An Acad Bras Cienc (2021) 93(Suppl. 3): e20210425 DOI 10.1590/0001-3765202120210425
Anais da Academia Brasileira de Ciências | *Annals of the Brazilian Academy of Sciences*
Printed ISSN 0001-3765 I Online ISSN 1678-2690
www.scielo.br/aabc | www.fb.com/aabcjournal

105 anos 1916 • 2021

ENGINEERING SCIENCES

Treatment of soy sauce wastewater with biomimetic dynamic membrane for colority removal and chemical oxygen demand lowering

FANG WANG, XIAO LUO, JIA GUO & WENXIANG ZHANG

Abstract: Soy sauce wastewater has been produced in soy sauce production and consumption. To reuse this kind of water resource, the chemical oxygen demand (COD), colority should be removed or lowered. Biomimetic dynamic membrane (BDM), GO&Laccase@UF membrane, was prepared by filtering mixture of graphene oxide (GO) and laccase through ultrafiltration (UF) membrane. Compared to UF membrane, the prepared BDM showed great performance in removal of COD and colority, due to the higher laccase activity with existence of GO. The removal rate of colority reached ~80% by one step filtration operation. Moreover, the multiple cycle test evidenced that the value of COD and colority in the permeate after 5 consecutive cycles with the same GO&Laccase@UF membrane still meet the standard for reuse water. This work indicates the promising of BDM for wastewater from food industry.

Key words: Soy sauce waste, biomimetic dynamic membrane, filtration, colority removal.

INTRODUCTION

Soy sauce is an oriental fermented condiment consumed widely in Asian countries such as China, Thailand, Japan, and Korea. However, the production and consumption of soy sauce result in large amount of soy sauce wastewater, which mainly contains high Chemical Oxygen Demand (COD), Biochemical Oxygen Demand (BOD), total suspended solid (TSS), protein and intense dark brown color due to the presence of caramel pigments and the occurrence of the Maillard reactions producing melanin or melanoidin (Harun et al. 2018, Sittiwat et al. 2001). Soy sauce wastewater mainly comes from the process of koji making, fermentation, backwashing and packaging, including production site and equipment cleaning wastewater, raw material soaking wastewater, and product waste overflow. The annual output of soy sauce in China is about 8 million tons, and 1 ton of soy sauce may produce about $6m^3$ ~ $9m^3$ of soy sauce wastewater. Without proper disposal, the emission of soy sauce wastewater may lead to serious environmental pollution, as well as waste of water resource.

To prevent pollution and to recycle valuable resources of soy sauce wastewater, various researches were carried out to develop efficient and economic methods for soy sauce wastewater treatment and reusing (Hyun-Hee et al. 2017, Battisti et al. 2019). Hyun-Hee et al. (2017) compared efficiency of three oxidation agent, Fenton (Fe^{2+}), Fenton-like (Fe^{3+}), and ozone (O_3), to remove the color and lower the COD of soy sauce wastewater. The best color removal of 81.1% and COD lowering of 64.9% were obtained via O_3 oxidation due to the degradation of organics caused by the large amount hydroxyl radical. Anam et al. (2012) applied a marine photosynthetic bacterial consortium, *Rhodobium marinum*, to produce hydrogen from soy sauce wastewater, which was regarded as a cheap carbon source. By using the soy sauce wastewater medium, the maximal hydrogen production could reach up to 200±67 mL H_2. Harun et al. (2018) studied effect of hydraulic retention time (HRT) on the performance of aerobic granular sludge for soy sauce wastewater treatment. Results evidenced that a HRT of 24h with aerobic and anaerobic/anoxic reaction time of 3.88 and 7.77h respectively could lead to optimal performances for COD removal.

Membrane technology has been widely used in food processing, waste water treatment and biomass refining, due to its benefit profits as low operation cost, high productivity, and high product quality (Zhu et al. 2018, García-Serrano et al. 2019, Bhattacharjee et al. 2017, Campos et al. 2016, Zhong et al. 2021). The application of direct pressure-driven membrane processes for wastewater treatment could be recalled to 1990s (Butler & MacCormick 1996). In the case of soy sauce wastewater treatment, Jang et al. (2018) investigated a combined nanofiltration (NF) and H_2O_2/O_3 process to reduce color and COD of soy sauce wastewater. The proposed method resulted in 98.1% color removal and 98.2% COD reduction. Lv et al. (2016) proposed an pilot membrane bioreactor (MBR) to treat the wastewater of soy sauce factory. By MBR treatment with combination of coagulation and ox-idation, the residual COD and color of soy sauce wastewater was effectively reduced until meeting the discharge limit.

