



Fabrication of Wood-Plastic Composites as Biocarriers in Moving Bed Biofilm Reactors

N.D. VU^{1,2,*}, T.T.T. BUI¹, Q.T. PHAM¹, M.N. NGUYEN¹, V.T. NGUYEN¹ and T.A.H. NGUYEN³

¹Faculty of Chemistry, VNU University of Science, Vietnam National University, Hanoi, Vietnam

²Research Center for Environmental Technology and Sustainable Development, VNU University of Science, Vietnam National University, Hanoi, Vietnam

³Master's Program in Environmental Engineering, VNU Vietnam Japan University, Vietnam National University, Hanoi; Luu Huu Phuoc St., Nam Tu Liem Dist., Hanoi, Vietnam

*Corresponding author: Tel: +84 0936187622; E-mail: vungocduy@hus.edu.vn

Received: 12 September 2021;

Accepted: 17 November 2021;

Published online: 20 April 2022;

AJC-20757

In present study, a novel biocarrier was fabricated from wood and high density polyethylene (HDPE) using a single screw extruder. The effect of wood:plastic mass ratio on physico-chemical properties of the obtained wood plastic composite (WPC) was evaluated. While the tensile and flexural strengths were decreased, the sample density was increased with higher wood contents. The wood:plastic mass ratio of 1:1 was considered as the best for the production of WPC biocarriers. The role of this material in moving bed biofilm system was tested in a batch mode reactor having volume of 2 L with 20% filling by the biocarrier. The treatment efficiencies of organic matter, ammonia and phosphate were enhanced nearly two times. The results are attributed to heterogenous and porous surface of WPC, which enhances bacteria adhesion and pollutant removal. It demonstrates that WPC can be a potential biocarrier for use in moving bed biofilm reactors (MBBRs).

Keywords: Biocarrier, Wood plastic composite, Moving bed biofilm reactor, Wastewater treatment, Kinetics.

INTRODUCTION

Activated sludge process (ASP) has been playing an important role in wastewater treatment to remediate organic matters and other pollutants [1-3]. In this method, microorganisms metabolize organic compounds to derive energy and synthesize new cells under aerobic conditions [4]. During operation, most nutrients to feed micro-organisms are available in wastewaters, so the main cost of ASP is relevant to the energy consumption for aeration and oxygen supply. Therefore, ASP is one of the most environmentally friendly water treatment techniques, which is still paid much attention [5]. However, this traditional biological process has a main disadvantage of slow treatment rates that leads to long retention time of wastewaters in treatment systems [6]. This inherent characteristic limits the application of ASP in small areas due to its requirement of large construction spaces. To overcome this drawback, ASP should be modified to increase the rate of pollutants treatment. Recently, supporting materials have been used as biocar-

riers, which can freely move in bioreactors under agitation (aeration or mechanical mixing) [7,8]. In biological reactors, biocarriers supply surface and space for microorganisms to attach and accumulate [8]. That is the reason to name this process as moving bed biofilm reactor (MBBR). It is reported that MBBR has a considerable advantage over activated sludge process such as high treatment rate and compact design [9,10]. Nowadays, a variety of biocarriers have been produced and commercialized such as K1, K2, K3, Natrrix, biofilm-chip from AnoxKaldness (Sweden), Flocor RS and Flocor RM from FLOCOR-Henderson Plastics Ltd (UK), BioSphere and Spira from Seimens (USA) [11-13]. These products are mainly made of plastics (PE, HDPE, PP). In Vietnam, a limited quantity of these products is annually imported and sold with high prices. In order to reduce their cost, thereby enabling the wider application of MBBR, this study aims at fabricating a novel biocarrier, which was derived from wood-plastic composite and evaluating its wastewater treatment performance in the lab-scale, batch mode MBBR.

EXPERIMENTAL

Preparation and characterization of wood-plastic composite (WPC): In this study, WPC materials were manufactured from saw dust and high density polyethylene (HDPE). The Oak saw dust was collected from Dai Mo carpentry village, Tu Liem, Hanoi, Vietnam. The saw dust was grounded into powder, screened through a 0.2 mm sieve and heated at 105 °C until it was dried. HDPE (density = 0.97 g/cm³) was collected from Minh Khai plastic village, Van Lam, Hung Yen, Vietnam.

Composite samples were prepared using a single screw extruder (from Industrial DILONG, China). The extruder was set to work at mixing rates in the range of 85-90 rpm and temperature of 160 °C, which were considered as the best mixing conditions *via* the screening experiments. Five different wood: plastic mass ratios were investigated for WPC preparation as presented in Table-1.

