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Enzymatic regeneration of modified cork with sodium dodecyl through the cationic dye removal from aqueous solution

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ABSTRACT

This study investigated a new and a simple process for regeneration of modified cork with sodium dodecyl sulfate (SDS/cork) by enzymatic process using soluble turnip peroxidase (STP) during the elimination of methyl blue (MB) in artificial wastewater. The recycling of the biosorbate and their regeneration investigated under optimal conditions of the two processes: biosorption on SDS/cork and STP. The enzymatic regeneration of the SDS/cork process was carried under pH (6.5), temperature (40°C), concentration of hydrogen peroxide (15 mM), and the contact time witch it is 90, 85, 80, 75 and 60 min for five enzymatic activities 11, 9, 7, 5 and 3 units/mL, respectively. The results indicated that the enzymatic regeneration of SDS/cork present by high performance and efficiency mode in the term of the number of reuse witch it has been reached 17th time for enzymatic activity 11 units/mL, the quasi-stability in the adsorption efficiency of cationic dye and for the global loss in the cork mass 0.04 g.

Keywords: Enzymatic regeneration; Desorption performance; SDS/cork powder; Cationic dye

1. Introduction

Biosorption is very promising process to removal of various dyes from wastewater. Low cost, more effective, abundant, readily available natural biosorbents and friendly process from environment [1–4]. Many times, it is also desirable to recover the solute from biosorbent. Thus, biosorbent recovery and subsequent regeneration and reuse are important attributes of this process [3]. Various regeneration techniques such as thermal, chemical [5], bioregeneration, hybrid technique, microwave regeneration and electrochemical techniques have been used effectively for regeneration of various forms of adsorbents [5–8].

This regeneration technique generally needs to consume large amounts of water and energy [9,10]. It represents a difficult technique to carry out, and yet not ecological or respectful of nature. So, we have to find a different way to regenerate those biosorbents.

In this study, enzymatic regeneration technique using the STP a new regeneration technique was investigating for eliminate a cationic dye, methyl blue (MB), onto sodium dodecyl sulfate (SDS/cork) powder. This technique is a new,

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fast, easy, more efficient, regeneratable, can be treated selective substances effluent existing in liquid form [11] and eco-friendly technique. The recycling of the adsorbate and their regeneration were carried under the optimum conditions of the two processes: adsorption on SDS/cork and STP. In this study, a new regeneration technique was to investigate cationic dye removal on SDS/cork powder using a STP. This technique is a new, fast, easy, more efficient, regeneratable, can be treated effluent from selectively existing substances and eco-friendly [11].

The objective of use the modified cork by SDS is to enhance the biosorption properties of MB. Biosorbent recycling and regeneration were carried out under optimum conditions for both processes: biosorption on SDS/cork and STP. Various modification techniques have been applied: acid activation, heat and chemical treatment, and chemical modification with inorganic materials [12–14]. Surface modification using the SDS surfactant is both environmentally friendly and inexpensive compared to other methods [13,15,16].

2. Materials and methods

2.1. Chemical products

4-Aminoantipyrine ($C_{11}H_{13}N_3O$, 99%) purchased from Fluka Chemie; Acetone (C_3H_6O, 99.5%) purchased by Prolabo Chemicals; Phenol (C_6H_6O, 99%) imported by Prolabo Chemicals; Hydrogen potassium monopotassium phosphate (136.06, 99%) imported by Biochem Chemopharma; Hydrogen peroxide (H_2O_2, 10%) was delivered by Sigma-Aldrich, SNC Boufama and Associates Z.A.C Mila 43000; Potassium hydroxide (KOH, 85%) imported by Sigma-Aldrich; Methylene blue (319.86, 85%) imported by Riedel-de Haën; The cork used in this study was supplied from the Wilayah of Jijel (Algeria).

2.2. Materials

The pH meter type Innolab with magnetic stirring and equipped with a combined glass electrode; Buchi Rotavapor R-200 brand; Optizen 2120UV brand UV-visible Spectrophotometer, computerized PC for the storage and processing of spectra; Memmert brand oven, magnetic stirring bars of different sizes were obtained from Cole-Parmer Canada Inc. (Montreal, QC); scanning electron microscopy (SEM) type Tescan Vega 3 SBU Easy Probe.

