, heat, and oxidizing agents and are not biologically degradable.[2] Given their structural properties and significance in environmental pollution, dyeing agents merit investigation in terms of wastewater treatment options.[3] Although the physicochemical treatment methods such as chemical precipitation, oxidation, and electrocoagulation for color removal from wastewater in the textile industry are numerous,[4] their use remains limited, given their high cost and inapplicability to all dyes. Biodegradation is seen as a low cost, ease to use, and environmentally friendly method for dye removal from wastewater.[5−8] In this context, ligninolytic fungi are considered a very promising alternative to treat textile wastewater because of their ability to produce nonspecific extracellular enzymes that are able to degrade recalcitrant organic pollutants.[9−12] Among them, the untapped ascomycete *Morchella esculenta* has been selected to perform the present study because of its ability to produce ligninolytic enzymes and easy cultivation.

The use of immobilized fungal cultures is advantageous because they are more resilient to environmental perturbations such as pH and exposure to toxic chemical concentrations than free cell cultures.[13,14] Polymer inclusion membranes (PIMs) are a type of liquid membranes used in separation and purification techniques because of their high selectivity and stability, which together with their mechanical properties make their performance superior to other membranes such as supported liquid membranes.[15−18] The greatest challenge, however, is overcoming the current toxicity or structure during the transport, which can perpetuate environmental risks.[19] In order to overcome this drawback, in the present work, *M. esculenta* pellets were used as carriers and degraders instead of the traditional chemical carriers used.[15,16,20−25] Thus, a novel biomembrane, named eco-green biomembrane (EgBM), in which the chemical carriers were replaced by fungal pellets of *M. esculenta,* was developed. The EgBM was achieved not only by the transport of reactive textile dyes used in the donor phase but

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also by the biodegradation and biosorption of the dyes. To the best of our knowledge, this approach is unprecedented.

2. EXPERIMENTAL SECTION

2.1. Chemicals. Chemical and microbiological reagents were obtained from Aldrich Chemical Co. (Milwaukee, WI, USA) and Sigma (St. Louis, MO, USA). Analytical grade chemicals and other solvents were purchased from Merck (Darmstadt, Germany). The textile azo dye Cibacron Brilliant Red 3B-A (color Index number 18105; DyStar Company, Raunheim, GERMANY), used in cotton dying, was used to perform the biodegradation experiments. The chemical structure of the dye is depicted in Figure 1.

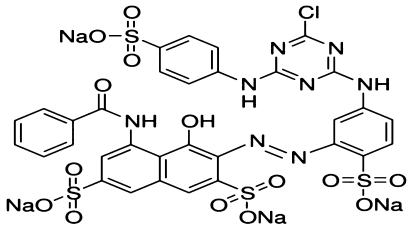

Figure 1. Chemical structure of the reactive textile dye.

2.2. Microorganism and Media Composition. The white-rot fungus *M. esculenta*, obtained from the culture collection of the Chemistry Department, Faculty of Science, Pamukkale University (Turkey), was used to perform the present study. *M. esculenta* was maintained on Petri plates containing malt extract agar (MEA) at 4 °C and was subcultured every month.

The growth medium consisted of NaCl (0.9% w/v) and malt extract (2% w/v) at pH 4.5. The production medium composition was as follows: glucose (10 g/L), $NH_4H_2PO_4$ (1.0 g/L), $MgSO_4{\cdot}7H_2O$ (0.05 g/L), $CaCl_2$ (0.01 g/L), and yeast extract (0.025 g/L). The media were autoclaved at 121 °C for 20 min before use.

2.3. Cultivation Conditions. The cultures were performed in 250 mL cotton-plugged Erlenmeyer flasks containing 100 mL of growth medium. Inoculation two plugs (diameter approx. 0.3 mm) of *M. esculenta*, grown on MEA Petri plates for 7 days, per erlenmeyer were used as inoculum. The flasks were incubated on a shaker at 175 rpm and 26 °C for 4 days in darkness. Then, single or double pellets, depending on the experiment, were homogenized with glass beads on Vortex for 15 min in 5 mL of 0.1 M of acetic acid−ammonium acetate buffer (pH 4.5). This homogenized pellet suspension was lyophilized (Techmech Freeze Dryer, TM350) and stored in the fridge for its use in the preparation of the EgBM.