TABLE-1

WOOD:PLASTIC RATIOS FOR COMPOSITE FABRICATION

Sample name	S30	S40	S50	S60	S70
Wood powder, % by weight	30	40	50	60	70
HDPE, % by weight	70	60	50	40	30

The effect of wood:plastic ratios on the physico-chemical properties of obtained composites was evaluated by measuring tensile/flexural strengths, density and SEM.

Tensile/flexural strengths: After mixing, the materials were compressed in flat form with a thickness of 3-4 mm (using Carver CMG 30 H, compressing force = 5 tons, temperature = 150-160 °C). The attained samples were cut into standard pieces (L × W = 150 × 20 mm and L × W = 80 × 10 mm) for measurement of tensile strength and flexural strengths, respectively. The strengths were determined with Zwick Z2.5 machine (Germany) at rate of 50 mm/min, whereas flexural strengths were measured using ASTM DIN 53503 standard. Each measurement was triplicated to get an average value.

Density measurement: Density of WPC was measured using the water displacement method. Accordingly, a specimen of WPC with a given weight (m = 20 g) was dipped into 100 mL volumetric cylinder containing 50 mL water. The volume of the tested specimen was equivalent to the change of water level in the cylinder. Then density (d) was calculated by following equation:

$$d = \frac{m}{V_2 - V_1} \quad (1)$$

where m is the weight of the tested specimen (g); V₁ and V₂ are water volumes in the cylinder before and after adding the specimen (mL), respectively.

SEM: The microscopic morphology of composite samples was observed with Tabletop Microscopes TM4000II, Hitachi, Japan.

Moving bed biofilm reactor experiment

Biocarrier preparation: One of the most important characteristics of a material for being used as a biocarrier is

the density. The density of the material should be lighter than that of water to ensure the free movement of biocarriers in the solution. This is the selection criterium of the optimum wood: plastic ratio for the WPC production.

The HDPE biocarrier was also prepared for comparison with WPC biocarrier. Both biocarriers were made using the single screw extruder with a 2.5 mm round hole die. The formed extrudate was then cut to form pellets with a diameter of 2.5 mm and a height of 3 mm (Fig. 1).



Fig. 1. Appearance of HDPE (A) and WPC (B) biocarriers

Bacteria source: To prepare for MBBR experiments, a bacteria source was produced by raising bacterial germ (obtained from Microtechnology and Environment Joint Stock Company, Vietnam) in a 10 L reactor. A 100 g of germ was dissolved in 10 L of tap water and continuously aerated using a Hailea ACO 208 aerator (25 W). The sludge solution was fed once per day with a nutrient solution, which contained sugar, ammonia and phosphate with the COD:N:P ratio of 100:5:1 and the initial COD value of approximately 500 mg/L. Every day, soluble COD and total COD values were analyzed. Subsequently, bacteria concentration was calculated by the difference between the total COD and soluble COD values. The sludge was transferred into moving bed biofilm reactors when the bacteria concentration reached 3500 mg COD/L.

Kinetic experiment: The enhancement of wastewater treatment in MBBR by using WPC as biocarriers was evaluated. For comparison purpose, 02 lab-scale MBBRs were set up, one MBBR was filled with WPC pellets, whereas the other MBBR was filled with HDPE pellets. The volume of biocarriers in one reactor accounted for 20% of its volume. The reactors were made of transparent PVC tube with a diameter of 100 mm and a height of 400 mm. Oxygen was supplied using Hailea ACO 208 aerator (25 W) with an air rate of 5 L/min. These systems were run in the batch mode with bacteria concentration of 3500 ± 150 mg COD/L. In the first 2 weeks, a nutrient solution (COD:N:P ratio of about 100:5:1) was added to support the adhesion and growth of bacteria on the surface of biocarriers. This step was to maintain the constant bacteria concentration.

After starting period, the kinetics of COD, NH₄⁺, PO₄³⁻ removal were investigated. A mixture of nutrients was fed to the bacteria in reactors before taking samples every day. In the COD treatment experiment, the initial COD value was chosen to be around 1000 mg/L. The pH of biological solution was kept to be in the range of 7.0-7.5 by using 1 M sulfuric acid or 1 M sodium hydroxide. Organic treatment efficiency was evaluated by taking samples at time intervals of 20 min in 1 h after

adding nutrients. Ammonia and phosphate are normally removed at lower rates as compared to COD, hence their concentrations were measured in every 2 h.

