Desalination and Water Treatment
www.deswater.com

doi:10.5004/dwt.2021.27196

224 (2021) 144–153
June

Development of microbial biofilms on cellulosic fibers for organic matter removal in river water treatment

Wen-Pei Low[a,*], Mohd Fadhil Md Din[b], Fung-Lung Chang[a], Siti Nur Fatihah Binti Moideen[c], Yee Yong Lee[d], Santhana Krishnan[b]

[a]*Department of Civil Engineering, Faculty of Engineering and Quantity Surveying (FEQS), INTI International University, 71800 Nilai, Negeri Sembilan, Malaysia, emails: wenpei.low@newinti.edu.my (W.-P. Low), funglung.chang@newinti.edu.my (F.-L. Chang)*
[b]*Centre for Environmental Sustainability and Water Security (IPASA), Research Institute for Sustainable Environment (RISE), School of Civil Engineering, Faculty of Engineering, Universiti Teknologi Malaysia (UTM), Johor Bahru 81310, Malaysia, emails: mfadhil@utm.my (M.F.M. Din), kcsanthana@utm.my (S. Krishnan)*
[c]*Graduate School of Environmental Studies, Tohoku University, 6-6-06 Aza-Aoba, Aramaki, Aoba-ku, Sendai, Miyagi 980-8579, Japan, email: snfatihahm@gmail.com*
[d]*Department of Civil Engineering, Faculty of Engineering, Universiti Malaysia Sarawak, 94300 Kota Samarahan, Sarawak, email: yylee@unimas.my*

Received 4 September 2020; Accepted 22 February 2021

ABSTRACT

The present study focuses on the usage of natural cellulosic fibers like coconut fibers (CF) and oil palm fibers (OPF) as an organic substrate for biofilm formation in removing pollutants as opposed to numerous studies that utilized non-organic substrates like plastic and synthetic membrane. The corresponding adsorption ability was tested toward the organic matters (OM) removal in the contaminated river water. The experimental results showed that CF and OPF possessed a higher concentration of phenolic and alcoholic hydroxyl groups by hydrogen bonds have led to a thinner extracellular polymeric substance being formed. The rate at which OM is removed for biofilm attached on coconut fiber (BCF) and biofilm attached on oil palm fiber (BOPF) were identified to be 94.07% and 87.01%, respectively. At 3% outflow, the global mass transfer rate BCF and BOPF were 1.01 and 0.84 d^{-1}. Further to that, the internal mass transfer was found to have an effective diffusivity of pollutants to biofilm. Yet, the mass transfer decreases with the decrease of OM concentration in water. Therefore, it is evident that natural cellulosic fibers are highly effective alternative carriers that can be used for biofilm growth in removing excess concentration of OM in river water.

Keywords: Microbial biofilm; Cellulosic fibers; Organic matter; River water; Global mass transfer

1. Introduction

Over the years, research on a wide range of water treatment technologies and materials has increased dramatically in the scientific world. Biofilm research is one of the many branches of science and technology especially for water and wastewater treatment that has gained popular interest [1,2]. Unlike conventional water and wastewater treatment methods that require high energy cost, chemical consumption, and a large volume of disposal [3], the biofilm approach is considered to be relatively low cost yet simple [4,5]. However, biofilm formation can be disastrous depending on its microbial community structures and the location of the formation [6]. One of the disastrous conditions where the formation of biofilm accumulates is in the cooling towers [7], drinking water distribution systems [8],

* Corresponding author.

and in heat exchangers [9] which will cause heat transfer resistance or corrosion, thus affect the efficiency of the system. However, it is undeniable that biofilm is also useful and desirable for different types of the condition in bioremediation applications where the microorganisms can convert or degrade some toxic pollutants into less toxic forms [10]. In recent studies, the "good" biofilm applications for water treatment have been highlighted and further investigated in order to provide valuable input to the natural environment and society [11]. The popularity of using biofilm has undoubtedly increased, but the trend on the substrates transfer to biofilm is yet to be developed.

It is known that most of the biofilm growth is associated with solid surfaces [12]. The conventional methods used for biofilm formation focussed only on the plastic media, rock media, granular carriers, and synthetic membranes [13]. Moreover, the formation of biofilm is strongly dependent on the topography of the material [14], nutrient loading rate, solid retention time, and ambient temperatures [15]. However, among the various types of common biofilm carriers mentioned beforehand, natural materials could be an alternative material that has been overlooked by researchers. In fact, the high specific area and wetting ability with rich nutrients are essential factors that can enhance the microorganisms adhesion process [16].

Consequently, cellulosic agricultural waste materials are seeming like one of the most promising natural materials that possess potential biofilm formation ability. These include materials like rice husk, wheat husk, groundnut shells, coconut shells, oil palm shells, cotton seed hulls, and waste tea leaves, just to name a few [17–19]. The basic components of the cellulosic agricultural waste material include hemicellulose, lignin, extractives, lipids, proteins, simple sugars, water hydrocarbons, and starch-containing a variety of functional groups that facilitates the formation of biofilm [20]. In Malaysia, the agricultural sector is the backbone of the economy that contributed RM 99.5 billion to the gross domestic product (GDP) in the year 2018 [21]. Based on this study, oil palm is a major contributor in the agricultural sector to the GDP, which is 37.9% followed by other agricultural crops (25.1%) [21]. Besides, Malaysia is also the top 10 coconut-producing countries in the world where coconut is the fourth important crop after the oil palm, rubber, and rice [22,23]. The cultivation area of coconut is about 82,917 ha in the year 2017 and the per capita consumption of coconut as fruit in Malaysia is the highest (17.0 kg/y) [22,23]. According to these statistics, it is therefore undeniably that the number of natural waste materials like coconut fibers (CF) and oil palm fibers (OPF) can be of abundance over a period of time. This consequently, threatened the natural biodiversity and environment, apart from generating issues related to the disposal of these fibers over limited landfill areas. Due to that, proper management of these agricultural waste materials is crucial in order to minimize the usage of the landfill areas.

Nevertheless, a previous study by Sabzali et al. [25] documented the use of biofilm cultivation over a carrier for pollutants degradation. However, concern associated with cost-effectiveness arises as the artificial supports of the biofilm carrier are expensive and have many problems in transportation and storage [24]. In view of that, it is interesting to further discover the capability of coconut fiber and OPF as natural carriers for biofilm development. The lignin and cellulosic content in natural fibers can be a food source to allow the growth of microorganisms which can later be attached to the medium itself [25–27]. Instead of using synthetic food sources for microorganisms, the natural fiber also ensures nutrients from the biofilm carrier are safe and being organic to the environment. In fact, it is easier for the biofilm to grow in the natural cellulosic fibers, owing to the innate condition as opposed to the artificial materials. Furthermore, it is also undeniable that natural cellulosic fibers have good adsorption ability especially in treating the pollutants in the water. The ability of these cellulosic fibers in adsorbing metal ions has been verified in existing literature [28–30]. The research works focused on examining the accumulation of OM and nutrients from the contaminated water have also been documented [31,32]. However, the adsorption efficiency changes directly proportional to the retention time of natural fibers in the river water. This is attributed to the growth and adherence of microorganisms on the fibers that in return affect the cellulosic nature in the fibers, hence the overall performance with respect to time.