2.4. Preparation of the EgBM. The EgBM consisted of three basic components: cellulose triacetate (CTA) (Mn = 72.000−74.000) as a base polymer, which acted as a support material, 2-nitrophenyl octyl ether (2-NPOE) as a plasticizer, which provided flexibility and mechanical stability to the biomembrane, and *M. esculenta* pellets as the carrier and degrader. 2-NPOE was selected as a plasticizer, according to previous studies by our research group.[26−29]

The EgBM was prepared as follows: 0.20 g of CTA was dissolved in 15 mL of dichloromethane under shaking for 3 h. 2-NPOE (0.3 mL) and single or double pellets, depending of the experiment, of *M. esculenta* were added into 10 mL of dichloromethane and stirred for 3 h. After this, both solutions were mixed under stirring for 6 h. Finally, the obtained solution was evaporated on a glass plate at room temperature, and cold water was added. The surface area and the thickness of the synthesized EgBM were 9.08 cm^2 and on average 50−60 μm, respectively.

2.5. Transport and Biodegradation Experiments. The EgBM reactor was used as indicated in Figure 2 for the transport

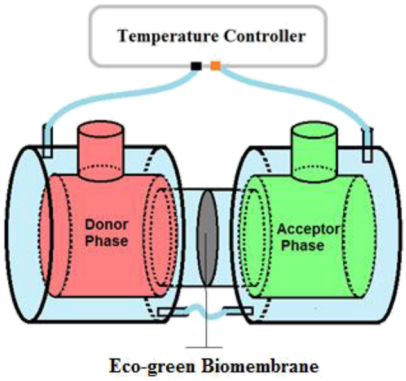

Figure 2. EgBM apparatus.

and biodegradation of the textile dye Cibacron Brilliant Red 3B-A (at three different concentrations; 2, 3, and 4 mg/L) from an aqueous solution. The EgBM reactor is composed of two equal chambers, and the exterior surfaces of the chambers are coated to preserve a constant temperature (25 °C). EgBM is stated between these two equal chambers (45 mL). The donor phase contains a textile dye solution, and the acceptor phase contains a laccase enzyme solution. Thus, the dye solution was the donor phase, and the production medium was the acceptor one. Both phases were magnetically stirred at a constant rate (500 rpm). All the experiments were performed at a constant temperature (25 °C) by means of a temperature controller (Polyscience, Model: 912, USA). Samples were taken periodically from both phases during 3 days and analyzed by UV−vis spectrophotometry (Spectrophotometer Shimadzu 1600A) at a wavelength of 519 nm, which is the wavelength of the maximum visible absorbance of Cibacron Brilliant Red 3B-A (Figure 3). Control experiments with no *M. esculenta* were conducted in parallel. Biodegradation of textile dye by the free fungal cell experiment was performed according to our previous study.[30] Biosorption studies were performed with dead cells. How much dye adsorption had been achieved on the dead cell surface during the experimental period was investigated. All results were calculated based on the biosorption values that are obtained.

2.6. Determination of Laccase Activity. Laccase is an extracellular, copper-containing polyphenol oxidase group enzyme based on the oxidation of phenolic compounds using molecular oxygen as an electron acceptor.[31] The laccase enzyme uses only dissolved oxygen while the other peroxidase group enzymes require hydrogen peroxide, which has toxic and inhibition effects as an oxidizing agent. Because of this feature, laccase enzymes have been a very widespread use in wastewater treatment processes. In this study, the biotransformation of a textile dye was investigated by using this feature of the laccase enzyme. The laccase activity was determined by measuring the enzymatic oxidation of 2,2′-azinobis-(3-ethylbenzothiazoline-6-sulfonic acid) (ABTS) at 420 nm ($\varepsilon = 3.6 \times 10^4$ cm^{-1} M^{-1}). The reaction mixture contained 300 μL of extracellular fluid, 300 μL of 1 mM ABTS, and 0.1 M acetate buffer (pH 4.5). One activity

