ACS OMEGA

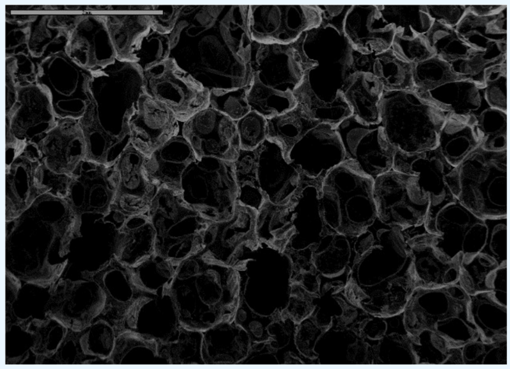
http://pubs.acs.org/journal/acsodf
Article

Methods Influence in Surface Area Result from Polyurethane Used as Support Media

Luana Mattos de Oliveira Cruz,* Rosana Oliveira Menezes, Tammy Salgado Duarte, and Daniel Augusto Camargo Bueno

Cite This: *ACS Omega* 2024, 9, 14766−14770

ABSTRACT: We evaluated if different measurement methods influence the surface area results from a polyurethane sponge used as support media in biofilm reactors. The surface area values are normally used to characterize and present advantages from supported medias. However, the methodology to determine it is barely discussed. We compared two specific surface area methodologies: Brunauer−Emmett−Teller (BET) and analysis of images obtained by a scanning electron microscope (SEM). Specific surface area by BET was 93769.1 m^2 m^{-3} (average); for SEM methodology, 10586.6 m^2 m^{-3}. The BET value was higher than expected in reality, and the SEM method result was more suitable and used as data input in a mathematical modeling.



■ INTRODUCTION

A support media is frequently used in the reactors so that they can form a biofilm on a surface or adsorb contaminants. In biofilm formation process, it provides the accumulation of active cells, attached to the support material through the production of extracellular polymeric substances (EPS).[1]

As an advantage, the support media increases the sludge retention time and the resistance to physical forces, preventing the cells from being easily washed out of the system before its doubling time. In addition, biofilm has greater protection against toxic substances and greater activity with a consequent increase in the rate of substrate removal since attached cells are continuously exposed to new substrates.[2,3] Thus, the support medium can enhance removal efficiency from many compounds.[4]

Since the support media is a structure that will be the basis for the development of the biofilm, it is important to choose the material carefully.[5]

Polyurethane sponge has been widely used as a support media in the treatment of effluents,[6−10] because of its favorable physical and chemical characteristics, such as high porosity, lightness, and resistance.[11] In addition, the sponge has a high surface area for the development of biofilm and low internal diffusion of oxygen, which contributes to the coexistence of aerobic and anoxic/anaerobic zones and favors the metabolic diversity in the system, which is necessary to remove nutrients, for example.[8,12]

Because it has a high percentage of empty spaces (about 90%), the development of biofilm occurs in almost all surface area of the sponge; thus, the determination of this parameter is essential to know the potential area for biofilm development[13] in order to optimize its application in reactors that treat effluents.

High specific surface area is normally used to characterize and present advantage from each material used as supported media.[14−17] However, the applied methodology to determine it is barely discussed and cited.[4,18−21] It can also provide important information when elaborating mathematical models.[22,23]

Moon et al.[11] calculated the sponge-specific surface area by extracting information from microscopic images of its structure. In addition, this parameter can also be determined using the method developed by Brunauer, Emmett, and Teller, known as BET, which is based on the adsorption−desorption of an inert gas (normally nitrogen) on the internal and external surfaces of a porous material.[24] The last has been used in many studies to quantify the specific surface area from different support media.[17,25−28]

In this study, we have evaluated if these different methodologies influence in the surface area results from the support media (mini-BioBob polyurethane sponge) that was