Analytical methods: To analyze the remaining concentrations of organic, nitrogen and phosphorous in reactors, samples were filtered through a 0.45 μm cellulose acetate membrane filter (obtained from Advantec MFS) after collection. The COD and NH_4^+ concentrations were analyzed using 5220D and 4500 methods-Standard Methods for the Examination of Water and Wastewater (20th edition). The phosphate ions was measured using 365.3 method-USEPA. Each measurement was duplicated to take average data. Bacteria concentration (expressed by mg COD/L) was determined by subtracting dissolved COD value from total COD value.

RESULTS AND DISCUSSION

Characterization of wood-plastic composite: Specimens for determining tensile and flexural strengths are given in Fig. 2. The obtained results of the strengths for different wood:plastic ratios are presented in Fig. 3.



Fig. 2. Samples wood-HDPE composites for determining mechanical strengths

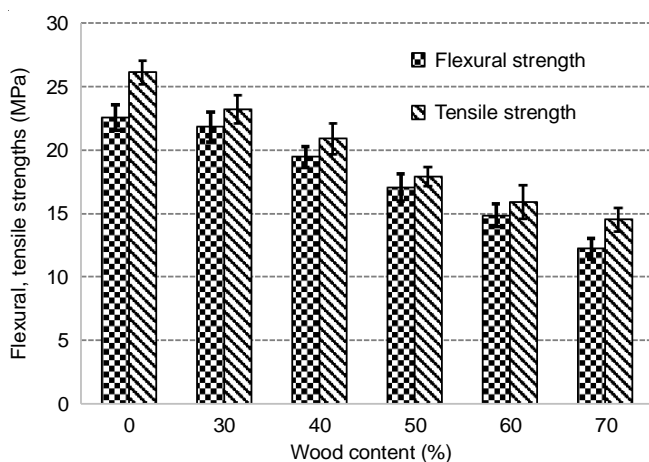


Fig. 3. Flexural/tensile strengths of WPC samples at different wood content

It is clear from Fig. 3 that both tensile and flexural strengths decrease as increasing wood contents in the samples. Tensile strength reduces 44% from 26.1 down to 14.5 MPa, flexural strength reduces nearly the same size (45%) from 22.6 down to 12.2 MPa. The impact of wood content on the strengths can

be explained by the incompatibility between wood and HDPE. HDPE is a hydrophobic material, while wood has hydrophilic property that causes weak adhesion between two components [14]. However, these strength values are good enough for using WPC as a biocarrier, which is suspended and does not suffered strong forces when moving in water.

Densities of composite samples with different ratios are given in Table-2. It can be seen that the density is proportional to wood content. The S30 and S40 samples were observed to be lighter than HDPE. This result is due to the presence of air bubbles inside these samples during mixing. The S50 sample has nearly the same density with HDPE, $d = 0.97 \text{ g/cm}^3$. This value meets requirement on density ($d = 0.95\text{-}0.97 \text{ g/cm}^3$) for a material to be suspended in the biological solution. Hence, wood:HDPE mass ratio of 1:1 (or 50%:50%) was chosen to preparing WPC biocarrier.

TABLE-2
DENSITY OF COMPOSITE SAMPLES
WITH DIFFERENT WOOD CONTENTS

Sample name	S30	S40	S50	S60	S70
Density (g/cm^3)	0.89 ± 0.02	0.94 ± 0.02	0.97 ± 0.02	1.10 ± 0.03	1.14 ± 0.03

Morphology of HDPE and WPC (50% wood) biocarriers are presented in Fig. 4. While HDPE reveals a rather smooth surface, WPC exhibited porous structure. This characteristic can be considered as an advantage of WPC over HDPE as biocarriers since it favours the accumulation of bacteria in MBBRs.

MBBR treatment: Two reactors filled with HDPE and WPC biocarriers were run in the same conditions as given in Table-3. For each target pollutant, the kinetic experiments was triplicated and the obtained data are presented as follows:

TABLE-3
CONDITIONS FOR BIOLOGICAL EXPERIMENTS IN MBBRs

Parameters	Value
Reaction volume (L)	2
Bacteria concentration (mg COD/L)	3500 ± 150
Biocarrier filling (vol. %)	20
Aeration rate (L/min)	5
pH	7.0-7.5
Temperature ($^{\circ}\text{C}$)	26 ± 1
Initial COD (mg COD/L) for organic treatment experiment	1000 ± 80
Initial NH_4^+ (mg N/L) for ammonia treatment experiment	30 ± 1.5
Initial PO_4^{3-} (mg P/L) for phosphate treatment experiment	5 ± 0.5