Despite of the profits and the excellent potential of membrane technology in various domains, the important obstacle, membrane fouling, is now greatly limiting the application of technology (Zhu & Mhemdi 2016, Loginov et al. 2017, Li et al. 2019, Grimi et al. 2010). Among approaches for fouling control during membrane process, fabrication of biomimetic dynamic membrane (BDM) is regarded as an promising method for wastewater treatment with low fouling due to the “online and in-situ” enzymatic degradation of foulant (Chen et al. 2019). For example, Chen et al. (2019) fabricated BDM by physical adsorption of nanotubes and laccases on commercial polymer membrane to treat dye wastewter. The prepared BDM showed desired performance with excellent dye removal rate, stable flux, as well as great antifouling capacity. Graphene oxide (GO) has also been widely used for membrane modification due to its high density of oxygen containing functional goups wich can improve the hydrophilicity, as well as the unique layer structure for water flux improvement (Dikin et al. 2007). Also, GO can enhance stability and activiey of enzymes by binding enzymes to the GO nanosheets (Novak et al. 2016, Dong et al. 2016).

The aim of this work was to prepare BDM by immobilizing mixture of GO and laccase on surface of ultrafiltration (UF) membrane to form a dynamic layer, and evaluate its performance on soy sauce wastewater treatment in view of COD and colority removal. Moreover, filtration performance after mutiple operation cycles were studied for longterm running properties of prepared BDMs.

MATERIALS AND METHODS

Preparation of BDM

The virgin hydrophilic polysulfone ultrafiltration (UF) membrane with a molecular weight cut-off (MWCO) of 100kDa (purchased from MICRODYN-NADIR Membranes Inc., Germany) was placed on the bottom of stirred Amicon 8020 membrane module (Millipore Corporation, USA) and cleaned by filtering deionized water. The effective membrane area was 13.4 cm^2. GO purchased from CheapTubes.com (Cambridgeport, Vermont, USA) was mixed with laccase from Aspergillus

Oryzae, purchased from Kool Chemical Technology Co., Ltd. (Beijing, China), in 150 mL of deionized water. The dosage of GO was 25 g/m^2, while 50 g/m^2 for laccase according to previous study (Zhu et al. 2020). The GO suspension was dispersed by sonication for 20 min using a water bath sonicator (Aquasonic 250HT). Then the mixed GO and laccase solution were filtrated through UF membrane to form the BDM named GO&Laccase@UF.

Treatment of soy sauce wastewater via BDM

Commercial soy sauce was purchased from supermarket in Wuhan, China, to prepare model soy sauce wastewater by dilution according to Jang et al. (2018). The COD, and colority of the prepared wastewater were 200 mg/L and 59, respectively. 50 mL prepared soy sauce wastewater was used for BDM filtration until 40 mL permeate was obtained. The Amicon 8020 cell was used for treatment (Figure 1). The transmembrane pressure was maintained at 1 bar by compressed N_2, and the stirring speed of agitator of the filtration cell was 50 rpm. The permeate volume was recorded with time and each 10 mL of permeate was sampled for quality analysis.

Analytical methods

The chemical composition of membrane surface was analyzed with Fourier transform infrared spectra (660-IR, Varian, Australia). COD was measured using EasyBox Kits (HuangKai Microbia, GuangZhou, China) in order to quantify organic matter concentration. The colority of the wastewater and permeate was measure according to a standard method (GB 11903-1989 (China 1989)) using K_2PtCl_6 and $CoCl_2.6H_2O$ as standards.

The filtration flux (J) was calculated by using Eq. (1).

$$J = \frac{V}{S \cdot t} \quad (1)$$

where S is the effective membrane area, t is the filtration time, and V is the permeate volume during t time.

The removal rate (R, %) is calculated by the following equation:

$$R = \left(1 - \frac{C_p}{C_f}\right) \times 100\% \quad (2)$$

where C_f and C_p represent the concentration of color substances in feed and permeate, respectively.

Data analysis

All tests were repeated at least three times. The errors were controlled below 5% and average values were calculated and demonstrated in the Figures and Tables.

RESULTS AND DISCUSSION

BDM membranes characterization

The FTIR spectrograms of pristine UF membrane, laccase, and prepared GO&Laccase@UF membrane were presented in Figure 2. The characteristic peak of UF membrane from 700 cm^{-1} to 2000 cm^{-1} disappeared after modification with laccase and GO, evidencing that the surface of UF membrane was effectively modified and covered by GO&Laccase layer. Moreover, GO&Laccase@UF membrane showed large peaks of oxygen groups at 996 cm^{-1} and 3295 cm^{-1}, representing the -C-O group and -O-H in both GO and laccase. These results evidenced the modification of the membrane surface.