Therefore, the present work focuses on investigating the adsorption performance of natural fibers and biofilm-attached natural fibers on OM removal in contaminated water. The mass transfer of the pollutants during the adsorption process of the biofilm-attached fibers is then analyzed by using a modified mass transfer model. Finally, the study provides an overview of the possibility of the natural waste materials (CF and OPF) in treating organic matter from river water, hence exploring the sustainable practices that encourage further research by using these natural waste materials (CF and OPF) as a carrier for biofilm formation.

2. Methodology

2.1. Materials preparation for biofilm development

In this study, two different cellulosic fibers – CF and OPF were selected as the media for biofilm development and adherence. The CF and OPF were prepared by simple washing and soaking in distilled water for 24 h prior to usage as biofilm carriers. Thereafter, the fibers were placed in a rectangular wired basket hung over a water container for biofilm growth and adherence. The water in the container was collected from Desa Bakti River and is replaced every 2 d to ensure the fibers are fully submerged whilst maintaining the nutrients required by the microorganisms to survive. The growth of the biofilms was monitored in the laboratory on a weekly basis. Once the biofilms had substantially grown, the biofilm-attached fibers are now ready for pollutants adsorption in the pre-fabricated model.

2.2. Fabricated column model

The research station, together with the fabricated column model is shown in Fig. 1. The site of which the model was setup is considered to be a semi-developed area consisting of minimal road networks and building blocks. The fabricated column model (Patent Number: 2013701675) used in this study consists of three prefabricated cylindrical

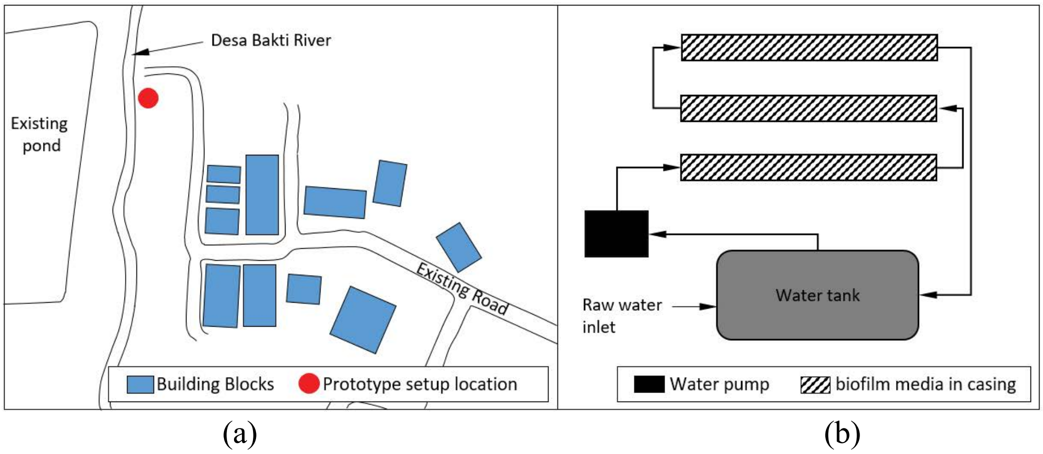

Fig. 1. Illustration showing (a) the location of the prototype setup and (b) the details of the fabricated column model.

columns that can accommodate the biofilm media, a storage tank, and water pumps.

The amount of biofilm attached to coconut fibers (BCF) and biofilm attached on oil palm fibers (BOPF) used in the study is 86 and 60 g, respectively, whilst the contaminated water sample in the model was maintained as the same source and limits to an approximate amount of 0.2 m^3 for each experiment replication. Table 1 shows the characteristics of the contaminated water sample in the model.

The treatment process lasted for 8 d and the water in the storage tank was consistently circulated with the help of the water pumps attached.

2.3. Microscopic observation and Fourier-transform infrared spectroscopy analysis on biofilm growth

The inverted biological microscope was chosen to monitor the biofilm growth on the CF and OPF. The image observed under the microscopic is fixed to zoom in at 20 × 0.4 lenses. The monitoring of biofilm development over the fibers was visually observed using the microscope on a weekly basis. Fibers were randomly selected from the column model for microscopic observation. Images of the biofilm growth were later captured by a digital image analyzer and transferred into a computer.

The Perkin Elmer Frontier Fourier-transform infrared spectroscopy (FTIR) (manufacturer location from United States) spectrometer of wavelength between 4,000 and 650 cm^{-1} was used to analyze the natural fibers before and after the biofilm growth. The spectrometer is configured with an advanced Far-IR capability that offers a flexible sampling option where non-destructive measurement can be carried out on the biofilm attached fibers. The samples were placed on the diamond crystal plate of the device with the pointed end pointing toward the sample to identify the organic materials.

2.4. Analytical methods

2.4.1. Rate of expression

The change in physical, chemical, and biological reactions of adsorbent to pollutants is rate-dependent [33]. A simple mass balance method was used for the pollutant adsorption analysis by the biofilm attached cellulosic fibers. It was identified that the effect of pollutant reduction time is crucial in determining the reaction, via the first-order rate, as shown in Eq. (1):

Table 1
Characteristics of the contaminated water sample in the model

Water characteristics	Value
Average flow rate, L/s	0.12–0.15
pH	5.82–6.73
Salinity, %	0.08–0.1
Chemical oxygen demand (COD), mg/L	45–111.33

$$q_t \frac{(C_0 - C_t) \times Q \times t}{m} \quad (1)$$

where C_0 is the initial concentration of the pollutant (mg/L), C_t is the concentration of the pollutant at the time (mg/L), Q is the flow rate of the water (L/s), t is the reaction time (s), and m is the mass of adsorbent (g).