Organic removal: The kinetics of organic removal was investigated in 1 h after adding nutrients to the reacting reactors. The variations of dissolved COD values *versus* time are presented in Fig. 5a for HDPE biocarrier and Fig. 5b for WPC. The obtained data confirm that the system worked stable in triplicated experiments. A faster COD decrease was observed in Fig. 5b. After 1 h, the COD treatment efficiency of WPC based MBBR reached 86%, which was higher than that of HDPE based MBBR (67%). Since two MBBRs were operated in the

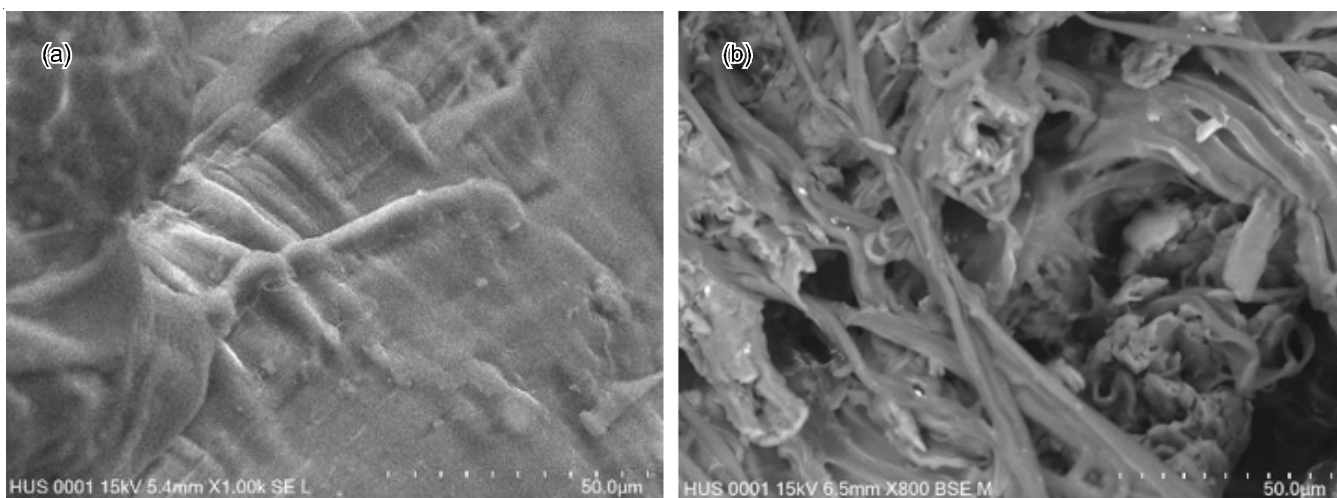


Fig. 4. SEM images of HDPE (a) and WPC (b) biocarriers

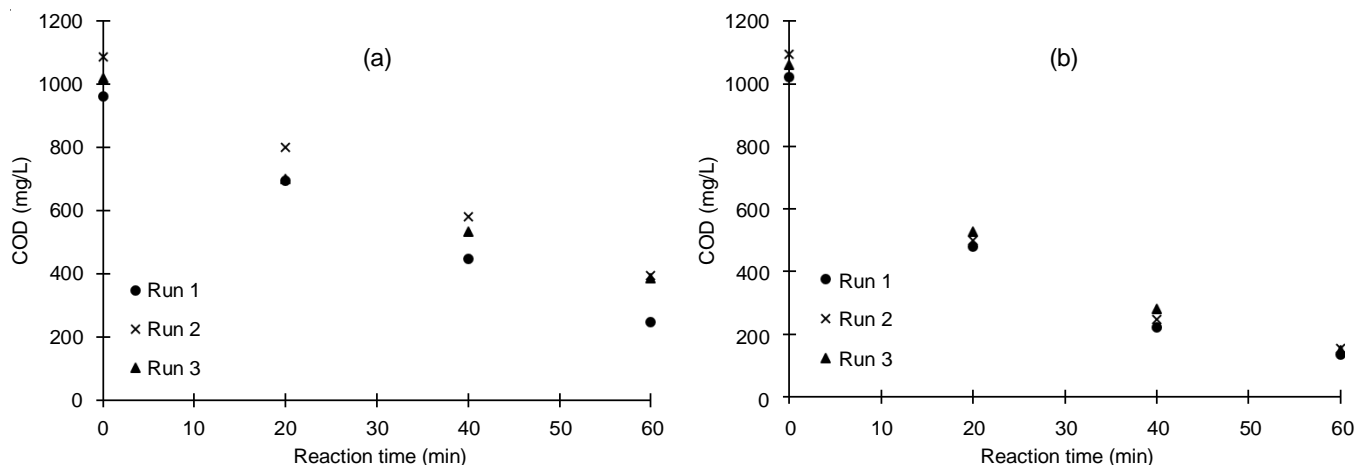


Fig. 5. Changes of COD values over the time in the MBBRs filled with HDPE (a) and WPC (b) biocarriers