Received: August 17, 2023
Revised: October 23, 2023
Accepted: January 10, 2024
Published: March 22, 2024

https://doi.org/10.1021/acsomega.3c06098
ACS Omega 2024, 9, 14766−14770

used in a lab-scale experiment (Anammox-Trickling Filter).[29] In addition, residual humidity (RH) tests and the volumetric accommodation index of mini-BioBobs were also carried out. All data are important to describe the involved process in the reactors, the biofilm formation, and provide information when elaborating mathematical models.[22,23]

■ MATERIALS AND METHODS

We evaluated the sponge media (mini-BioBob), which was filling a lab-scale Anammox-trickel filter (A-TF) (Menezes, 2019). The A-TF was operated to remove nitrogen from a synthetic effluent (Figure 1a). The polyurethane sponge (mini-BioBob from Bioproj Tecnologia Ambiental Ltd) is inside a polypropylene ring.[30] Its size is 15 mm per 25 mm (Figure 1b).

a)

Figure 1. (a) Trickling filter filled with the support material before inoculation; (b) support media mini-BioBobs and their size in detail.

Residual Humidity. Initially, 30 porcelain capsules were oven-dried at 103−105 °C (until weight stabilization), and their weights were registered. In each of them, a mini-BioBob was inserted, and the sets were weighed one by one. The capsules together with the mini-BioBobs were oven-dried at 103−105 °C (until weight stabilization), and their weights together were recorded again. The wet (wM) and dry (dM) masses of the support media were obtained by discounting the capsule mass.[31]

Residual humidity (RH %) was obtained by the ratio of the water mass to the dry material mass using eq 1. This test was carried out to verify whether the RH inherent in the mini-BioBob could interfere in its mass. In addition, the objective was to verify whether, when oven-dried in stove at 103−105 °C, as necessary in some environmental analyses, the mini-BioBob would be damaged.

$$\mathrm{RH}\ (\%) = \frac{\mathrm{watermass}}{\mathrm{drymaterialmass}} = \frac{\mathrm{wM} - \mathrm{dM}}{\mathrm{dM}} x100 \tag{1}$$

Volumetric Accommodation Index. This experiment was performed using a 1000-mL glass cylinder due to its diameter similar to that of the lab-scale TF reactor (approximately 6.4 cm). A hundred mini-BioBobs were randomly inserted (simulating a reactor compartment), and the volume they occupied was measured (without accommodation—Vwa). Subsequently, sudden movements were made with the cylinder so that the material was accommodated as much as possible, and then the new volume was measured (Va). Aiming at a greater representativeness of the data, three repetitions were executed during this experiment.

The volumetric accommodation index was obtained by the ratio between the difference of the volume without and with accommodation (volume of the difference) and the volume without accommodation (eq 2). This test was carried out in order to verify the mini-BioBobs capacity to better accommodate themselves inside the reactor. This calculation may support the reactor design, which can be smaller as much as the sponges are accommodated.

$$\text{Volumetric accommodation index}\ (\%) = \frac{\mathrm{Vwa\text{-}Va}}{\mathrm{Vwa}} \times 100 \tag{2}$$

Specific Surface Area. It is important to note that the following tests were carried out only for the polyurethane sponge without the polypropylene ring.

Brunauer–Emmett–Teller (BET). Two tests were performed using this method. The first was based on the results of the certificated test provided by the "*Materials Characterization and Development Center*" (*Centro de Caracterização e Desenvolvimento de Materiais* – CCDM). The test was carried out through nitrogen gas molecule adsorption on the material surface, using the equipment Micromeritics Flow Sorb II 2300.

The test request was originally made to determine the specific surface area of BioBob, which is the standard support material used in real-scale reactors constructed by the company (Bioproj Tecnologia Ambiental Ltd.) that supplied the mini-BioBobs for this research. As the only difference between the two materials is the size, so the sponge is the same, we could consider this result as valid for this research.