The accumulation of organic pollutant mass adsorbed per mass of adsorbent (in g/g) vs. time (in d) is crucial to identify different reactions that will affect the organic pollutant reduction in water since the water sample is circulated through the fabricated column model. As the initial flow rate (Q_0) was kept constant for 8 consecutive days, the contamination can be reduced significantly where the pollutants are adsorbed and trapped into the adsorbent. The empirical model developed from previous work [32] was proposed to be used in this study to describe the adsorption dynamics of BCF and BOPF, as shown in Eq. (2):

$$\ln q_t \text{ acc} = \frac{C_0 \times v}{H \times \rho} \times \ln(t) - \frac{\ln\left(\frac{C_t}{C_0 - C_t}\right) \times \nu}{H \times k_{\text{BA}} \times \rho} \quad (2)$$

where k_{BA} is the Adams–Bohart model's constant (L/mg d), H is the bed depth (m), v is the linear flow velocity of water (m/d), t is the reaction time (s), and ρ is the density of the adsorbents (g/L).

2.4.2. Resistance mass transfer

In order to identify the process of pollutants reaction on BCF and BOPF, the resistance mass transfer method was used in analyzing the experimental data. The study utilized the developed mathematical models proposed from previous work which is capable to determine the mass transfer for adsorption of pollutants onto natural adsorbents [32]. The model is presented in Eqs. (3) and (4) as follows:

$$\ln(k_g) = \frac{\ln\left(\frac{C_t}{C_0 - C_t}\right) \times \ln\left(\frac{C_t}{C_0}\right) \times N_0}{C_0 \times \ln\left(\frac{C_0}{C_t} - 1\right) \times k_f} + \ln\left\{\ln\left(\frac{C_0}{C_t}\right)\right\} \tag{3}$$

$$k_g = k_d + k_f \tag{4}$$

where k_g is the global mass transfer factor (d^{-1}), k_d is the porous diffusion factor or internal mass transfer factor (d^{-1}), k_f is the film mass transfer factor or external mass transfer factor (d^{-1}), and N_0 is the sorption capacity (mg/L).

3. Results and discussion

3.1. Microscopic observation of BCF and BOPF

To better understand the effect of microbial growth and adhesion on fiber surfaces, careful observation via microscope on CF and OPF as natural biofilm media is necessary. Monitoring a continuous culture is essential in order to demonstrate the development and attachment of mixed culture biofilm growth that is related to the influence of time length the surface was exposed to river water. The biofilm growth on CF and OPF was monitored continuously over the course of 4 weeks. The ability of CF and OPF used to immobilize microbial growth on the surface observed under the microscope is as shown in Fig. 2.

During initial attachment, the bacteria contacted the fiber's substratum and only a small amount of bacteria successfully attached to the surface of the fibers. This is associated with the initial repulsion of the cell pole between the microbes and substratum [34]. The attachment phase later became significant following the increasing amount of naturally mixed culture biofilm observed on the surface of CF and OPF in the second weeks onwards of the experiment. The presence of a hydrophobic functional group in fibers such as the carbon skeleton and lignin further assisted in biofilm formation and development onto the substratum surface [35]. It was observed that the attachment of natural biofilm consists of mostly algae and bacteria. This is anticipated as the river water containing a high concentration of organics and nutrients enhanced algae biofilm growth under sufficient sunlight [36]. The algae-bacteria biofilm growth on CF and OPF from Desa Bakti River used to accumulate the excess organic and nutrients from the same water source is needed to be carried out in order to recognize the direct interaction of biofilm and pollutants from the same cultures. In fact, the algae biofilm was proven to be feasible for wastewater treatment where it can be utilized for nutrients, heavy metals, and micropollutants removal [37].

3.2. Active sites determination on BCF and BOPF

FTIR spectra analysis was applied to study the biofilm formation and *in-situ* behavior of the fibers without destroying the samples. The functional group change before and after the biofilm growth was monitored. Fig. 3 illustrates the FTIR spectra of CF and OPF [31] whilst Fig. 4 illustrates the FTIR spectra of biofilm attached to CF and OPF.

Referring to Fig. 3, both CF and OPF spectra are obtained with rather identical wavenumbers where the peaks in the vicinities contain the characteristic of a cellulose and lignin system, despite the insignificant difference in the amount of light absorption [31]. This is due to the lignin contains different types of fibers that have resulted in a slight difference in their chemical structure. The low percentage of FTIR's transmittance reveals that the amount of absorbed light by the compound related to bond vibrations is high

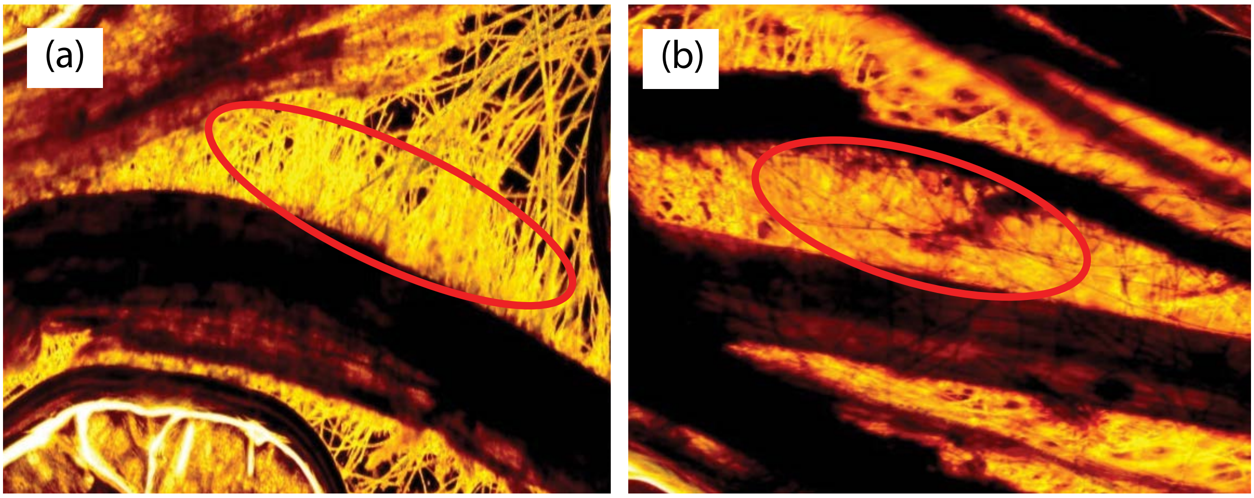

Fig. 2. Mixed culture biofilm growth by algae and bacteria on the surface of (a) CF and (b) OPF under magnification of 20 × 0.4.