same conditions except for the biocarriers, the difference in their COD reduction rates can be attributed to the characteristics of biocarriers. Specifically, this can be explained by the fact that the higher roughness/porosity of WPC as compared to HDPE led to the better attachment of bacteria on the WPC surface. Bacterial adhesion on the biomaterial surface plays an important role in forming biofilms. It is reported that the bacteria attachment is influenced by many properties of the carrying materials, such as surface roughness, chemical composition, surface charge and hydrophobicity [15]. A rough surface promotes the bacteria colonization and protects the biofilm from the moving forces [15,16]. Moreover, the roughness results in a large surface area for bacteria adhesion. Fig. 4 reveals that WPC has a porous surface structure and higher roughness degree as compared to HDPE. In respect of interaction, since the heterotrophic bacteria, which are responsible for organic treatment, are hydrophobic, they are favoured to interact with non-polar surfaces [17]. In the WPC, HDPE was mixed well with wood powder to create both hydrophobic (HDPE) and hydrophilic (wood powder) surfaces. Hydrophobicity and porosity made WPC to be a good material for heterotrophic bacteria to adhere and develop.

To quantify the different between two tested biocarriers, a simple kinetic model, the first-order kinetic law, was applied to model COD removal:

$$\ln\left(\frac{\bar{C}}{C_0}\right) = -kt \quad (2)$$

In which: \bar{C}_0 and \bar{C} are average COD values at initial and time t ; k is the first order rate constant.

The plots of $\ln\left(\frac{\bar{C}}{C_0}\right)$ versus t are presented in Fig. 6. The obtained straight lines indicate that the first-order kinetic model is appropriate for describing the COD treatment in this study. The rate constants were slopes of these lines, which were 0.0343 and 0.0177 min^{-1} for WPC and HDPE biocarriers, respectively. It means that the reaction rate of WPC was two-fold higher than that of HDPE.

Ammonia removal: In aerobic conditions, ammonia is not only utilized to build new biomass but also biologically oxidized to nitrate. Nitrification occurs in 2 steps by ammonia oxidizing bacteria (AOB) and nitrite oxidizing bacteria (NOB) [18]:

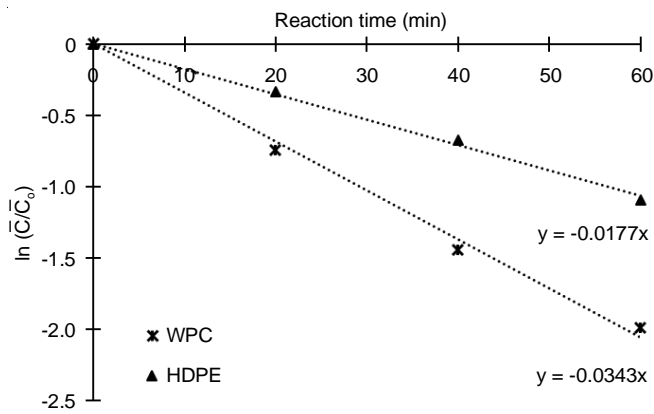
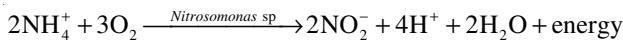
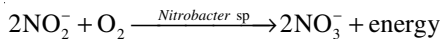


Fig. 6. Plots of $\ln\left(\frac{\bar{C}}{C_0}\right)$ versus reaction time for COD removal

Step-1:



Step-2:



The treatment of ammonia in MBBR is mainly contributed by these kinds of bacteria. Unlike hydrophobic property of organic oxidizing bacteria, both AOB and NOB were reported to be hydrophilic [19]. Wood consists of cellulose, hemicellulose and lignin, which contain many polar groups (-OH, -COOH) in their molecular structures. Therefore, wood component is expected to make WPC to be a good biocarrier for AOB and NOB. To confirm this assumption, experiments with the two prepared biocarriers (WPC and HDPE) were carried out in the same conditions with initial NH_4^+ concentration of about 30 mg N/L. Biomass concentration was kept to be stable (about 3500 mg COD/L). Sugar and phosphate concentrations were adjusted to remain COD:N:P ratio of 100:5:1. In this experiment, variation of ammonia concentration was observed in 2 h. Kinetic data are showed in Fig. 7. It can be seen that a faster treatment rate was obtained with WPC biocarrier. The average NH_4^+ removal efficiency of the WPC based MBBR after 2 h was 60%, which was nearly two-fold higher than that of HDPE.