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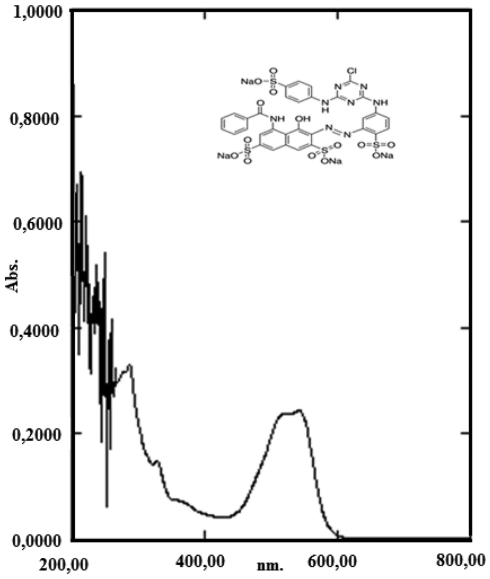

Figure 3. Wavelength scanning of the reactive dye in the UV region.

unit (U) was defined as the μmoles of ABTS oxidized per min, and the activities were expressed in U/L.

2.7. Calculations of Biodegradation, Decolorization, and Biosorption. The decolorization/biosorption/biodegradation percentage and rate were calculated according to the equations given below.

$$R = [(\mathrm{Co} - \mathrm{C})/\mathrm{Co}]\cdot 100$$

(Decolorization percentage, R(%)) (1)

Decolorization rate

$$= (\mathrm{Co} - \mathrm{C})/\text{incubation time(in the presence of a living cell)} \quad (2)$$

$$\text{Biosorption percentage} = [(\mathrm{Ao} - \mathrm{A})/\mathrm{Ao}]\cdot 100 \quad (3)$$

$$\text{Biosorption rate} = (\mathrm{Ao} - \mathrm{A})/\text{incubation time(in the presence of dead cells)} \quad (4)$$

Biodegradation percentage

$$= \text{decolourization percentage} - \text{biosorption percentage} \quad (5)$$

2.8. Fourier-Transform Infrared Spectroscopy. Fourier-transform infrared spectroscopy (FT-IR) spectra before and after degradation were obtained by using a PerkinElmer spectrometer BX FT-IR (ATR) system. The laccase enzyme production medium was used as a background spectrum.

2.9. Scanning Electron Microscopy. Membranes with and without fungus were examined by scanning electron microscopy (SEM) (Zeiss LS 10) at 20,000 kV under vacuum at 10^{-6} Torr.

3. RESULTS AND DISCUSSION

3.1. Effect of the Amount of Fungus on Dye Transport and Degradation. To determine the EgBM capacity, it is important to optimize the amount of fungus to be immobilized. For this, EgBM was synthesized with different amounts of fungal pellets. When more than two pellets were used, a nonuniform biomembrane was obtained. Consequently, experiments with single and double pellets were conducted. The results obtained are shown in Table 1 and Figure 4. High dye decoloration was attained operating with both EgBM (*i.e.*, single and double pellets). Thus, decoloration was 87.2% ± 0.6 and 98.6% ± 0.5 after 60 min for single and double pellets, respectively. In addition, laccase enzyme activities peaked at 24 h for both types of EgBM with values of 13.8 ± 0.01 for the single-pellet EgBM and 28.7 ± 0.02 for the double-pellet EgBM. The double-pellet EgBM performed better, and therefore it was selected to to be used in the subsequent experiments because a higher carrier concentration favours ion transport and higher laccase enzyme activities.