However, a second test was carried out by the Biomass Characterization, Analytical and Calibration Resources Laboratory (LRAC) from the University of Campinas (UNICAMP) with the mini-BioBobs which was used in the laboratory-scale TF reactor. The analysis methodology was similar to that described above; yet, it was performed on the Micromeritics ASAP (Accelerated Surface Area and Porosimetry System 2010) equipment.

Microscopic Analysis. The calculation was based on the methodology proposed by Moon et al. (2010) in which the authors adopted the following considerations: a polyurethane sponge is a three-dimensional rectangular structure composed of many cells; the fibers that form the sponge are straight and cylindrical; and the diameter and length of the fiber between two crossing points are uniform. After these considerations, we have analyzed the images that were obtained by a scanning electron microscope (SEM), and we have calculated the results with the equations described in the previous studies.[11] Through this methodology, it was also possible to obtain the total volume of the fibers, the void fraction, and the pore size.

https://doi.org/10.1021/acsomega.3c06098
ACS Omega 2024, 9, 14766−14770

RESULTS AND DISCUSSION

Although the BET and ASAP values were closer, they were much higher than expected for this material surface area. On the other hand, SEM methodology result was more suitable, and this methodology seems more appropriate to describe this parameter and to be used as input data in mathematical models.[22,23]

Residual Humidity. The average value found was close to zero. Therefore, RH was considered insignificant in the mini-Biobobs, and the humidity cannot interfere in the media mass. In addition, the material was not damaged when it was oven-dried at 103−105 °C. Hence, when performing total solids analysis, it is not necessary to remove the biomass from the support material, which can facilitate the analysis process.

Volumetric Accommodation Index. Table 1 shows the results obtained in the volumetric accommodation test for each repetition as well as the average value.

Table 1. Results from the Volumetric Accommodation Test

	accommodation results	
repetition	(mL/L)	(%)
1	120	12.0
2	132	13.2
3	122	12.2
average	125 ± 6	12.5 ± 0.6

After the material accommodation, we could verify that 12.5 ± 0.6% of the volume occupied at first was free. Thus, considering the possible accommodation, the number of mini-BioBobs used in the reactor may be greater, providing a larger area for the development of biofilm. We can also infer, as a second alternative, that when designing a reactor, its volume may be smaller, proportionally to the accommodation of the support media.

Specific Surface Area. In the test provided by the Materials Characterization and Development Center (CCDM), BioBob was analyzed by Brunauer−Emmett−Teller (BET). Its unit mass was 2.9055 ± 0.0001 g, and in 1 m^3 of BioBob, there could be 5500 units of the product. Thus, the specific surface area of BioBob equals to 5.883 $m^2\ g^{-1}$, and the specific surface area per unit volume approximately equals to 94011.5 $m^2\ m^{-3}$.

This result obtained from the real scale media is similar to the one achieved when using the mini-BioBob at the Biomass Characterization, Analytical and Calibration Resources Laboratory (LRAC - UNICAMP) via ASAP (also using BET analysis). The surface area resulted in 2.2317 $m^2\ g^{-1}$. As a unit average mass is 0.185 g, in 1 m^3, there can be 226,360 units of the product. Thus, the specific surface area per unit of volume was approximately 93486.7 $m^2\ m^{-3}$.

When analyzing the images provided by the SEM (Figure 2), we obtained 0.06 mm as fiber diameter average value and 52.23 fibers in a length of 1 cm of sponge. Applying the calculations described in Moon et al.,[11] it was possible to obtain a specific surface area equals to 10586.6 $m^2\ m^{-3}$. Other results are shown in Table 2.

If we compare both methodologies to determine the specific surface area (BET and with calculation from SEM images), we notice that they resulted in very different values from each other, and using the BET method, the value found was about 9 times greater than that one using the images methodology from SEM.