This clearly indicates the advantage of WPC over HDPE as biocarriers.

The better NH_4^+ treatment can be explained by the presence of wood in the WPC biocarrier. Previous studies reported that nitrification rate on the hydrophilic surface was higher than that on the hydrophobic surface [19,20]. In another research, Khan *et al.* [21] evaluated the effects of four different plastics on ammonia oxidation to form nitrate. Their results showed a positive correlation between surface hydrophilicity and total biomass attachment. In present study, WPC was supposed to have heterogeneous surface due to the mixture of two parent components. Wood created the hydrophilic property to attach ammonia oxidation bacteria. Moreover, the porosity of WPC also gives a large surface area and space for bacterial colonization.

Phosphate removal: Phosphate treatment was tested in the same conditions as ammonia. Fig. 8 presents the decrease of phosphate concentrations in two parallel MBBRs. A similar trend to the ammonia removal was obtained for phosphate removal. When WPC was used as biocarriers, the phosphate removal rate of the MBBR was higher. After 2 h of reaction, the average phosphate removal efficiencies reached 60% and 20% for the WPC and HDPE based MBBRs, respectively.

As reported earlier [22,23], the phosphate was mostly treated by phosphorous accumulating organisms (PAOs) in biological processes. These organisms only grow in some certain conditions. Therefore, traditional activated sludge systems ineffectively remove phosphate from wastewater due to the lack of PAOs. Recently, granular sludge was discovered to accumulate phosphate well [24]. Bassin *et al.* [25] reported that PAOs develop in anoxic zone with the granular structure. In this study, it is supposed that anoxic zones were formed on the biocarrier surface for PAOs growth as the result of WPC porosity.

Conclusion

The wood-HDPE composite was fabricated and applied as a biocarrier in moving bed biofilm reactors (MBBRs). To begin with, the effect of wood:HDPE ratio on the physico-chemical properties of the WPC was evaluated. When wood