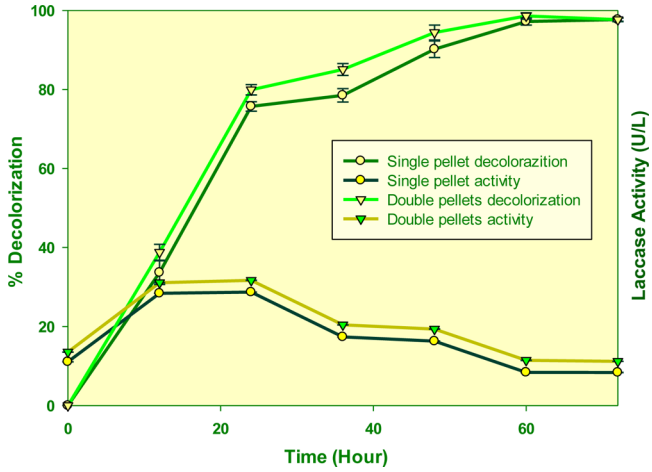

Figure 4. Decolorization and laccase activity of the donor phase per single and double pellets in the EgBM.

Table 1. Biodegradation and Enzymatic Changes in Different Pellet Quantities (sd. Standart Deviation; *n*. Replicate Numbers; h. Hour)[a]

	pellet quantity		decolorization % ± sd n = 3	biosorption % ± sd n = 3	biodegredation % ± sd n = 3	laccase activity U/L ± sd n = 3
donor phase	single	72 h	97.66 ± 0.4	16.35 ± 0.1	81.30 ± 0.3	6.42 ± 0.02
	pellet	60 h	87.20 ± 0.6	14.95 ± 0.3	82.24 ± 0.5	8.39 ± 0.01
	(0.039 g)	24 h	75.70 ± 0.5	7.94 ± 0.1	67.76 ± 0.3	13.83 ± 0.01
	double	72 h	96.72 ± 0.5	17.28 ± 0.3	79.43 ± 0.4	8.36 ± 0.03
	pellet	60 h	98.60 ± 0.8	15.42 ± 0.1	83.18 ± 0.6	11.19 ± 0.01
	(0.073 g)	24 h	79.91 ± 0.5	7.94 ± 0.1	71.96 ± 0.4	28.72 ± 0.02

[a]Donor phase: 3.0 mg/L dye solution in enzyme production medium EgBM composition with the single pellet: 35.67% 2-NPOE, 22.79% CTA, 41.54% *M. esculenta* EgBM composition with the double pellet: 25.2% 2-NPOE, 16.1% CTA, 58.7% *M. esculenta* Acceptor phase: enzyme production medium, temperature 298 K.

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3.2. Effect of the Dye Concentration on Dye Transport and Biodegradation. Regarding membrane capacity in the transport process, which is related to the concentration of the donor phase, the amount of the substance transported *via* the membrane is limited. Accordingly, the maximum transport of target analytes will be determined *via* membrane optimization. Because transport efficiency drops as membrane transport capacity rises because of membrane stability, different concentrations of the dye solution in the donor phase were used. Thus, the biodegradation of the textile dye Cibacron Brilliant Red 3B-A by EgBM at three different concentrations of 2.0, 3.0, and 4.0 mg/L in the donor phase was tested. The most effective removal occurred at a concentration of 3.0 mg/L after 60 h (Figure 5a, Table 2). As can be seen in Figure 5b, laccase