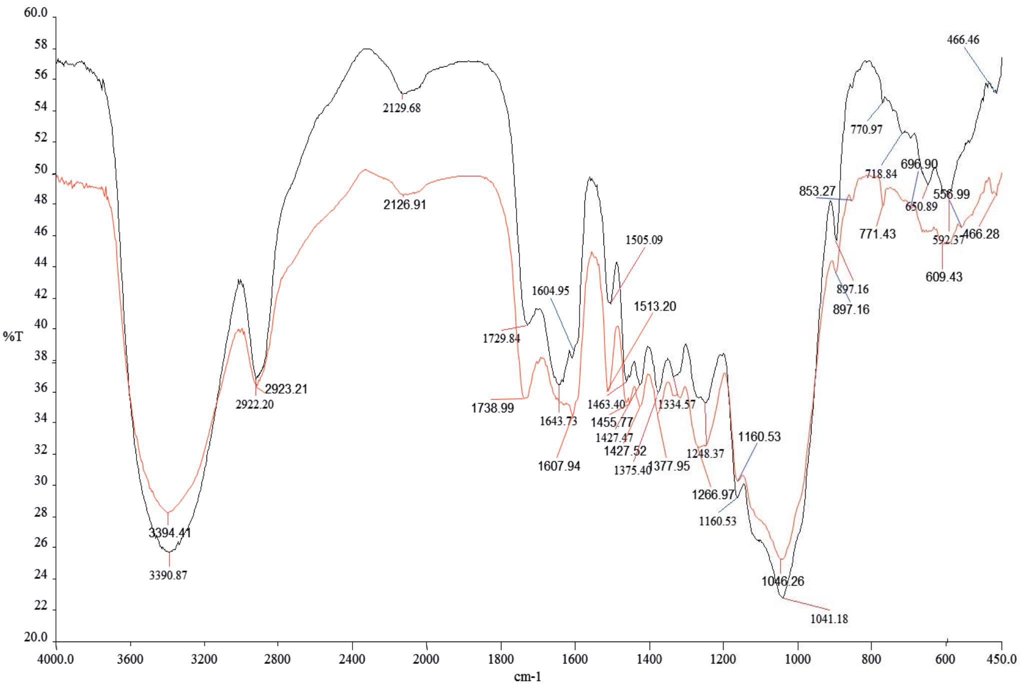

Fig. 3. FTIR spectra of CF (red) and POF (black) [31].

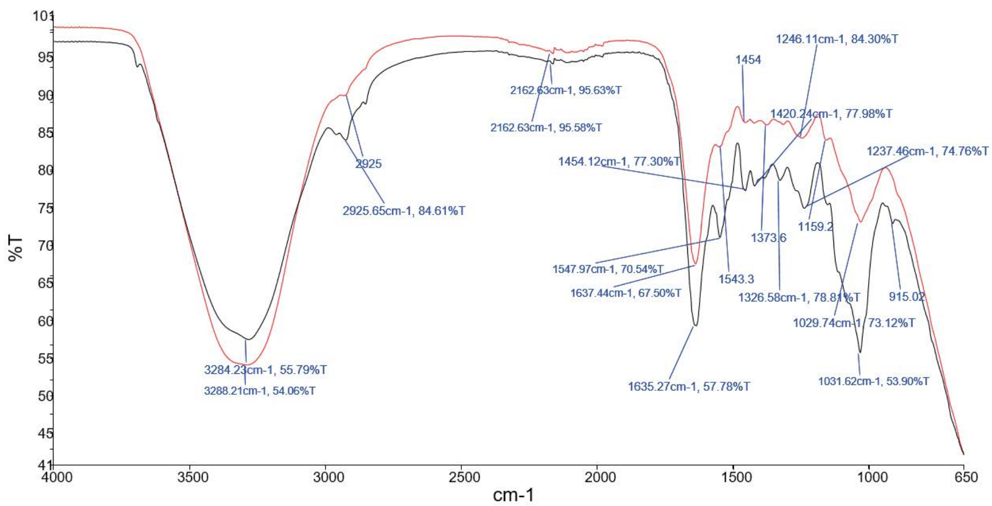

Fig. 4. FTIR spectra of natural BCF (red) and BOPF (black).

[38]. Overall, the OPF shows a slightly higher percentage of FTIR's transmittance compared to CF, except at 3,394–3,393 cm^{-1} (phenolic and alcoholic hydroxyl groups by hydrogen bonds) and 1,047–1,041 cm^{-1} (carboxylic group).

In Fig. 4, the average FTIR spectra of BCF and BOPF display similar sharp absorption peaks with slightly different transmittance percentages. The major active functional group of both biofilms attached fibers were characterized into three regions such that N–H and O–H groups (3,288–4 cm^{-1}), C=O group (1,637–5 cm^{-1}) and C–O, C–C, and C–OH groups (1,031–1,029 cm^{-1}). The typical position of these FTIR spectra are grouped into polysaccharides or carbohydrates (1,200–900 cm^{-1}), proteins (1,700–1,300 cm^{-1}) and glucose, and adsorbed water molecules (2,800–3,400 cm^{-1}) [39–43]. Typically, the quantification of polysaccharides and proteins showed that these classes of biomolecules formed the extracellular polymeric substance (EPS) by mass with an increase in protein relative to the polysaccharides (carbohydrate) [44]. Under the interaction between EPS formation and growth, the attachment on OPF shows a slightly higher concentration compared to the attachment on CF. This might be that the CF has a slightly higher percentage of FTIR's transmittance on the band centered at 3,394–3,393 cm^{-1} and 1,047–1,041 cm^{-1} compared to

OPF where CF showed a higher concentration of phenolic and alcoholic hydroxyl groups by hydrogen bonds as compared to OPF. The phenolic and alcoholic hydroxyl groups exhibit in the natural fibers slightly affect the biofilm formation of the microorganisms [45,46]. Hence, it leads to a higher concentration of EPS attachment on OPF than CF.

3.3. Comparison of adsorption loading rate of biofilm attached fibers (BCF and BOPF) and natural fibers (CF and OPF)

Mixed species of natural biofilm play an important role in enhancing the removal of OM from river water. After 4 weeks of biofilm developing on CF and OPF, the potential of mixed-species natural biofilms were tested in a fabricated column model for treating OM compounds in Desa Bakti river water. Fig. 5 shows the relationship between OM volumetric loading rate to time for CF, OPF, BCF, and BOPF provided in the system using the chemical oxygen demand (COD) examination. The volumetric loading rate is calculated by dividing the product of COD concentration (mg/L) and influent flow with the total volume of the water sample. Generally, an increase in the initial concentration of COD in the water determined an increase of volumetric loading rate of COD as the volume and flow rate of water are fixed in the experiment.