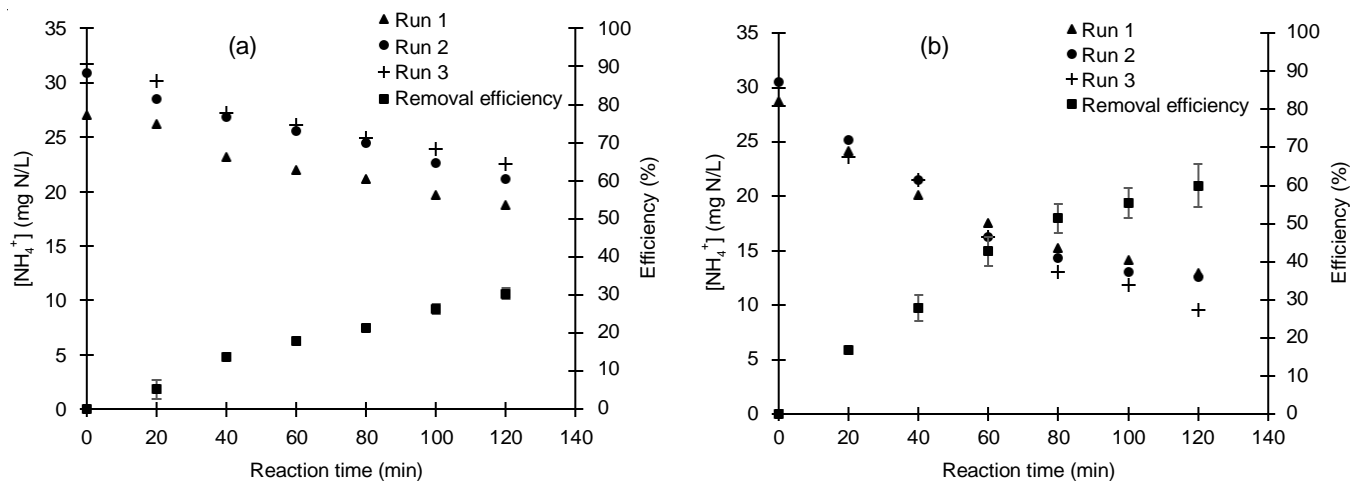


Fig. 7. Ammonia removal in MBBRs using HDPE (a) and WPC (b) biocarriers

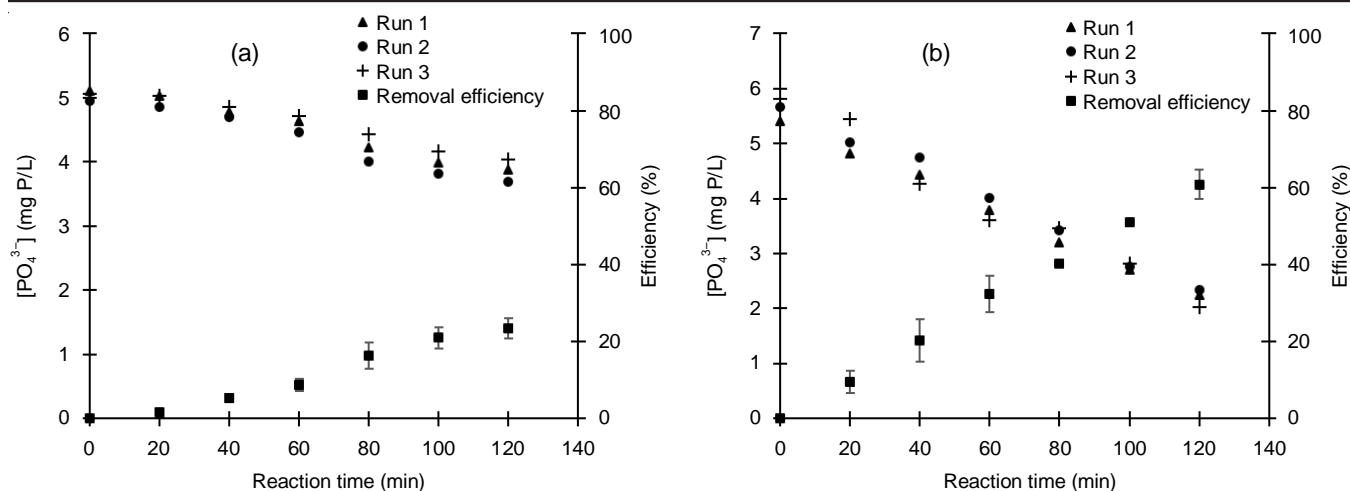


Fig. 8. Phosphate removal in MBBRs using HDPE (a) and WPC (b) biocarriers

content was changed from 30% to 70%, the WPC density increased from 0.89 to 1.14 g/cm³. The optimal wood content of 50% resulted in the WPC density of 0.97 g/cm³, which is suitable for being used as a biocarrier. This WPC revealed a porous structure, whereas HDPE exhibited a non-porous surface. In the batch mode and with 20% of the reactor volume filled with biocarriers, the WPC based MBBR demonstrated almost two-fold greater removal efficiencies of COD, NH₄⁺ and PO₄³⁻ than the HDPE based MBBR. This can be attributed to the heterogeneous and porous surface of WPC, which have both hydrophobic and hydrophilic properties, thereby enabling attachment of different bacteria responsible for the treatment of various pollutants. Further researches should be conducted on the optimization of the shape, configuration and size of WPC biocarriers. Additionally, recycling of wood and plastic wastes as the WPC biocarriers is expected to reduce the solid waste disposal requirement while enhance wastewater decontamination.

ACKNOWLEDGEMENTS

The authors are grateful for the financial support from Vietnam National University, Hanoi (Research project No QG.19.07). Thanks are also due to Master's program in the Environmental Engineering, VNU Vietnam Japan University and Vietnam National University, Hanoi for technical support.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