2.3. Methyl blue biosorption study

The removal of MB realized by adding 0.08 g SDS/cork into 20 mL dye solution with pH equal to 6, temperature maintained at 40°C and contact time of 90 min. The residual dye concentration was determined by UV-Vis spectrophotometer at the corresponding max λ_{value} at 665 nm and the biosorption efficiency (R) of the cationic dye was determined using the Eq. (1):

$$\text{Biosorption Efficiency}(R) = \frac{(C_I - C_F)}{C_I} \times 100 \quad (1)$$

where C_I is the initial MB concentration (mg/L) and C_F is the final MB concentration (mg/L) in solution.

2.4. Modification of the biosorbent surface using SDS

To modify the surface of the virgin cork powder, 20 g of cork powder was dispersed in 100 mL of SDS solution (2.9 g/L) at room temperature using a magnetic stirrer to achieve homogeneity. The mixture was centrifuged, filtered, washed multiple times by water osmosis and dried at 60°C for 24 h. SDS/cork powder was stored in an airtight container until it was used [17].

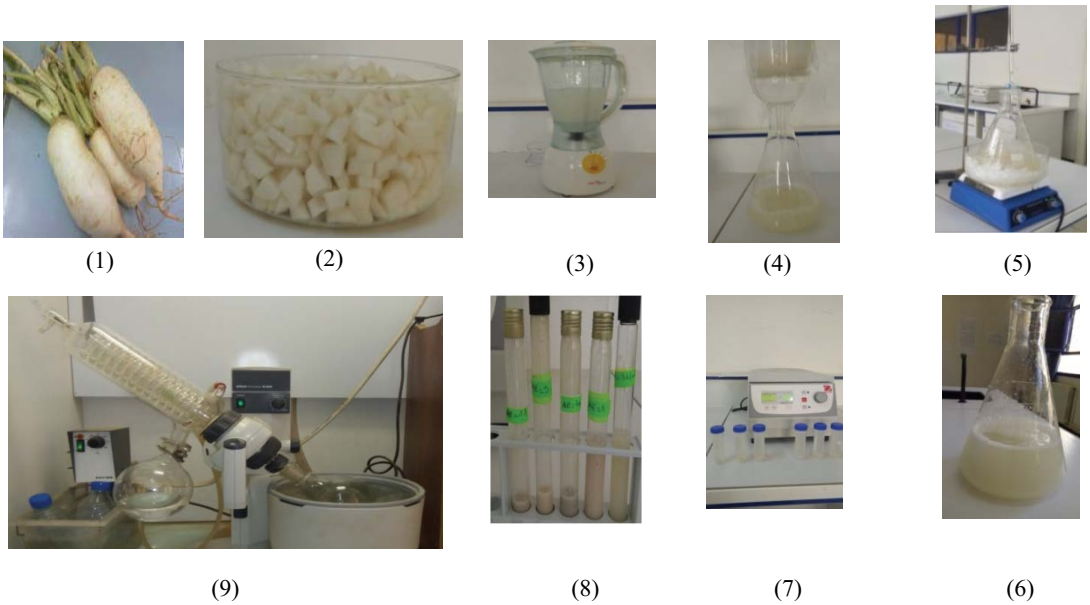


Fig. 1. Extraction and purification steps of STP. (1) Turnip, (2) Turnip peel, (3) Mixation, (4) Filtration, (5) Purification by acetone, (9) Recovery of acetone, (8) STP, (7) Centrifugation, and (6) Mixture: Acetone + Enzyme.

2.5. Removal of methyl blue study by STP

The efficiency of MB oxidation by enzymatic process was performed using batch experiments. A known amount of biosorbent was introduced in flasks containing an initial MB concentration. The mixture was stirred during a determined time. At equilibrium time the absorbance of supernatants was determined at λ_{max} = 664 nm. The performance of the bioprocess was calculated using Eq. (1).

2.6. Extraction and purification of turnip peroxidase

The purified enzyme was initially extracted from the white turnip such as mass of turnip peel equal to the half of water mass. This mixture is filtered with gauze, the permeate is called the crude extract enzyme (CEE) which is stored in the fridge at 4°C. The CEE is purified with cold acetone (4°C) according to the relationship $V_{acetone} = V_{CEE}$. The mixture of CEE and acetone is kept in the fridge at 4°C for 2 h to facilitate the separation of the enzyme by centrifugation at 6,000 rpm for 15 min. The pellet to be recovered is dissolved in various volumes of monopotassium phosphate buffer solution (pH = 6.5), to have different enzymatic activities from STP and it is stored in the fridge at 4°C [18].