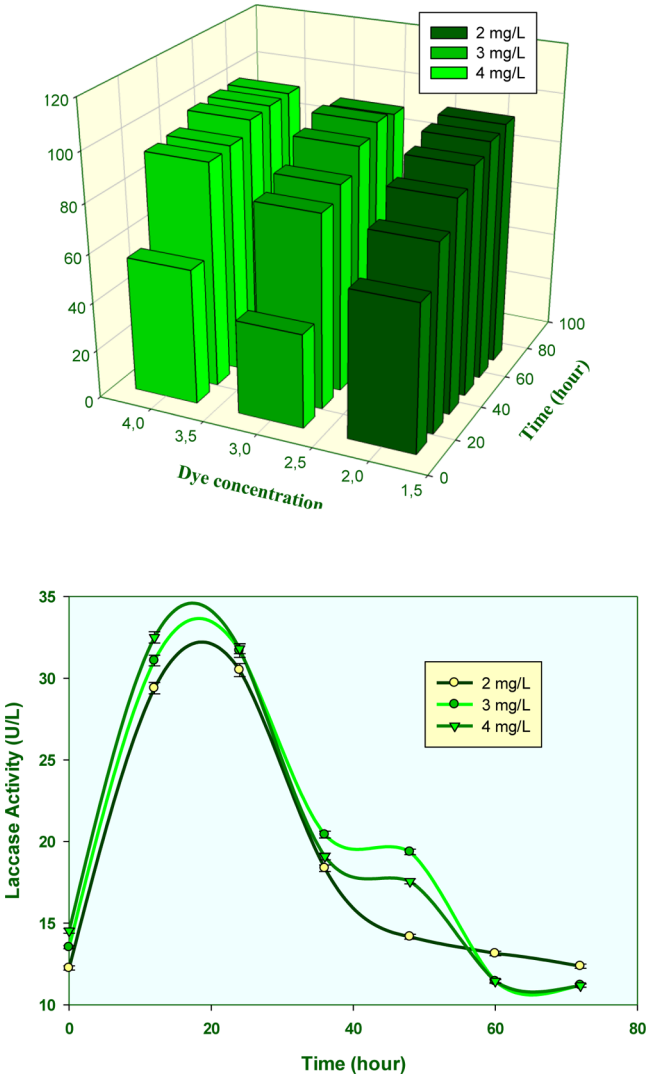

Figure 5. (a) Effect of decolorization in the donor phase for three different (2.0−4.0 mg/L) dye concentrations. (b) Laccase activity of the donor phase for different dye concentrations.

activities peaked at 24 h and from there onward, they declined. The laccase activity of the acceptor phase decreased with the increasing time during the transport process. The reason of decreasing this is thought that the laccase activity is inhibited by the intermediate products and possible metabolites that formed in the medium. This decreasing is compatible with the study reported by Rodríguez Couto et al.[32] They investigated the

Table 2. Alteration of Decolorization for Different Dye Concentrations in the Donor Phase[a]

	time (hour)	2.0 mg/L	3.0 mg/L	4.0 mg/L
decolorization % ± sd n = 3	12	60.74 ± 0.4	38.79 ± 0.3	55.61 ± 0.5
	24	77.04 ± 0.5	79.91 ± 0.5	92.08 ± 0.8
	36	87.41 ± 0.6	85.05 ± 0.6	93.05 ± 0.7
	48	94.07 ± 0.8	94.39 ± 0.7	98.06 ± 0.9
	60	97.78 ± 0.8	98.60 ± 0.8	96.71 ± 0.8
	72	98.26 ± 0.8	96.72 ± 0.5	97.87 ± 0.8

[a]Donor phase: dye solution in enzyme production medium with three different concentration 2.0−4.0 mg/L EgBM composition with double pellets: 25.2% 2-NPOE, 16.1% CTA, 58.7% *M. esculenta* Acceptor phase: enzyme production medium, temperature 298 K.

effect of ions on laccase stability, and observed that the laccase activity was affected negatively by increasing the experimental time and amount of ions in the medium.

3.3. Effect of the Type of Acceptor Phase Solution on Dye Transport and Biodegradation. To assess the effect of the acceptor phase on dye transport, three different acceptor phases were considered: laccase production medium, laccase production medium and dye (3 mg/L), and DW. Laccase activities peaked at 24 h and declined thereafter proportionally; after 72 h, activities remained steady (Table 3). Consequently, 24 h was selected as the optimum. As is shown in Table 3, the highest laccase activity values were 28.7 ± 0.02, 29.6 ± 0.04, and 11.5 ± 0.03 U/L for the laccase production medium, laccase production medium and dye, and DW at 24 h, respectively.

The decoloration values attained were 98.6 ± 0.4% for the laccase production medium, 94.4 ± 0.5% for the laccase production medium and dye, and 89.1 ± 0.5% for DW at 60 h.