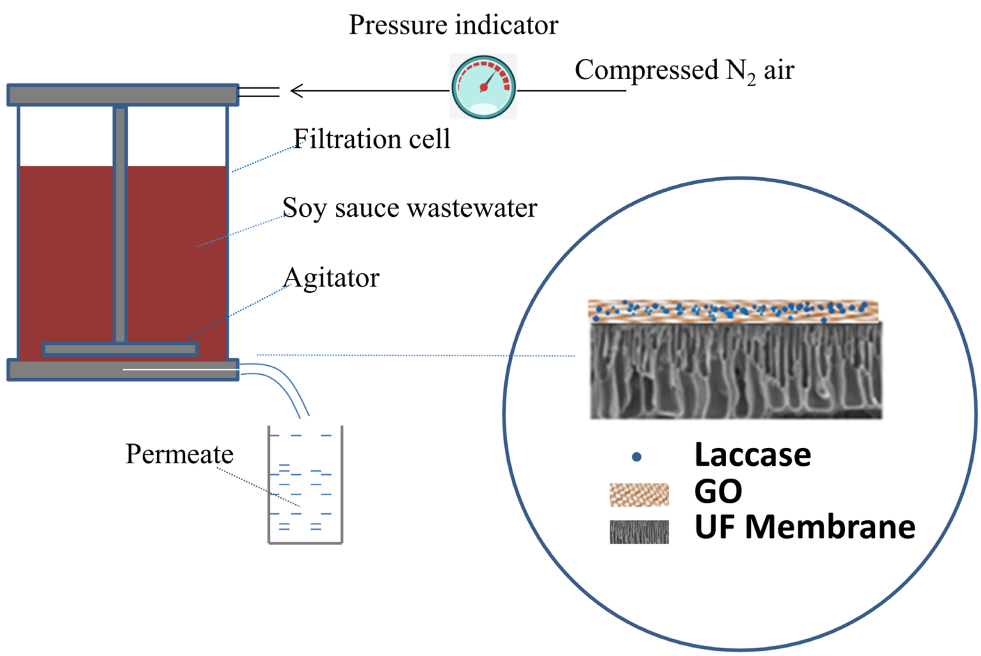

Figure 1. Schematic diagram of the filtration set-up.

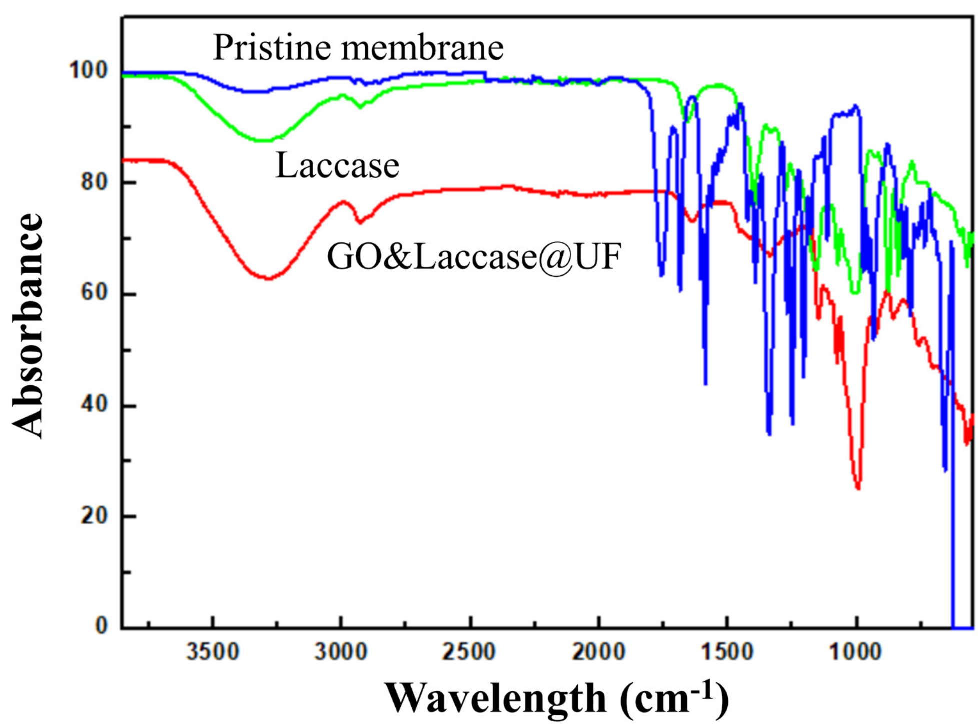

Figure 2. FTIR spectrum of different membranes.