- O. Modin, F. Persson, B.M. Wilen and M. Hermansson, *Crit. Rev. Environ. Sci. Technol.*, **46**, 635 (2016); <https://doi.org/10.1080/10643389.2016.1149903>
- H. Guven, H. Ozgun, M.E. Ersahin, R.K. Dereli, I. Sinop and I. Ozturk, *Environ. Sci. Pollut. Res.*, **26**, 1770 (2019); <https://doi.org/10.1007/s11356-018-3665-8>
- M. Sarkar, V.K. Sangal and H. Bhunia, *Environ. Eng. Res.*, **25**, 400 (2020); <https://doi.org/10.4491/eer.2019.114>
- R. Chen, L.F. Ren, J. Shao, Y. He and X. Zhang, *RSC Adv.*, **7**, 2841 (2017); <https://doi.org/10.1039/C7RA09225C>
- D. Orhon, *J. Chem. Technol. Biotechnol.*, **90**, 608 (2015); <https://doi.org/10.1002/jctb.4565>
- M.A. Musa and S. Idrus, *Sustainability*, **13**, 4656 (2021); <https://doi.org/10.3390/su13094656>
- H.T. Nhut, N.T.Q. Hung, T.C. Sac, N.H.K. Bang, T.Q. Tri, N.T. Hiep and N.M. Ky, *Environ. Eng. Res.*, **25**, 652 (2020); <https://doi.org/10.4491/eer.2019.285>
- Y. Dong, S.Q. Fan, Y. Shen, J.X. Yang, P. Yan, Y.P. Chen, J. Li, J.S. Guo, X.M. Duan, F. Fang and S.Y. Liu, *Sci. Rep.*, **5**, 12400 (2015); <https://doi.org/10.1038/SREP12400>
- S.M. Safwat, *Int. J. Res.*, **6**, 85 (2019);
- J.D. Rouse, O. Burica, M. Strazar and M. Levstek, *Wat. Sci. Technol.*, **55**, 135 (2007); <https://doi.org/10.2166/wst.2007.251>
- A. Barwal and R. Chaudhary, *Rev. Environ. Sci. Biotechnol.*, **13**, 285 (2014); <https://doi.org/10.1007/s1157-014-9333-7>
- L. Deng, W. Guo, H.H. Ngo, X. Zhang, X.C. Wang, Q. Zhang and R. Chen, *Bioresour. Technol.*, **208**, 87 (2016); <https://doi.org/10.1016/j.biortech.2016.02.057>
- S.K. Al-Amshawee, M.Y. Yunus and A.A. Azoddein, *IOP Conf. Ser. Mater. Sci. Eng.* **736**, 072006 (2020); <https://doi.org/10.1088/1757-899X/736/7/072006>
- R. Gu, B.V. Kokta, D. Michalkova, B. Dimzoski, I. Fortelny, M. Slouf and Z. Krulis, *J. Reinf. Plast. Compos.*, **29**, 1 (2010); <https://doi.org/10.1177/0731684410378543>
- M. Katsikogianni and Y.F. Missirlis, *Eur. Cells Mater.*, **8**, 37 (2004); <https://doi.org/10.22203/ecm.v008a05>
- M. Gharechahi, H. Moosavi and M Forghani, *J. Biomater. Nanobiotechnol.*, **3**, 541 (2012); <https://doi.org/10.4236/jbnt.2012.324056>
- A. Krasowska and K. Sigler, *Front. Cell. Infect. Microbiol.*, **4**, 1 (2014); <https://doi.org/10.3389/fcimb.2014.00112>
- H. Fujitani, A. Kumagai, N. Ushiki, K. Momiuchi and S. Tsuneda, *Front. Microbiol.*, **6**, 1159 (2015); <https://doi.org/10.3389/fmicb.2015.01159>
- Y.H. Kim, J.H. Cho, Y.W. Lee and W.K. Lee, *Biotechnol. Technol.*, **11**, 773 (1997); <https://doi.org/10.1023/A:1018460805328>
- M.M.T. Khan, L.K. Ista, G.P. Lopez and A.J. Schuler, *Environ. Sci. Technol.*, **45**, 1055 (2011); <https://doi.org/10.1021/es101389u>
- M.M.T. Khan, T. Chapman, K. Cochran and A.J. Schuler, *Water Res.*, **47**, 2190 (2013); <https://doi.org/10.1016/j.watres.2013.01.036>
- C. Tarayre, H.T. Nguyen, A. Brognaux, A. Delepierre, L.D. Clercq, R. Charlier, E. Michels, E. Meers and F. Delvigne, *Sensors*, **16**, 797 (2016); <https://doi.org/10.3390/s16060797>
- L.L. Blackall, G.R. Crocetti, A.M. Saunders and P.L. Bond, *Antonie van Leeuwenhoek*, **81**, 681 (2002); <https://doi.org/10.1023/a:1020538429009>
- R.J. Seviour, T. Mino and M. Onuki, *FEMS Microbio. Rev.*, **27**, 99 (2003); [https://doi.org/10.1016/S0168-6445\(03\)00021-4](https://doi.org/10.1016/S0168-6445(03)00021-4)
- J.P. Bassin, R. Kleerebezem, M. Dezotti and M.C.M. Loosdrecht, *Water Res.*, **46**, 3805 (2012); <https://doi.org/10.1016/j.watres.2012.04.015>