2.7. Activity measurement

The measurement of enzyme activity was assayed by the Am-NH_2 method [19] as follows, in vial of 50 mL put: 1 mL of phenol (0.1 M); 1 mL of H_2O_2 (0.1 M) and 1 mL of 4-aminoantipyrine (0.01 M); the rest is supplemented with a pH = 6.5 buffer solution of 0.01 M monopotassium phosphate. A volume of 4 mL of this reaction mixture (50 mL) should be placed in a test tube plus a 0.2 mL of STP. This reaction is followed by UV-Vis spectroscopy after the addition of 0.2 mL of STP at λ_{max} = 517 nm in order to plot the OD = *f*(time) pattern [19,20]. The enzyme activity (EA) is determined by the equation next:

$$\mathrm{EA}\left(\mathrm{U/mL}\right) = \frac{\Delta \mathrm{OD}}{\Delta t} \times V_r \times 37.125 \times 10^6 \quad (2)$$

where OD is the optical density; EA is the enzyme activity (U/mL); V_r is the reaction volume (4.2 mL); t is the time (s).

2.8. Desorption and reusability for methyl blue dye removal

Desorption experiments were conducted using three processes: distilled water, reverse osmosis water and enzymatic process. Such as, batch tubes putting 0.08 g of SDS/cork witch it is in excess of the optimal mass value to eliminate the mass loss effect, a 20 mL of MB solution of concentration 100 mg/L prepared in a buffer solution of potassium phosphate (0.01 M) at the pH 6.5. This mixture maintains at temperature of 35°C and a stirring speed of 250 t/min for 90 min. This solution was subsequently filtered with a microfilter (0.45 μm) to leave the SDS/cork powder in the solution of reusability (distilled water, reverse osmosis water and enzymatic mixture). For enzymatic reusability, a mixture contains 0.2 mL of STP with different enzymes activities (3, 5, 7, 9 and 11 units/mL), 1 mL of the corresponding hydrogen peroxide concentration (15 mM for enzymatic activities not more than 9 units/mL and 20 mM for an enzymatic activities exceeding 9 units/mL) and 2.8 mL of the buffer solution at pH = 6.5 and temperature of 40°C. Following this treatment, the SDS/cork powder was cleaned after desorption step in different process with distilled water, filtered through a microfilter (0.45 μm) and then oven dried at 40°C for 8 h overnight for reuse. All experiments were performed in optimal conditions.