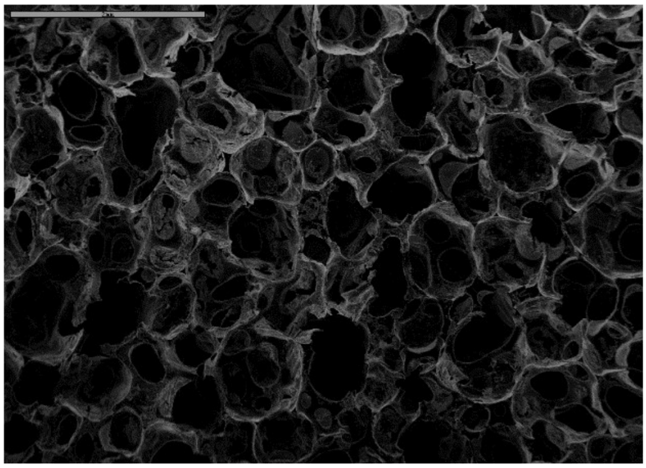


Figure 2. Polyurethane sponge image obtained by SEM.

Table 2. Results from Analyzed Samples Using the Method Described by Moon et al.[11]

parameters	values
length of a fiber connecting two crossing points (mm)	0.128
surface area of a short fiber segment (mm^2)	0.024
total of short fibers	435,630
total surface area (mm^2)	10586.652
specific sponge surface area ($m^2\ m^{-3}$)	**10586.652**
volume of a long fiber (mm^3)	0.028
volume of a short fiber (mm^3)	0.000364
total of big fibers	2728
total of small fibers	293,148
total volume of fibers (mm^3)	183.953
void fraction (%)	81
pore size (mm)	0.129

The BET methodology has been extensively employed in research,[17,25−28] as it is considered a good method for determining the specific surface area. However, it can introduce inaccuracies in the analysis of polyurethane sponges. This material possesses micropores, and when subjected to pressure, additional pores can be induced within its structure. Consequently, the areas where nitrogen can adhere may yield surface area values higher than what is genuinely anticipated for this material.

Concerning the analysis method for SEM images, several factors require consideration. In this approach, numerous approximations are needed, including the quantification of fiber counts and diameter measurements. Hence, it is crucial that a single individual conduct the analysis. Additionally, it was assumed that all constituent fibers of the sponge were cylindrical and that all pores possessed a cubic shape.

Therefore, we can deduce that distinct methodologies yield varying determinations of the specific surface area of the sponge.

The different values can also be confirmed if we compare the results shown in studies that used a polyurethane sponge as support media.

In Table 3, we verify that the reported specific surface area range is from 193 to 20,000 $m^2\ m^{-3}$. Moreover, only the study from de Oliveira Netto and Zaiat[17] mentioned BET as the methodology they used to determine this parameter.

https://doi.org/10.1021/acsomega.3c06098
ACS Omega 2024, 9, 14766−14770

Table 3. Specific Surface Area Reported in Studies that Used Polyurethane Sponge as Support Media

ref	reactor	specific surface area (or similar)	unit
17	combined anaerobic−aerobic packed-bed reactor	43.8	$m^2\ g^{-1}$
15	cyclic-activated sludge system	5000	$m^2\ m^{-3}$
14	three different reactors[a]	0.195	m^2 (surface area)
19	trickling filter	20,000	$m^2\ m^{-3}$
31	moving bed biofilm reactor	15,470	$m^2\ m^{-3}$
18	moving bed biofilm reactor	900	$m^2\ m^{-3}$
8	trickling filter	400	$m^2\ m^{-3}$
9	trickling filter	193−326	$m^2\ m^{-3}$

[a]Sponge biofilter (SBF), sponge batch reactor (SBR), sponge-submerged membrane bioreactor (SSMBR).

As we have pointed out previously, although specific surface area is considered as an advantage to apply sponge as support media, the nonuniformity in methodology and unit makes it difficult to analyze the studies and compare with other material.

It also interferes in first data input in mathematical modeling[22,23] which could help to describe and predict the reactor's performance trends. Thus, the determination of this parameter is essential to know the potential area for biofilm development in order to optimize its application in reactors that treat effluents.