The efficient treatment of COD from river water by using biofilm attached fibers and original fibers were compared in this study using the fabricated column model mentioned in the methodology section. During the experiment, the BCF and BOPF can remove up to 94.07% and 87.01% of COD, respectively, after the 8th experiment days. On the contrary, for original fibers (CF and OPF) without biofilm attached, the COD removal rate is 91.02% and 82.35%, respectively. The results reveal better performance on BCF and BOPF adsorption capability for OM removal from river water treatment. It can be observed that the removal rate of organic and nutrients decreased gradually with decreasing organic and nutrient pollutants load in the water. The overall view of the result seems that BCF has better OM removal capacity compared to BOPF, which further proven that the overall mass transfer of organic and nutrients in BCF is higher than BOPF. Moreover, it can also be seen that BCF and BOPF performed better in organic matter adsorption as compared to CF and OPF. Theoretically, natural cellulosic fiber has lignocellulosic properties that are proved to possess good adsorption ability for water pollutants removal [47]. However, the presence of biofilm further strengthened the biosorption capacity since fibers covered with biofilm can enhance the capture of particulate nutrients from the contaminated water, hence the accumulation of adsorbate on the hosting medium [48]. Thus, the empirical mass transfer models were applied to evaluate the detailed mechanism of biological adsorption and filtration action.

3.4. Biosorption analysis using empirical models

The adsorption rate of OM to the biofilm is quantified through the external and internal mass transfer rate across the biofilm surface. In this study, the use of an empirical model is the basis of further adsorption analysis which will be able to describe the natural mass transfer performance during the adsorption of OM from river water onto the BCF and BOPF. The application of the model equation shown in Fig. 6 includes the cumulative results of substrates removal, q_t acc, which is calculated from the linear dependences of the empirical model as outlined in Eq. (2).

A plot of $\ln q_t$ acc vs. $\ln t$ as in Fig. 6 yields a straight line with a good correlation for the gradient and intercept (R^2 > 0.99). This indicates the linear regression analysis of using the empirical model is also appropriate in studying the adsorption mechanisms of OM onto the BCF and BOPF.

The results obtained from Fig. 6 are important to understand the overall reaction of biofilm kinetics for river water treatment. In BCF and BOPF, the substrates will diffuse and travel through a complicated network of passages before being utilized by the algae-bacteria. The gradient of the graph represents the adsorbate-biofilm affinity related to biofilm structure/density, solubility/polarity, properties of adsorbate, and properties of mixed-species biofilm. Meantime, the intercept of the graph reveals the potential mass transfer link with the driving force of the organic and nutrients concentration in the water to the biofilm developed fibers (BCF and BOPF).

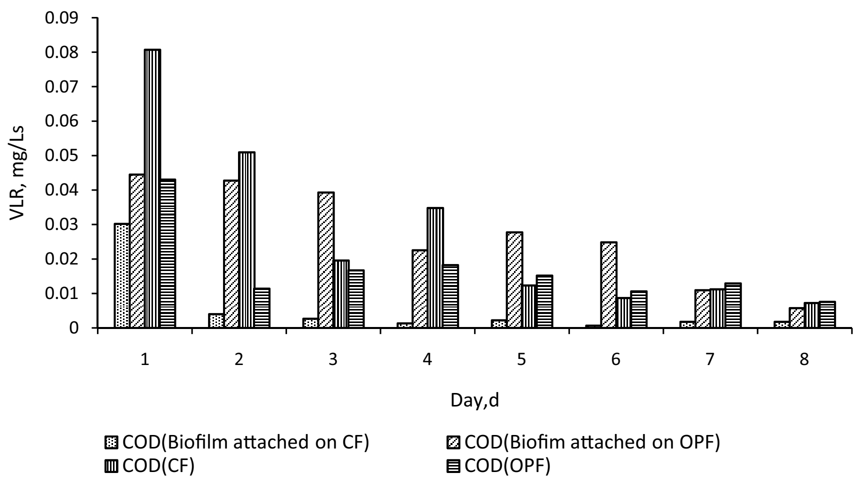

Fig. 5. Relation between OM (COD) loading rate vs. time (d) for biofilm attached on CF and POF.

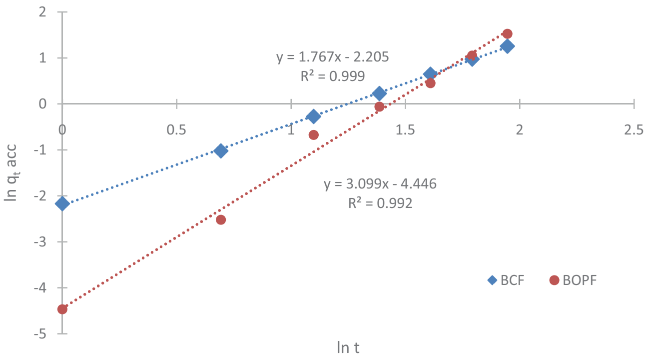

Fig. 6. Plot of lnq_t acc vs. ln$t$ for the mass accumulation of OM onto BCF and BOPF.

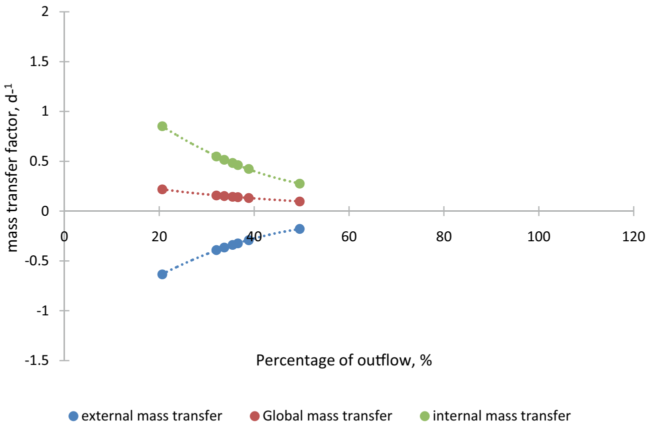

Fig. 7. Global, internal, and external mass transfer factor vs. percentage of outflow for the adsorption of OM (COD) onto BCF.

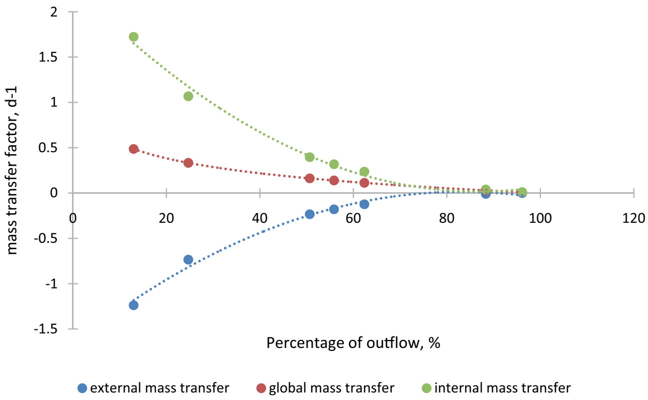

Fig. 8. Global, internal, and external mass transfer factor vs. percentage of outflow for the adsorption of OM (COD) onto BOPF.