According to the results attained, the phase acceptor of the production medium led to the highest laccase activity. However, the three acceptor phases tested led to similar decoloration values. However, the results indicate that the EgBM works double-sided.

3.4. Fourier-Transform Infrared Spectroscopy. To determine whether metabolites have formed following biotransformation, FT-IR spectroscopy of the acceptor phase after degradation and an initial reactive textile dye sample was performed to analyze degradation products. In Figure 6a, the spectrum of the original dye is presented. Absorption bands appeared around 2924 cm^{-1}, which can be attributed to stretching vibrations of the aromatic C−H groups of the dye. The absorption band located around 1540 cm^{-1} was attributed to the stretching vibration of the N═N azo group. Absorption bands also appeared around 1047 cm^{-1}, which were attributed to stretching vibrations of the S═O sulfoxide groups, as well as around 613 cm^{-1}, which were attributed to stretching vibrations of C−Cl halogen groups. In the spectrum of the degraded dye, wide splay absorption bands appeared around 3412 cm^{-1}, which were attributed to stretching vibrations of O−H groups, and absorption bands also appeared around 1635 cm^{-1}, which were attributed to C═N.[33,34] This indicates the disappearance of the characteristic band of the azo and successful biodegradation of toxic groups as well as those corresponding to the −C−Cl and sulfoxide groups denoting dye transformation (Figure 6b).

The obtained results are very similar to those attained by the free process (Table 4), but immobilized cells can be reutilized making the overall process more economically advantageous.

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Table 3. Comparison of the Laccase Activities for Three Different Acceptor Phase Media[a]

laccase activity (U/L) ± sd n = 3							
time (hour)	0	12	24	36	48	60	72
enzyme production medium	8.58 ± 0.03	19.75 ± 0.01	28.72 ± 0.01	22.80 ± 0.04	17.02 ± 0.02	11.19 ± 0.02	8.36 ± 0.03
enzyme production medium and dye	16.55 ± 0.05	32.75 ± 0.07	29.56 ± 0.04	24.28 ± 0.03	21.81 ± 0.03	19.00 ± 0.01	17.53 ± 0.01
water	0.000 ± 0.01	15.95 ± 0.04	11.47 ± 0.03	10.19 ± 0.02	9.03 ± 0.03	8.75 ± 0.02	8.03 ± 0.01
decolorization % ± sd n = 3							
time (hour)	0	12	24	36	48	60	72
enzyme production medium	0.000	38.79 ± 0.3	79.91 ± 0.5	85.05 ± 0.5	94.39 ± 0.4	98.60 ± 0.8	96.72 ± 0.5
enzyme production medium and dye	0.000	55.61 ± 0.4	79.91 ± 0.5	85.51 ± 0.4	89.25 ± 0.5	94.39 ± 0.5	96.26 ± 0.6
water	0.000	58.41 ± 0.4	79.91 ± 0.5	84.86 ± 0.4	86.26 ± 0.6	89.07 ± 0.5	91.02 ± 0.7

[a]Donor phase: 3.0 mg/L dye solution in enzyme production medium EgBM composition with double pellets: 25.2% 2-NPOE, 16.1% CTA, 58.7% *M. esculenta* Acceptor phase: three different medium; enzyme production medium, enzyme production medium and dye, water, temperature 298 K.