Filtration and removal performance of BDM membranes

The average flux of pristine UF and GO&Laccase@ UF was presented in Figure 3(a). Compared to pristine UF membrane, BDM membrane showed lower flux, mainly due to the GO&Laccase layer formed on the membrane surface. Although, the flux of prepared BDM was only 80 $L.m^2.h^{-1}$, which was half of the flux of pristine UF membrane, The colority removal rate reached~80%. While the colority removal rate was as low as 10% for pristine UF membrane, as seen in Figure 3(b).

The color substances in soy sauce wastewater can undergo enzymatic browning under the oxidation of laccase and produce melanin, which could be then adsorbed and removed during filtration, reducing the color of permeate. The GO&Laccase layer was regarded as functional layer for coloriy removal, but also a fouling layer for liquid permeability. This can explain both the good removal and relatively worse permeability of BDM membranes.

The value of COD and colority of feed (model soy sauce wastewater), permeate of UF membrane and BDM were presented in Table I. As can be seen, UF showed no reduction on COD value. BDM showed significant COD removal ability, reducing the value of COD from 200 mg/L for the feed to 30~60 mg/L for the permeate. The value of COD is most common used in quantifying the amount of oxidizable pollutants found in wastewater. The colority of permeate of GO&Laccase@UF was 9, indicating the better removal ability of GO&Laccase@UF. This phenomenon may be explained by the benefits provided by GO due to enrichment and catalytic function. As a good adsorbent, GO enriched laccase and colorant around its surface, accelerating the enzymatic reaction at the concentrated area. Moreover, GO contributed to fast "regeneration" of laccase by acting as its "second T2/T3 active site", avoiding the decrement of native intermediate for oxidized laccase (Fu & Zhu 2013, Parhizkar et al. 2017, Zhu et al. 2020, Zhang et al. 2019). Moreover, the value of COD and colority of permeate obtained by prepared BDM meet the standard of Integrated wastewater discharge standard of China (GB 8978-1996), COD<100 mg/L and colority<50. From the photos of permeate obtained from filtration with UF and GO&Laccase@UF (Figure 4) one can easily tell the benefit of BDM in colority removal.

The evolution of flux and colority of permeate in filtration of soy sauce wastewater with GO&Laccase@UF was presented in Figure 5. The flux calculated for every 5 mL permeate was record and it decreased from 93 Lm^2h^{-1} to 60 Lm^2h^{-1} for accumulation of 40 mL permeate, evidencing existence of membrane fouling during filtration, even with the degradation of foulant generated by laccase. This also indicate the necessary of combing other antifouling strategies such as rotating disk, threshold flux control and ultrasonic filed (Luo et al. 2012a, b, 2010, 2013). However, the colority removal rate only decreased by 5-15%. This may be explained by interception and adsorption of the colorant by the fouling layer, as well as the continuous degradation of pollutants by laccase.

Filtration performance of BDM GO&Laccase@UF in multiple cycles

To evaluate the long-time performance of GO&Laccase@UF, the treatment of soy sauce wastewater was carried out 5 times with consecutive application of the same GO&Laccase@UF membrane. For each cycle 50 mL feed was filtered until no permeate came out from the filtration cell. The permeate flux decreased obviously from the first to the fifth cycle (Figure 6), due to the membrane fouling. The colority removal decreased gradually with reusing of the BDM (Figure 7). This may be explained by the saturation of the adsorbent on the membrane surface.

It should be noted that, after 5 cycle re-application, the value of COD and colority of the permeate still meet the stadard of reuse water (Table II), indicating that the prepared BDM GO&Laccase@UF could provide idea long-term performance in aspect of colority removal.