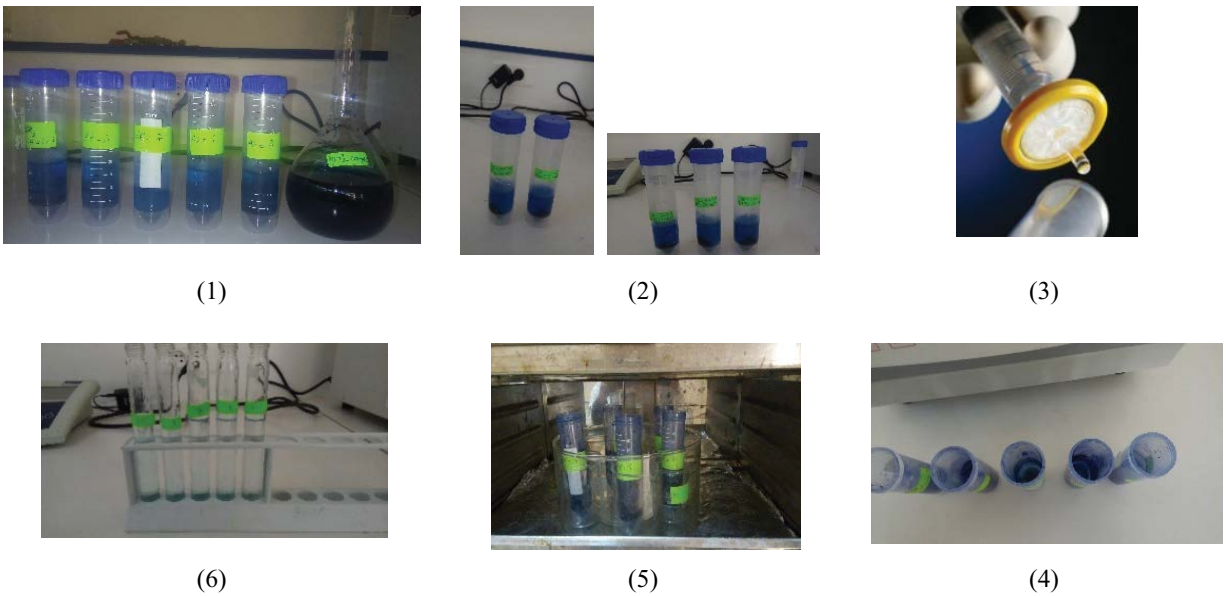


Fig. 2. Enzymatic regeneration process. (1) Enzymatic regeneration of artificial wastewater continent MB, (2) Centrifugation of mixture: SDS/cork and wastewater, (3) Filtration of mixture by millipore with a 0.45 μm pore size, (4) Recover adsorbate after a microfiltration step, (5) Drying, and (6) Wastewater after biosorption treatment.

2.9. Characterization

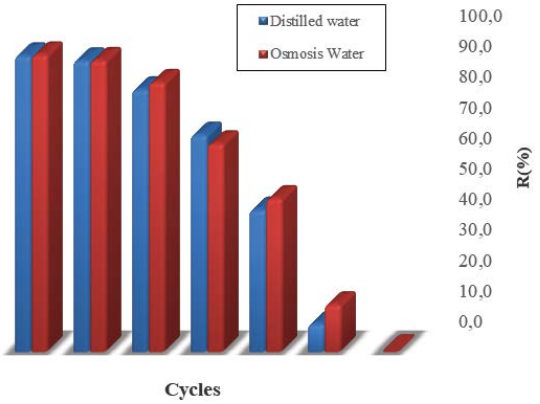
Cork powder morphology has been characterized by an electron scanning microscope.

3. Results

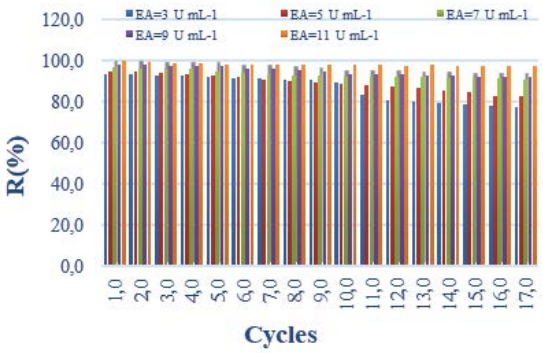
3.1. Desorption and reusability for removal dye

From Fig. 3b it is clear that the enzymatic process has the most effective and efficient regeneration mode where the number of reuses has been reached 17th time for the enzyme activity 11 units/mL with a quasi-stability in the biosorption efficiency of MB with an overall weight loss is 0.04 g (Fig. 4). SDS/cork's regenerative efficiency decreases with enzyme activity. On the other hand, the other conventional processes (distilled water and osmosis water) have weak regenerative substrate processes, so that the biosorption efficiency has been reduced to less than 50%, and it has been cancelled after the 8th reuse (Fig. 3a).

Then, the previous results on regenerating SDS/cork or other by different processes demonstrate that enzymatic regeneration presents the best process as a function



(a)



(b)

Fig. 3. Cyclic regeneration of SDS/cork powder by (a) distilled water, osmosis water and (b) different enzymes activities of STP. pH = 6.5, T = 40°C, [H_2O_2] = 15 mM for EA = 3, 5, 7, 9 U/mL and [H_2O_2] = 20 mM for EA = 11 U/mL.

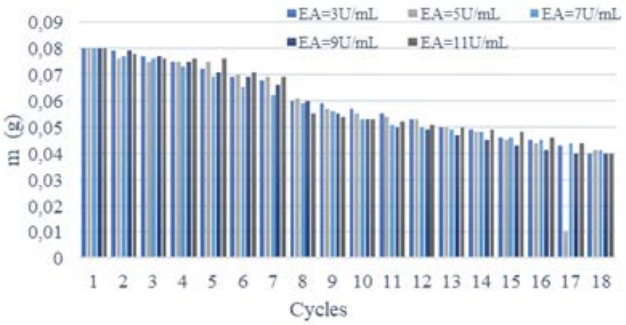


Fig. 4. Loss of biosorbent mass during regeneration cycles.