From the results in Fig. 6, it is clear that the straight-line slope of BOPF (3.0991 mg/g d) is higher than BCF (1.7674 mg/g d). This is due to the higher influent concentration of OM that has induced a higher value of slope in the graph in the presence of a higher driving force for the adsorption onto the biofilm. Apart from that, the consistent value of COD from day 1 to 3 (shown in Fig. 4) exhibits by BCF compared to BOPF due to OM concentration may have become limited as the experiment progress, hence causing a gentle gradient in COD adsorption as referring to Eq. (2).

3.5. Global, external, and internal mass transfer factor in BCF and BOPF

The global, external, and internal mass transfer factors for BCF and BOPF are shown in Figs. 7 and 8. Hyperbolic concave curves are formed for both curves (k_g and k_d), indicating the rate of global and internal mass transfer of BCF and BOPF decreases. On the contrary, the hyperbolic convex curve is formed for curve k_f, indicating the rate of film mass transfer of BCF and BOPF increases. In spite of that, all curves (k_g, k_d, and k_f) converge toward the end which shows the mass transfer decreases with increasing repulsion force when the concentration of substrate eventually becomes a limiting factor in the water treatment process. The detailed results of the mass transfer (global, internal, and external) to the percentage of outflow are also presented in Table 2.

A higher value of the mass transfer factor indicates the higher rate of nutrient transport onto the biofilm. From Table 2, it was identified that the overall mass transfer of BOPF is slightly lesser than BCF. This is due to the thicker EPS in OPF that has induced a slower diffusion rate of OM onto the biofilm [49].

Substrates in river water are initially transported from water to the biofilm (external mass transfer), which later continue to move through the biofilm matrix and consumed by the algae or bacteria in the biolayer (internal mass transfer) [50]. At the same time, the negative external mass transfer coefficient of pollutants adsorption on BCF and BOPF means that mass transfer limitation exists and is weak due to the interface of water with biofilm. The competition among the pollutants molecules in river water would impede solute mobility, resulting in a longer time needed to reach the inner active surface of biofilm on CF and OPF upon comparing to the diffusion in biofilm pores. In fact, this condition is caused by the biofilm matrix being close to the substratum (CF and OPF) where the mass transfer is dominated by porous diffusion in biofilm. It is also identified that the film mass transfer of BOPF is higher than BCF. The higher initial concentration of OM molecules in river water prompts higher film mass transfer due to an increase in initial solute concentration. This usually enhances the intensity of OM-induced flow patterns [51].

The variation of k_d is also important to note as it controls the overall mass transfer resistance in biofilm attached to CF and OPF. Due to the rapid fixation of the adsorbate to the acceptor sites in biofilm, the porous diffusion resistance of OM does not contribute much to defer the overall mass transfer and thus a higher value of k_d. This indirectly means the mass transfer is not dependent on film diffusion. Organic carbon is an important source used for nutrients uptake by algae and bacteria in the biofilm. The highest concentration of OM in the river water induced the highest internal mass transfer in the biofilm on CF and OPF. However, it is not anticipated that the internal diffusivity of BOPF is less than BCF even if the initial concentration of COD in the river water is higher. The decrease of the

Table 2
Values of k_g, k_f, and k_d determined by graphical method

Adsorbent	Percentage of outflow (%)					
	3	5	8	10	20	50
Global mass transfer factor (k_g), d^{-1}						
Biofilm attached on CF	1.0067	0.8601	0.7252	0.6612	0.4622	0.1992
Biofilm attached on OPF	0.8354	0.7139	0.6020	0.5489	0.3839	0.1658
Film mass transfer factor or external mass transfer factor (k_f), d^{-1}						
Biofilm attached on CF	–2.7260	–2.2750	–1.8600	–1.6629	–1.0509	–0.2418
Biofilm attached on OPF	–1.5468	–1.4692	–1.3558	–1.2822	–0.9382	–0.1462
Porous diffusion factor or internal mass transfer factor (k_d), d^{-1}						
Biofilm attached on CF	3.7327	3.1351	2.5852	2.3241	1.5131	0.4410
Biofilm attached on OPF	2.1262	2.0266	1.8817	1.7881	1.3561	0.4201

mass transfer might have related to the influence of other pollutants in the river water which affects the uptake rate of COD onto the biofilm matrix [52].

Overall, the higher surface roughness of OPF compared to CF for biofilm generation increases biofilm density in OPF than CF. This has led to a decrease in the effective diffusivity of biofilm which would further alter the intra-biofilm mass transfer rate. Such a statement is further supported by Fitch [53] who proven that an increase of biofilm thickness induced a decrease of the mass transfer due to the decreasing diffusion rate of the adsorbate within the biofilm. Thus, the relationship between internal mass transfer and the physical characteristics of biofilm is significant. This is because internal diffusivity is affected by modification of the internal structure of biofilms developed on CF and OPF in order to adapt to the condition of water, for instance, the concentration of substrates [50].

This lead to a conclusion where the results pointed out the presence of OM in river water is an important source that can be consumed by microbial biomass in biofilm. Diffusion in the biofilm matrix is the predominant mass transfer mechanism for the substrates transport process. In spite of that, there are still many other factors that need to be identified, especially environmental-related factors known to have a prominent influence on the growth of biofilm and substrates diffusivity rate.

4. Conclusion

The present study has demonstrated that both CF and OPF as biofilm carrier is effective for removal of OM from polluted river water. The recorded COD removal rates were around 94% and 87% within 8 experimental days for BCF and BOPF, respectively. In comparison, the natural cellulosic fibers (CF and OPF) were able to remove around 91% and 82% of COD. The mass transfer analysis shows that BCF has a higher global mass transfer rate than BOPF due to the thicker EPS that have induced a slower diffusion rate of pollutants to the biofilm. However, the film mass transfer of BOPF is higher than BCF as the initial OM concentration in the river water sample is higher. Besides the organic loading rate of the sample water, there were also other factors such as nutrients, or the existence of other pollutants in the river water that were identified to have a great influence on the adsorption rate of BCF and BOPF. Thus, it is concluded that the BCF and BOPF have excellent adsorption capacity that is capable of replacing the costly adsorption materials in removing OM from polluted river water.

Acknowledgments

The authors would like to acknowledge INTI International University for the financial support used to carry out this research and publication. The Universiti Teknologi Malaysia (UTM): PDRU Grant-Vot No. Q.J130000.21A2.04E53 and MRUN R.J130000.7805.4L886 are also acknowledged.