Therefore, the stark contrast in the outcomes from these two techniques underscores the importance of selecting the appropriate methodology for the material under investigation. The choice between BET and SEM image-based calculations should be guided by the specific characteristics of the material and the level of precision required. These discrepancies emphasize the need for researchers to critically assess the underlying assumptions and potential sources of error in their chosen analysis methods, ultimately recognizing that different approaches may yield varying determinations of the specific surface area, as observed in our study.

■ CONCLUSIONS

We have determined that the two methods for assessing the specific surface area (BET and calculation from SEM images) yield significantly different values. The BET method produced a value approximately nine times greater than the one obtained through SEM image analysis.

While the BET and ASAP values were somewhat similar, they were considerably higher than what was anticipated for this material's surface area. Conversely, the SEM methodology provided a more fitting result, and it appears to be a more suitable approach for describing this parameter and utilization as input data in mathematical models.

■ AUTHOR INFORMATION

Corresponding Author

Luana Mattos de Oliveira Cruz − *School of Civil Engineering, Architecture and Urban Planning − FECFAU, UNICAMP (University of Campinas), 13083-852 Campinas, SP, Brazil*; orcid.org/0000-0003-3795-9111; Phone: +55 19-3521-2377; Email: luanamoc@unicamp.br

Authors

Rosana Oliveira Menezes − *School of Civil Engineering, Architecture and Urban Planning − FECFAU, UNICAMP (University of Campinas), 13083-852 Campinas, SP, Brazil*

Tammy Salgado Duarte − *School of Civil Engineering, Architecture and Urban Planning − FECFAU, UNICAMP (University of Campinas), 13083-852 Campinas, SP, Brazil*

Daniel Augusto Camargo Bueno − *School of Civil Engineering, Architecture and Urban Planning − FECFAU, UNICAMP (University of Campinas), 13083-852 Campinas, SP, Brazil*

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.3c06098

Notes

The authors declare no competing financial interest.
All authors have approved the final article and have materially participated in the research and/or article preparation.

■ ACKNOWLEDGMENTS

The authors would like to thank FAPESP (São Paulo Research Foundation, process number 2016/21586-1) for financing this study. We would also like to thank Bioproj Tecnologia Ambiental Ltd for the support media donation.

■ REFERENCES

(1) Sheng, G.-P.; Yu, H.-Q.; Li, X.-Y. Extracellular Polymeric Substances (EPS) Of Microbial Aggregates In Biological Wastewater Treatment Systems: a Review. *Biotechnology Advances* **2010**, *28* (6), 882−894.

(2) Nozhevnikova, A. N.; Simankova, M. V.; Litti, Y. V. Application of the Microbial Processo of Anaerobic Ammonium Oxidation (ANAMMOX) in Biotechnological Wastewater Treatment. *Applied Biochemistry and Microbiology* **2012**, *48* (8), 667−684.

(3) Xiao, Y.; Zeng, G. M.; Yang, Z. H.; Liu, Y.; Ma, Y.; Yang, L.; Wang, R.; Xu, Z. Coexistence Of Nitrifiers, Denitrifiers And Anammox Bacteria In A Sequencing Batch Biofilm Reactor as Revealed by PCR-DGGE. *J. Appl. Microbiol.* **2009**, *106*, 496−505.

(4) Liu, J.; et al. Performance Evaluation of a Lab-Scale Moving Bed Biofilm Reactor (MBBR) Using Polyethylene as Support Material in the Treatment of Wastewater Contaminated with Terephthalic Acid. *Chemosphere* **2019**, *227*, 117−123.

(5) Florêncio, L.; De Almeida, P.; Mendonça, N.; Volshan Júnior, I.; Andrade Neto, C.; Piveli, R.; Chernicharo, C. Nitrificação em Reatores Aeróbios com Biomassa Aderida. In Mota, F. S. B.; Von Sperling, M. (Coord.) *Nutrientes De Esgoto Sanitário: Utilização e Remoção*; ABES: Rio de Janeiro, 2009; Chapter 8, pp 262−292.