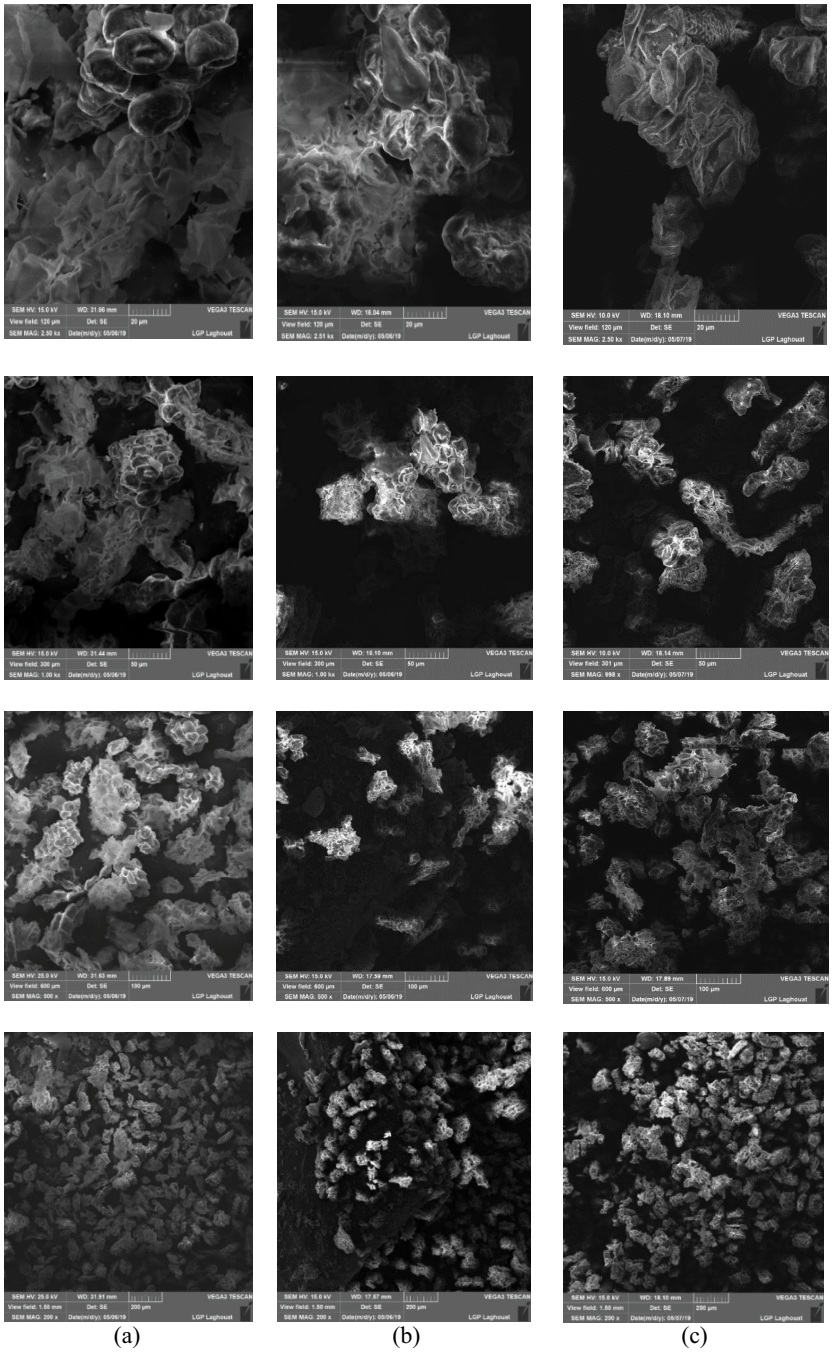
Table 1
Comparison between some sorbent's regeneration processes during adsorption of dyes

Sorbents	Processes	Dyes	Numbers of cycles	References
SDS/cork	STP	MB	17 cycles of reuse decreased only 5%	This study
Alginate/natural bentonite composite beads	Distilled water	MB and Congo red	5 cycles	[21]
Hectorite clay/alginate composite beads	Methanol	MB	6 cycles	[22]
Hydroxypropyl-β-cyclodextrin/polyethylene glycol 400, modified Fe_3O_4 nanoparticles	NaOH solution	Congo red	*R* achieved 60% after 4 cycles	[23]
Magnetic β-cyclodextrin-anhydride polymer	Ethanol solution containing acetic acid	MB and Rhodamine B	*R* decreased 10% after 5 cycles	[24]