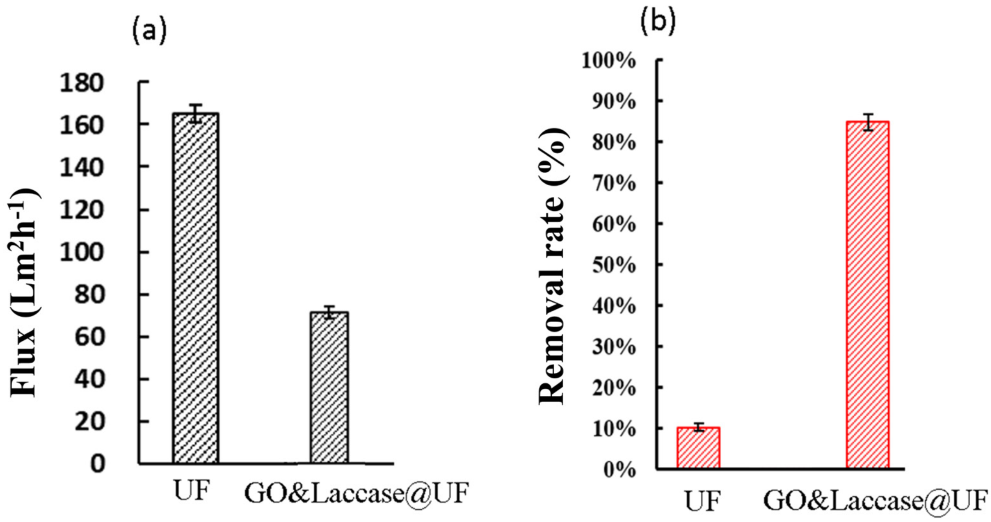

Figure 3. Flux (a) and colority removal rate (b) of different membranes.

Table I. COD and colority of permeate obtained from different membranes.

Permeate/Feed	COD (mg/L)	Colority
Feed	200	59
UF permeate	200	53
GO&Laccase@UF permeate	30~60	9

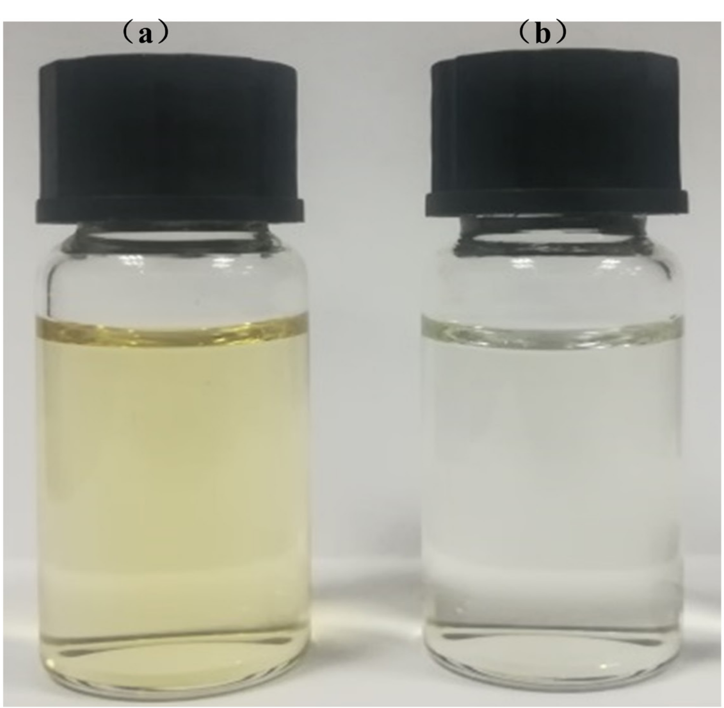

Figure 4. Photos of permeate obtained from filtration with UF (a) and GO&Laccase@UF (b).

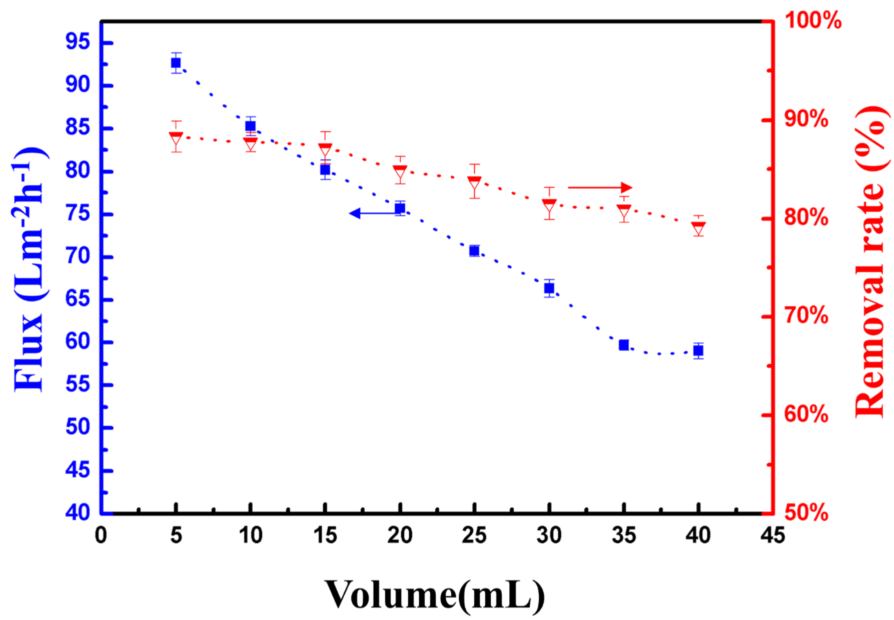

Figure 5. Flux and colority removal rate of GO-BDM@UF under continuous filtration of 50ml wastewater.