(6) Almeida, P. G. S.; Marcus, A. K.; Rittmann, B. E.; Chernicharo, C. A. L. Performance Of Plastic − And Sponge − Based Trickling Filters Treating Effluents From An UASB Reactor. *Water Sci. Technol.* **2013**, *67* (5), 1034−1042.

(7) Okubo, T.; Onodera, T.; Uemuraa, S.; Yamaguchic, T.; Ohashi, A.; Harada, H. On-Site Evaluation Of The Performance Of A Full-Scale Down-Flow Hanging Sponge Reactor As A Post-Treatment Process Of An Up-Flow Anaerobic Sludge Blanket Reactor For Treating Sewage In India. *Bioresour. Technol.* **2015**, *194*, 156−164.

(8) Sánchez Guillén, J. A.; Cuéllar Guardado, P. R.; et al. Anammox Cultivation in a Closed Sponge-Bed Trickling Filter. *Bioresour. Technol.* **2015**, *186*, 252−260.

(9) Sánchez Guillén, J. A.; Jayawardana, L. K.M.C.B.; et al. Autotrophic Nitrogen Removal over Nitrite in a Sponge-Bed Trickling Filter. *Bioresour. Technol.* **2015**, *187*, 314−325.

(10) Bressani-Ribeiro, T.; Almeida, P. G. S.; Volcke, E. I. P.; Chernicharo, C. A. L. Trickling Filters Following Anaerobic Sewage Treatment: State Of The Art And Perspectives. *Environmental Science Water Research & Technology* **2018**, *4*, 1721.

https://doi.org/10.1021/acsomega.3c06098
ACS Omega 2024, 9, 14766−14770

(11) Moon, C.; Lee, E. Y.; Park, S. Biodegradation Of Gas- Phase Styrene In A High- Performance Biotrickling Filter Using Porous Polyurethane Foam As A Packing Medium. *Biotechnology and Bioprocess Engineering* **2010**, *15*, 512−519.

(12) Fia, F. R. L.; et al. Treatment of Wastewater from Coffee Bean Processing in Anaerobic Fixed Bed Reactors with Different Support Materials: Performance and Kinetic Modeling. *J. Environ. Manage.* **2012**, *108*, 14−21.

(13) Tandukar, M.; Uemura, S.; Ohashi, A.; Harada, H. Combining UASB And The "Fourth Generation" Down-Flow Hanging Sponge Reactor For Municipal Wastewater Treatment. *Water Sci. Technol.* **2006**, *53* (3), 209−218.

(14) Guo, W.; Ngo, H. H.; Dharmawan, F.; Palmer, C. G. Roles of Polyurethane Foam in Aerobic Moving and Fixed Bed Bioreactors. *Bioresour. Technol.* **2010**, *101* (5), 1435−1439.

(15) Araujo Junior, M. M.; Lermontov, A.; Araujo, P. L. S.; Zaiat, M. Reduction Of Sludge Generation By The Addition Of Support Material In A Cyclic Activated Sludge System For Municipal Wastewater Treatment. *Bioresour. Technol.* **2013**, *143*, 483−489.

(16) Rahimi, Y.; Torabian, A.; Mehrdadi, N.; Shahmoradi, B. Simultaneous Nitrification-Denitrification and Phosphorus Removal in a Fixed Bed Sequencing Batch Reactor (FBSBR). *J. Hazard. Mater.* **2011**, *185* (2−3), 852−857.

(17) de Oliveira, N.; Antonio, P.; Marcelo, Z. Treatment of Domestic Sewage in an Anaerobic-Aerobic Fixed-Bed Reactor with Recirculation of the Liquid Phase. *Clean: Soil, Air, Water* **2012**, *40* (9), 965−971.