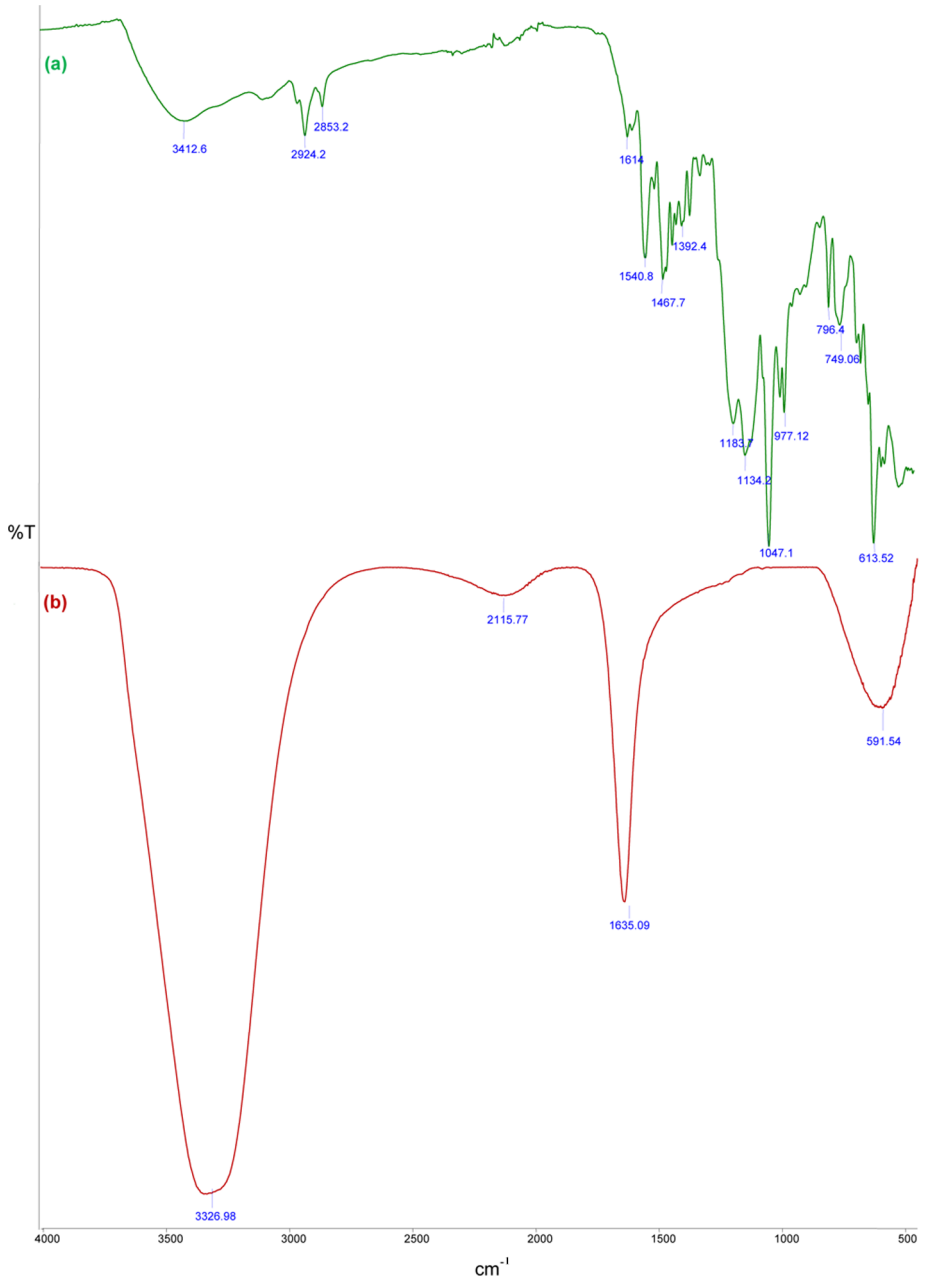

Figure 6. (a) FT-IR spectrum of reactive textile dye (b) FT-IR spectrum of reactive textile dye after the transport and biodegradation.

3.5. Scanning Electron Microscopy. In Figure 7(1a−2b), the SEM photos of the blank membrane (*i.e.*, with no cells) and the immobilized EgBM. Base polymer (CTA) and plasticizer (2-NPOE) were distributed well, and the blank membrane surface

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Table 4. Comparison of Biodegradation Results of Free and Immobilized *M. esculenta*[a]

	decolorization %	biosorption %	biodegradation %
immobilized *M. esculanta*	96.72 ± 0.5	17.28 ± 0.3	79.43
free *M. esculanta*	90.83 ± 0.2	18.48 ± 0.4	74.35

[a]Donor phase: 3.0 mg/L dye solution in enzyme production medium EgBM composition: 25.2% 2-NPOE, 16.1% CTA, 58.7% *M. esculenta* Acceptor phase: enzyme production medium, time 72 h, temperature 298 K.