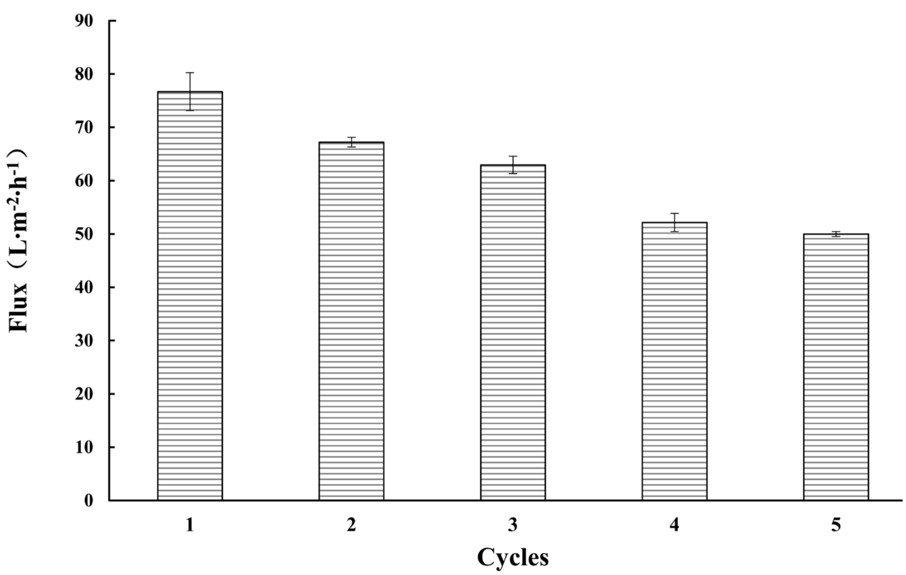

Figure 6. Permeation flux of BDM GO&Laccase@UF under 5 consecutive cycles.

CONCLUSIONS

BDM membrane, GO&Laccase@UF, was fabricated by immobilizing of GO and laccase on UF membrane for soy sauce wastewater treatment. Results showed that, compared to pristine UF membrane, BDM had great capacity for COD and colority removal, probably due to the higher laccase activity with existence of GO. The removal rate of colority reached ~80%. The COD of permeate from BDM was reduce to 30~60 mg/L, and the colority was ~9, leading to an achievement of standard for reuse water. The performance of one GO&Laccase@UF membrane for 5 consecutive cycles use evidenced the effect of membrane fouling on permeate flux. However, the removal ability remained acceptable after 5 cycles. This study may provide an innovative method for treatment of wastewater from food industry.

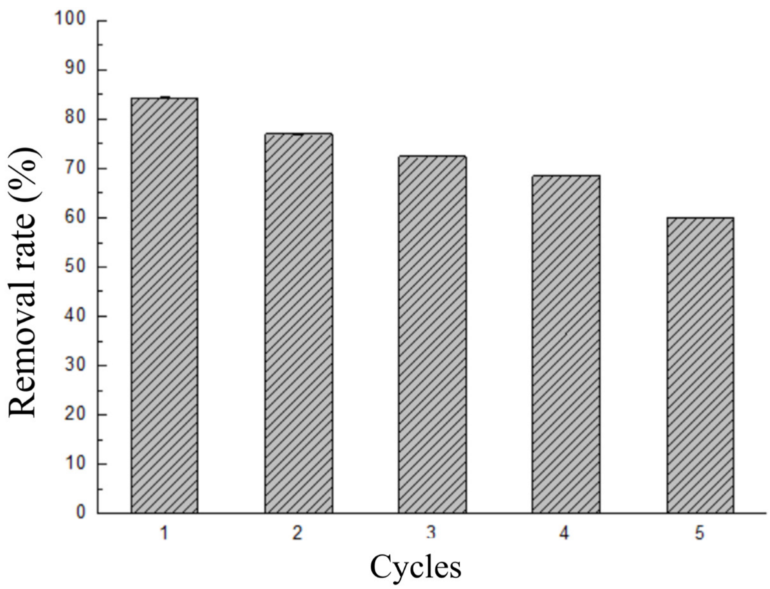

Figure 7. Colority removal rate of BDM GO&Laccase@UF under 5 consecutive cycles.