(18) Chu, L.; Wang, J. Comparison Of Polyurethane Foam And Biodegradable Polymer As Carriers In Moving Bed Biofilm Reactor For Treating Wastewater With a Low C/N Ratio. *Chemosphere* **2011**, *83* (1), 63−68.

(19) Zhang, X.; et al. Biofilm Characteristics in Natural Ventilation Trickling Filters (NVTFs) for Municipal Wastewater Treatment: Comparison of Three Kinds of Biofilm Carriers. *Biochem. Eng. J.* **2016**, *106*, 87−96.

(20) Zhang, S.; et al. Responses of Biofilm Characteristics to Variations in Temperature and NH4+-N Loading in a Moving-Bed Biofilm Reactor Treating Micro-Polluted Raw Water. *Bioresour. Technol.* **2013**, *131*, 365−373.

(21) Reboleiro-Rivas, P.; et al. Nitrogen Removal in a Moving Bed Membrane Bioreactor for Municipal Sewage Treatment: Community Differentiation in Attached Biofilm and Suspended Biomass. *Chemical Engineering Journal* **2015**, *277*, 209−218.

(22) Duarte, T. S. *Modelagem Matemática Aplicada À Remoção De Nitrogênio Em Um Filtro Biológico Percolador, Via Processo Anammox*; Master's thesis, University of Campinas: Campinas, SP, Brazil, 2020.

(23) Bressani-Ribeiro, T.; Almeida, P. G. S.; Chernicharo, C. A. L.; Volcke, E. I. P. Inorganic Carbon Limitation During Nitrogen Conversions In Sponge-Bed Trickling Filters For Mainstream Treatment of Anaerobic Effluent. *Water Res.* **2021**, *201*, No. 117337, DOI: 10.1016/j.watres.2021.117337.

(24) Fagerlund, G. Determination of Specific Surface by the BET Method. *Matériaux et Construction* **1973**, *6* (3), 239−245.

(25) Eldyasti, A.; Nakhla, G.; Zhu, J. Influence of Particles Properties on Biofilm Structure and Energy Consumption in Denitrifying Fluidized Bed Bioreactors (DFBBRs). *Bioresour. Technol.* **2012**, *126*, 162−171.

(26) Sabbah, I.; et al. Efficient Ammonia Removal from Wastewater by a Microbial Biofilm in Tuff-Based Intermittent Biofilters. *Ecological Engineering* **2013**, *53*, 354−360.

(27) Wan, Z.; Li, D.; Jiao, Y.; Ouyang, X.; Chang, L.; Wang, X. Bifunctional Mos2coated Melamine-Formaldehyde Sponges For Efficientoil−Water Separation And Water-Soluble Dye Removal. *Applied Materials Today* **2017**, *9*, 551−559.

(28) Tosi, P.; van Klink, G. P. M.; Hurel, C.; Lomenech, C.; Celzard, A.; Fierro, V.; Delgado-Sanchez, C.; Mija, A. Investigating The Properties Of Humins Foams, the Porous Carbonaceous Materials Derived from Biorefinery By-Products. *Applied Materials Today* **2020**, *20*, No. 100622.

(29) Menezes, R. O. *Operação De Um Filtro Biológico Percolador − Anammox Sem Recirculação Utilizando Espumas De Poliuretano Como Meio Suporte*. Master's thesis. Faculdade de Engenharia Civil, Arquitetura e Urbanismo: UNICAMP. Campinas, 2019.

(30) Teixeira, P. C.; Donagemma, G. K.; Fontana, A.; Teixeira, W. G. *Manual De Métodos de Análise do Solo*, 3rd ed.; Embrapa, 2017.

(31) Lim, J. W.; et al. Nitrogen Removal in Moving Bed Sequencing Batch Reactor Using Polyurethane Foam Cubes of Various Sizes as Carrier Materials. *Bioresour. Technol.* **2011**, *102* (21), 9876−9883.

https://doi.org/10.1021/acsomega.3c06098
ACS Omega 2024, 9, 14766−14770