References

[1] J. Liu, Y. Wu, C. Wu, K. Muylaert, W. Vyverman, H.Q. Yu, R. Muñoz, B. Rittmann, Advanced nutrient removal from surface water by a consortium of attached microalgae and bacteria: a review, Bioresour. Technol., 241 (2017) 1127–1137.
[2] A. Skoyles, S.R. Chaganti, S.O. Mundle, C.G. Weisener, Nitrification kinetics and microbial community dynamics of attached biofilm in wastewater treatment, Water Sci. Technol., 81 (2020) 891–905.
[3] G. Crini, E. Lichtfouse, Advantages and disadvantages of techniques used for wastewater treatment, Environ. Chem. Lett., 17 (2019) 145–155.
[4] B. Halan, K. Buehler, A. Schmid, Biofilms as living catalysts in continuous chemical syntheses, Trends Biotechnol., 30 (2012) 453–465.
[5] M. Asri, S. Elabed, S.I. Koraichi, N.E. Ghachtouli, Biofilm-Based Systems for Industrial Wastewater Treatment, C.M. Hussain, Ed., Handbook of Environmental Materials Management, Springer, Cham, 2018, pp. 1–21.
[6] Z. Lewandowski, H. Beyenal, Fundamentals of Biofilm Research, 2nd ed., CRC Press, New York, NY, 2013.
[7] E. Ilhan-Sungur, A. Çotuk, Microbial corrosion of galvanized steel in a simulated recirculating cooling tower system, Corros. Sci., 52 (2010) 161–171.
[8] M.J. Lehtola, I.T. Miettinen, M.M. Keinänen, T.K. Kekki, O. Laine, A. Hirvonen, T. Vartiainen, P.J. Martikainen, Microbiology, chemistry and biofilm development in a pilot drinking water distribution system with copper and plastic pipes, Water Res., 38 (2004) 3769–3779.