Table II. COD and colority of the permeate in five cycles by BDM GO&Laccase@UF.

Cycles	COD (mg/L)	Colority
1	30~60	9
2	30~60	14
3	30~60	16
4	30~60	19
5	30~60	24

Acknowledgments

The authors would like to acknowledge the financial support from the National Natural Science Foundation of China (51908136).

REFERENCES

ANAM K, HABIBI MS, HARWATI TU & SUSILANINGSIH D. 2012. Photofermentative hydrogen production using Rhodobium marinum from bagasse and soy sauce wastewater. Int J Hydrogen Energ 37: 15436-15442.

BATTISTI AC, SANTOS HMMFD, ALBERTON JS, GOMES LMF, RAUPP LK, GRACIANO MR, OLIVEIRA PEDE, SILVA JUNIOR JLD & DIAS RCE. 2019. Leachate and vinasse used in a biological process combined with Fenton's reaction: a green method for treatment of textile effluents. An Acad Bras Cienc 91: e20181156. https://doi.org/10.1590/0001-3765201920181156.

BHATTACHARJEE C, SAXENA VK & DUTTA S. 2017. Fruit juice processing using membrane technology: A review. Innov Food Sci Emerg 43: 136-153.

BUTLER R & MACCORMICK T. 1996. Opportunities for decentralized treatment, sewer mining and effluent re-use. Desalination 106: 273-283.

CAMPOS PR, MODENES AN, ESPINOZA-QUINONES FR, TRIGUEROS DE, BARROS ST & PEREIRA NC. 2016. Improvement on the concentrated grape juice physico-chemical characteristics by an enzymatic treatment and Membrane Separation Processes. An Acad Bras Cienc 88: 423-436.

CHEN W, MO J, DU X, ZHANG Z & ZHANG W. 2019. Biomimetic dynamic membrane for aquatic dye removal. Water Res 151: 243-251.

CHINA MOEAEOTPSRO. 1989. Water quality-Determination of Colority. GB 11903-11989.

DIKIN DA, STANKOVICH S, ZIMNEY EJ, PINER RD & RUOFF RS. 2007. Preparation and characterization of graphene oxide paper. Nature 448: 457-460.

DONG SP, XIAO HF, HUANG QG, ZHANG J, MAO L & GAO SX. 2016. Graphene Facilitated Removal of Labetalol in Laccase-ABTS System: Reaction Efficiency, Pathways and Mechanism. Scientific Reports 6.

FU H & ZHU D. 2013. Graphene oxide-facilitated reduction of nitrobenzene in sulfide-containing aqueous solutions. Environ Sci Technol 47: 4204-4210.

GARCIA-SERRANO P, ROMERO C, BRENES M & GARC A-GARC AP. 2019. Enrichment in phenolic compounds of black ripe olives through nano-filtration and vacuum evaporation techniques. Innov Food Sci Emerg 51: 73-79.

GRIMI N, VOROBIEV E, LEBOVKA N & VAXELAIRE J. 2010. Solid–liquid expression from denaturated plant tissue: Filtration–consolidation behaviour. J Food Eng 96: 29-36.

HARUN HA, HAMID H, SUNAR NM, AHMAD FH, ANUAR AN, ROSMAN NH & OTHMAN I. 2018. Performance of Aerobic Granular Sludge in Treating Soy Sauce Wastewater at Different Hydraulic Retention Time. Int J Eng Technol 7: 564-568.

HYUN-HEE J, GYU-TAE S & DAE-WOON J. 2017. Investigation of Oxidation Methods for Waste Soy Sauce Treatment. Int J Environ Res Public Health 14: 1190.

JANG H-H, SEO G-T & JEONG D-W. 2018. Advanced Oxidation Processes and Nanofiltration to Reduce the Color and Chemical Oxygen Demand of Waste Soy Sauce. Sustainability 10: 2929.

LI S, LUO J, HANG X, ZHAO S & WAN Y. 2019. Removal of polycyclic aromatic hydrocarbons by nanofiltration membranes: Rejection and fouling mechanisms. J Membrane Sci 582: 264-273.

LIU D, VOROBIEV E, SAVOIRE R & LANOISELL J-L. 2013. Comparative study of ultrasound-assisted and conventional stirred dead-end microfiltration of grape pomace extracts. Ultrason Sonochem 20: 708-714.

LOGINOV M, SAMPER F, SAN-GUIZIOU G, SOBISCH T, LERCHE D & VOROBIEV E. 2017. Centrifugal ultrafiltration for determination of filter cake properties of colloids. J Membrane Sci 536: 59-75.