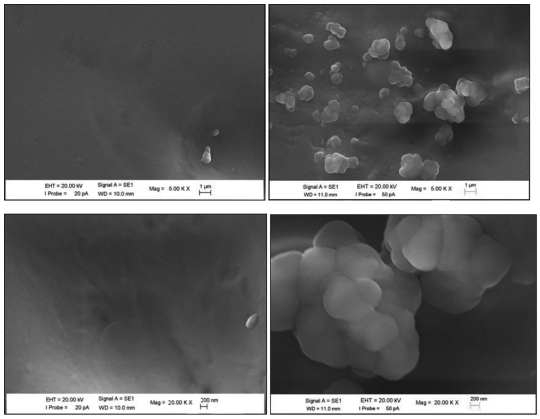

Figure 7. 1a) SEM photo of the blank membrane (1 μm, 5.00 KX), (1b) SEM photo of EgBM (1 μm, 5.00 K X). (2a) SEM photo of the blank membrane (200 nm, 20.00 KX), (2b) SEM photo of EgBM (200 nm, 20.00 K).

was smooth [Figure 7(1a,2a)]. After immobilizing the membrane with the fungus cells, *M. esculenta* cells were seen clearly and distinctly visible in the immobilized EgBM [Figure 7(1b,2b)], and *M. esculenta* cells can be clearly distinguished. SEM photos of EgBM showed that *M. esculenta* cells were immobilized into the membrane successfully. Furthermore, this photo also demonstrated that *M. esculenta* cells were well connected to the membrane structure.

3.6. Comparing Free and Immobilized *M. esculenta* to EgBM. To determine which method performs better, two different experiments with the same fungal cell quantity (two pellets) and textile dye concentration (3.0 mg/L) were conducted. Table 4 presents the experimental results; the immobilized *M. esculenta* degraded the textile dye better, but the values are similar to the free one because their immobilization caused by EgBM increased efficiency as well as stability values are too similar. Although both systems performed similar, the stability and reproducibility of the EgBM should be taken into consideration. If should be prefer to use fungus in free (not immobilized) anywhere the system will be unstable and could not convert to any engineering systems. For the sustainability of the EgBM protype microreactor, immobilizing *M. esculenta* into the EgBM presents big advantages for the applicability of the system in large scales.

Also, the use of the immobilized system presents the following advantages over the free one: repeated use, easy separation from the medium, less contamination risk, protection against environmental perturbations (*e.g.*, pH, toxic chemicals), and shear damage.[35−37]

4. CONCLUSIONS

This study has added a new dimension to biomembrane research by synthesizing a novel EgBM that joins the physical potential of PIM and the degrading ability of fungal enzymes. The decolorization percentage of reactive textile dye with the developed membrane achieved was 98.6% ± 0.8 in 60 h. Using this novel approach (*i.e.*, EgBM), not only the transport of the reactive textile dye but also their biodegradation (83.2% ± 0.6) by laccase enzymes and biosorption (15.4% ± 0.1) on fungal mycelium was successfully achieved. To take biomembrane studies a step further and improve the sustainability of industrial applications of biomembranes, we combined the physical potential of PIMs with fungal enzymes. The comparing free and immobilized *M. esculenta* experiments demonstrated that immobilization caused better decoloration values (96.72%) as well as biodegradation (79.43%). The developed biomembrane microreactor overcomes the problem of toxicity found in traditional separation[18,25,38] processes because of the use of chemical carriers. Instead, the fungus *M. esculenta* was used as a carrier and also as a degrader because it produces laccase enzymes. As a result, the present work can serve as a guide for further studies on both the transport and biodegradation of hazardous compounds to both humans and the environment.

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Notes

The authors declare no competing financial interest.

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