[9] E. Eguía, A. Trueba, B. Río-Calonge, A. Girón, C. Bielva, Biofilm control in tubular heat exchangers refrigerated by seawater using flow inversion physical treatment, Int. Biodeterior. Biodegrad., 62 (2008) 79–87.
[10] Y. Wu, T. Li, L. Yang, Mechanisms of removing pollutants from aqueous solutions by microorganisms and their aggregates: a review, Bioresour. Technol., 107 (2012) 10–18.
[11] G. You, C. Wang, P. Wang, J. Hou, Y. Xu, L. Miao, T. Feng, Insights into spatial effects of ceria nanoparticles on oxygen mass transfer in wastewater biofilms: interfacial microstructure, *in-situ* microbial activity and metabolism regulation mechanism, Water Res., 176 (2020), doi: 10.1016/j.watres.2020.115731.
[12] M. Jamal, W. Ahmad, S. Andleeb, F. Jalil, M. Imran, M.A. Nawaz, T. Hussain, M. Ali, M. Rafiq, M.A. Kamil, Bacterial biofilm and associated infections, J. Chin. Med. Assoc., 81 (2018) 7–11.
[13] M.A. Yun, K.M. Yeon, J.S. Park, C.H. Lee, J. Chun, D.J. Lim, Characterization of biofilm structure and its effect on membrane permeability in MBR for dye wastewater treatment, Water Res., 40 (2006) 45–52.
[14] Y.J. Oh, N.R. Lee, W. Jo, W.K. Jung, J.S. Lim, Effects of substrates on biofilm formation observed by atomic force microscopy, Ultramicroscopy, 109 (2009) 874–880.
[15] Y. Liu, Q.S. Liu, Causes and control of filamentous growth in aerobic granular sludge sequencing batch reactors, Biotechnol. Adv., 24 (2006) 115–127.
[16] A. Praveen, P. Sreelakshmy, M. Gopan, Coir geotextile-packed conduits for the removal of biodegradable matter from wastewater, Curr. Sci., 95 (2008) 655–658.
[17] R. Dungani, M. Karina, A.S. Subyakto, D. Hermawan, A. Hadiyane, Agricultural waste fibers towards sustainability and advanced utilization: a review, Asia J. Plant Sci., 15 (2016) 42–55.
[18] M. Rajinipriya, M. Nagalakshmaiah, M. Robert, S. Elkoun, Importance of agricultural and industrial waste in the field of nanocellulose and recent industrial developments of wood based nanocellulose: a review, ACS Sustainable Chem. Eng., 6 (2018) 2807–2828.
[19] M.U. Mahidin, Selected Agricultural Indicators, Malaysia, Press release from Department of Statistic Malaysia Official Website, 2019. Available at: https://www.dosm.gov.my/v1/index.php?r=column/cthemeByCat&cat=72&bul_id=SEUxMEE3VFdBcDJhdUhPZVUxa2pKdz09&menu_id=Z0VTZGU1UHBUT1VJMFlpaXRRR0xpdz09
[20] D. Sud, G. Mahajan, M.P. Kaur, Agricultural waste material as potential adsorbent for sequestering heavy metal ions from aqueous solutions – a review, Bioresour. Technol., 99 (2008) 6017–6027.
[21] P.K. Sharma, S. Ayub, C.N. Tripathi, Agro and horticultural wastes as low cost adsorbents for removal of heavy metals from wastewater: a review, Int. Ref. J. Eng. Sci., 2 (2013) 18–27.
[22] A. Habshah, Developing a Resilient and Sustainable Malaysian Coconut Industry: Policy Solutions, R. Laboh, Ed., Proceedings National Coconut Conference (NCC) 2018, 'Empowering Coconut Industry', Malaysia Agricultural Research and Development Institute (MARDI), Kinta Riverfront Hotel and Suites, Ipoh, Perak, Malaysia, 2018.
[23] Department of Statistic Malaysia, Supply and Utilization Accounts Selected Agricultural Commodities, Malaysia 2012–2016, Malaysia, 2017. Available at: https://dosm.gov.my/v1/index.php?r=column/cthemeByCat&cat=164&bul_id=UDROQlIWME5ETGZrcUE5VnAzcHJEQT09&menu_id=Z0VTZGU1UHBUT1VJMFlpaXRRR0xpdz09#
[24] A. Sabzali, M. Nikaeen, B. Bina, Evaluation of cigarette filters rods as a biofilm carrier in integrated fixed film activated sludge process, World Acad. Sci. Eng. Technol., 5 (2011) 583–588.
[25] C. Asasutjarit, S. Charoenvai, J. Hirunlabh, J. Khedari, Materials and mechanical properties of pretreated coir-based green composites, Composites, Part B, 40 (2009) 633–637.
[26] T. Nguyen, F.A. Roddick, L. Fan, Biofouling of water treatment membranes: a review of the underlying causes, monitoring techniques and control measures, Membranes, 2 (2012) 804–840.
[27] G.S. Lorite, R. Janissen, J.H. Clerici, C.M. Rodrigues, J.P. Tomaz, B. Mizaikoff, C. Kranz, A.A. de Souza, M.A. Cotta, Surface physicochemical properties at the micro and nano length scales: role on bacterial adhesion and *Xylella fastidiosa* biofilm development, PLoS One, 8 (2013) 4–12, doi: 10.1371/journal.pone.0075247.
[28] A. Celik, A. Demirbaş, Removal of heavy metal ions from aqueous solutions via adsorption onto modified lignin from pulping wastes, Energy sources, 27 (2005) 1167–1177.
[29] A. Jamshaid, A. Hamid, N. Muhammad, A. Naseer, M. Ghauri, J. Iqbal, S. Rafiq, N.S. Shah, Cellulose-based materials for the removal of heavy metals from wastewater–an overview, ChemBioEng Rev., 4 (2017) 240–256.
[30] D.S. Malik, C.K. Jain, A.K. Yadav, Removal of heavy metals from emerging cellulosic low-cost adsorbents: a review, Appl. Water Sci., 7 (2017) 2113–2136.
[31] M.F.M. Din, M. Ponraj, W.P. Low, M.A. Fulazzaky, K. Iwao, A.R. Songip, S. Chelliapan, Z. Ismail, M.H. Jamal, Removal rate of organic matter using natural cellulose via adsorption isotherm and kinetic studies, Water Environ. Res., 88 (2016) 118–130.
[32] W.P. Low, M.F.M. Din, F.L. Chang, S.N.F.B. Moideen, Y.Y. Lee, Empirical models of kinetic rate for river treatment analysis of cellulosic materials, J. Water Process Eng., 23 (2018) 257–264.
[33] Metcalf and Eddy, Wastewater Engineering Treatment and Reuse, 4th ed., Mc Graw Hill, New York, NY, 2003.
[34] S.L. Percival, S. Malic, H. Cruz, D.W. Williams, Introduction to Biofilms, S.L. Percival, D.C. Knottenbelt C.A. Cochrane, Eds., Biofilms and Veterinary Medicine, Springer, New York, NY, 2011, pp. 41–68.
[35] H. Palonen, Role of Lignin in the Enzymatic Hydrolysis of Lignocellulose: VTT Technical Research Centre of Finland, Finland, 2004.
[36] L. Christenson, Algal Biofilm Production and Harvesting System for Wastewater Treatment with Biofuels By-Products, Master of Science, Utah State University, Logan, Utah, 2011.
[37] A.F. Miranda, N. Ramkumar, C. Andriotis, T. Höltkemeier, A. Yasmin, S. Rochfort, D. Wlodkowic, P. Morrison, F. Roddick, G. Spangenberg, B. Lal, Applications of microalgal biofilms for wastewater treatment and bioenergy production, Biotechnol. Biofuels, 10 (2017) 1–3, doi: 10.1186/s13068-017-0798-9.
[38] P.S. Kalsi, Spectroscopy of Organic Compounds, 6th ed., New Age International Publishers, New Delhi, India, 2004.
[39] B. Doumèche, L. Galas, H. Vaudry, P. Di Martino, Membrane foulants characterization in a drinking water production unit, Food Bioprod. Process., 85 (2007) 42–48.
[40] A. Mishra, B. Jha, Isolation and characterization of extracellular polymeric substances from micro-algae *Dunaliella salina* under salt stress, Bioresour. Technol., 100 (2009) 3382–3386.
[41] R. Sanna, Structural and Morphological Characterization of Hydrozincite and Its Interaction With Organic Molecules, PhD Thesis, Cagliari University, Italy, 2011.
[42] C.J. Hirschmugl, K.M. Gough, Fourier transform infrared spectrochemical imaging: review of design and applications with a focal plane array and multiple beam synchrotron radiation source, Appl. Spectrosc., 66 (2012) 475–491.
[43] T. Qin-qin, L. Zhi-rong, D. Ying, Z. Xin-xing, Biosorption properties of extracellular polymeric substances towards Zn(II) and Cu(II), Desal. Water Treat., 45 (2012) 40–47.
[44] A. Omoike, J. Chorover, Spectroscopic study of extracellular polymeric substances from *Bacillus subtilis*: aqueous chemistry and adsorption effects, Biomacromolecules, 5 (2004) 1219–1230.
[45] V. Plyuta, J. Zaitseva, E. Lobakova, N. Zagoskina, A. Kuznetsov, I. Khmel, Effect of plant phenolic compounds on biofilm formation by *Pseudomonas aeruginosa*, Apmis, 121 (2013) 1073–1081.
[46] D.J. Walsh, T. Livinghouse, D.M. Goeres, M. Mettler, P.S. Stewart, Antimicrobial activity of naturally occurring phenols and derivatives against biofilm and planktonic bacteria, Front. Chem., 7 (2019) 2–3, doi: 10.3389/fchem.2019.00653.
[47] A. Naseer, A. Jamshaid, A. Hamid, N. Muhammad, M. Ghauri, J. Iqbal, S. Rafiq, N.S. Shah, Lignin and lignin based materials

for the removal of heavy metals from waste water-an overview, Z. Für Phys. Chem., 233 (2019) 315–345.
[48] T.R. Bott, L.F. Melo, Particle-Bacteria Interactions in Biofilms, L. Melo, T.R. Bott, M. Fletcher, B. Capdeville, Eds., Biofilms - Science and Technology, Springer Science & Business Media, Portugal, 2012, pp. 199–206.
[49] M.R. Mattei, L. Frunzo, B. D'acunto, Y. Pechaud, F. Pirozzi, G. Esposito, Continuum and discrete approach in modeling biofilm development and structure: a review, J. Math. Biol., 76 (2018) 945–1003.
[50] L. Melo, Biofilm physical structure, internal diffusivity and tortuosity, Water Sci. Technol., 52 (2005) 77–84.
[51] M. Wegener, A.R. Paschedag, M. Kraume, Mass transfer enhancement through Marangoni instabilities during single drop formation, Int. J. Heat Mass Transfer, 52 (2009) 2673–2677.
[52] J.L. Sotelo, G. Ovejero, A. Rodríguez, S. Álvarez, J. Galán, J. García, Competitive adsorption studies of caffeine and diclofenac aqueous solutions by activated carbon, Chem. Eng. J., 240 (2014) 443–453.
[53] M.W. Fitch, Membrane Bioreactor Technology, S. Zarook, S. Ajay, Eds., Biotechnology for Odor and Air Pollution Control, Springer Science & Business Media, Germany, 2005, pp. 195–212.