LUO J, DING L, WAN Y & JAFFRIN MY. 2012a. Threshold flux for shear-enhanced nanofiltration: Experimental observation in dairy wastewater treatment. J Membrane Sci 409-410: 276-284.

LUO J, DING L, WAN Y, PAULLIER P & JAFFRIN MY. 2010. Application of NF-RDM (nanofiltration rotating disk membrane) module under extreme hydraulic conditions for the treatment of dairy wastewater. Chem Eng J 163: 307-316.

LUO J, DING L, WAN Y, PAULLIER P & JAFFRIN MY. 2012b. Fouling behavior of dairy wastewater treatment by nanofiltration under shear-enhanced extreme hydraulic conditions. Sep Purif Technol 88: 79-86.

LV S, LIANG Z, LI X, FAN H & ZEN Y. 2016. Investigation on biomass performance of a submerged membrane bioreactor for treating soy sauce wastewater. Environ Prot Eng 42: 135-148.

NOVAK MJ, PATTAMMATTEL A, KOSHMERL B, PUGLIA M, WILLIAMS C & KUMAR CV. 2016. “Stable-on-the-Table” Enzymes: Engineering the Enzyme-Graphene Oxide Interface for Unprecedented Kinetic Stability of the Biocatalyst. Acs Catalysis 6: 339-347.

PARHIZKAR N, SHAHRABI T & RAMEZANZADEH B. 2017. A new approach for enhancement of the corrosion protection properties and interfacial adhesion bonds between the epoxy coating and steel substrate through surface treatment by covalently modified amino functionalized graphene oxide film. Corros Sci 123: 55-75.

SITTIWAT L, ROUNGDAO M, APINYA A & AMARET B. 2001. Roles of the Maillard reaction in browning during moromi process of Thai soy sauce. J Food Process Pres 23: 149-162.

ZHANG H, LUO J, LI S, WOODLEY JM & WAN Y. 2019. Can graphene oxide improve the performance of biocatalytic membrane? Chem Eng J 359: 982-993.

ZHONG W ET AL. 2021. Resources recycle of traditional Chinese medicine (TCM) wastewater 1: Effectiveness of the UF-MD hybrid system and MD process optimization. Desalination. 504: 114953.

ZHU Z, CHEN Z, LUO X, LIANG W, LI S, HE J, ZHANG W, HAO T & YANG Z. 2020. Biomimetic dynamic membrane (BDM): Fabrication method and roles of carriers and laccase. Chemosphere 240: 124882.

ZHU Z, LUO X, YIN F, LI S & HE J. 2018. Clarification of Jerusalem Artichoke Extract Using Ultra-filtration: Effect of Membrane Pore Size and Operation Conditions. Food Bioprocess Tech 11: 864-873.

ZHU Z & MHEMDI H. 2016. Dead end ultra-filtration of sugar beet juice expressed from cold electrically pre-treated slices: Effect of membrane polymer on fouling mechanism and permeate quality. Innov Food Sci Emerg 36: 75-82.

How to cite

WANG F, LUO X, GUO J & ZHANG W. 2021. Treatment of soy sauce wastewater with biomimetic dynamic membrane for colority removal and chemical oxygen demand lowering. An Acad Bras Cienc 93: e20210425. DOI 10.1590/0001-3765202120210425.

Manuscript received on March 22, 2021;
accepted for publication on June 22, 2021

FANG WANG[1,2]
https://orcid.org/0000-0003-2801-7982

XIAO LUO[3]
https://orcid.org/0000-0001-9002-9947

JIA GUO[1,2]
https://orcid.org/0000-0002-6422-2302

WENXIANG ZHANG[4,5]
https://orcid.org/0000-0001-9771-8884

[1]School of Chemical Engineering and Pharmacy, Wuhan Institute of Technology, 430205, Wuhan, China

[2]Key Laboratory of Green Chemical Process of Ministry of Education, Wuhan Institute of Technology, 430205, Wuhan, China

[3]College of Food Science and Engineering, Wuhan Polytechnic University, 430023, Wuhan, China

[4]Department of Civil and Environmental Engineering, Faculty of Science and Technology, University of Macau, 999078, Macau, China

[5]School of Environmental Science and Engineering, Guangdong University of Technology, 510006, Guangzhou, China

Correspondence to: **Jia Guo and Wenxiang Zhang**
E-mail: guojia@wit.edu.cn ; wxzhang@edu.mo

Author contributions

Dr. Fang Wang performed experiments and wrote the manuscript; Mr. Xiao Luo performed experiments; Prof. Jia Guo– commented and revised the manuscript; Dr. Wenxiang Zhang conceived and designed the experiments, revised the manuscript.