(Continued)

Table 1

Sorbents	Processes	Dyes	Numbers of cycles	References
Sericin/derived activated carbon	NaOH chemical activation	MB	*R* was maintained stable (90.1%) after 5 cycles	[25]
Graphene oxide/poly(vinyl alcohol)/TiO_2 microspheres	Irradiated under simulated solar light	MB	*R* remaining stable (88.9%) after 5 cycles	[26]
Polyethylenimine-modified cellulose	NaOH solution	Rose Bengal and MB	*R* was not decreased even after 10 cycles	[27]
Mesoporous titania/polyvinyl alcohol	Acid solution	MB	10 cycles	[28]



(a) (b) (c)

Fig. 5. SEM image of different cork form: (a) virgin cork, (b) SDS/cork before biosorption of MB and (c) SDS/cork after biosorption of MB.

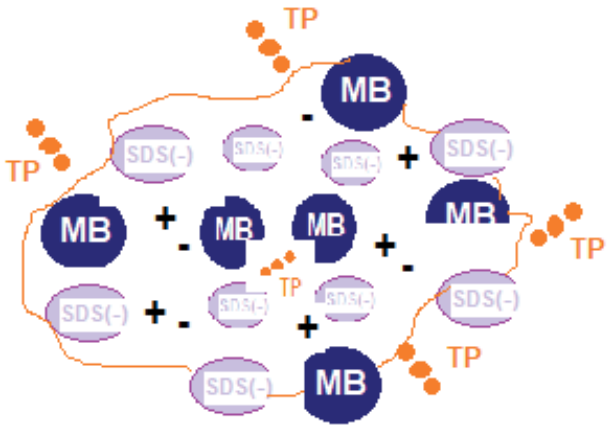


Fig. 6. Mechanisms of enzymatic regeneration of SDS/cork.

of cycle times and the stability of biosorption efficiency on biosorbent regeneration cycles (Table 1).

3.2. Scanning electron microscopy

SEM photographs shown in Fig. 5 were taken under high magnification 20, 50, 100 and 200 μm to observe the surface morphology of virgin cork (Fig. 5a), SDS/cork (Fig. 5b) and SDS/cork after biosorption of MB (Fig. 5c). These figures confirm that the cork powder has a roughened surface, which ensures a high porosity and surface area. The SEM images clearly show the presence of SDS and MB with an average diameter of about the micrometre. The SEM analysis confirmed that the MB was successfully attached to the surface of the unmodified and modified cork.

3.3. Mechanisms of enzymatic regeneration of SDS/cork

The surface charge of the SDS/cork is negative in the pH range between 4 and 10 due to the $-SO_3^-$ anion of the surfactant [29]. The cationic dye can be biosorbed onto the surface of the SDS/cork biosorbent through electrostatic interactions [17]. The STP leads to oxidizing the MB dye into quinone at all SDS/cork volumes. This reaction regenerates by continuing our biosorbent (Fig. 6).

4. Conclusion

In this study, a simple and nature-friendly technique was applied to regenerate enzymatically modified SDS/cork biosorbent using STP during the removal of MB from artificial wastewater. Biosorbent recycling and regeneration were investigated under optimal conditions for both processes: biosorption to SDS/cork and STP. As such, the physical biosorption process was performed with a mass of SDS/cork exceeding the optimum value = 0.08 g, [MB] = 100 mg/L, pH = 6, T = 40°C, a contact time = 90 min. The results showed that the increase in enzyme activity of STP leads to an increase in the number of retaliations with a quasi-stable biosorption efficiency of MB. So that the elimination percentage is reduced to 10% after the 17th reusing with enzymatic activity 11 units/mL under low SDS/cork mass loss over the entire regeneration cycle where it has not been exceeded 0.04 g. On the other hand, other conventional methods have poor methods of regenerating the substrate, with the result that the removal percentage has been reduced by more than 50% and it is been cancelled after the 6th reuse. In summary, we demonstrated the feasibility of recyclability and sustainability of our biosorbent for MB elimination deserves good applicability for wastewater treatment and environmental protection.

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