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Enhanced commercial and 3D-printed bio-carriers improve wastewater treatment performance: A critical mini-review

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Abstract. An advanced wastewater treatment technology, simple, uniform, reliable and stable in its operation, which at the same time is highly competitive from the economic and environmental point of view, is Moving Bed Biofilm Reactors (MBBR) performed with the contribution of bio-carriers. This review provides an overview of the most innovative and recent applications of several kinds of bio-carriers to improve wastewater treatment efficiency. In particular, the use of commercial plastic bio-carriers is presented, such as K1, K3, RK 04Z098, or bio-carriers of natural origin after modification of their surface, such as Loofah sponge coated with $Bi_{24}O_{31}Br_{10}$ photocatalyst and Basalt fibers modified with ferric citrate. Research has shown that the most critical parameter that determines the performance of the MBBR technology is the appropriate design of the carrier in terms of its specific surface, material, texture, and orientation. 3D-printing technology provides the solution on optimization of the bio-carriers' construction, having flexibility in the design and the possibility of choosing the desirable construction material. The utilization of 3D-printed bio-carriers to improve wastewater treatment performance is still in the early research stages, and almost all the research conducted in this direction is presented in this review.

Keywords: Enhanced bio-carriers; 3D-printed bio-carriers; Wastewater treatment; Moving Bed Biofilm Reactor

1. Introduction

The continuous upgrading and implementation of new stricter regulations for water quality as well as the discovery of new advanced wastewater treatment processes have made the mature technology of biomass growth on bio-carriers during aerobic wastewater treatment, one of the current trends in wastewater treatment.

Bio-carriers allow the immobilization of microorganisms on their surface, thus improving the efficiency of biological processes. They are inert materials with different shapes and sizes and are usually made of porous ceramics, polyethylene, polypropylene, etc. The adhesion of microorganisms to the surface of bio-carriers and their further growth create a thick biofilm on their surface and inside their structure as well. The component that binds and connects the microorganisms are extracellular polymeric substances (EPS) produced by the microorganisms. The nature of the bio-carriers' material, and in particular the texture of its surface and its porosity, have a significant impact on the performance of the biofilm, as it highly affects the rate of binding and growth of microorganisms.

Natural and readily available materials are often used as bio-carriers, which in some cases give satisfactory results, while in others it is considered necessary to modify them or even use new technologies, such as 3D printing, aiming to fabricate complex, biomimetic shapes and topologies with fidelity at the micron scale.

The aim of this review is to highlights the most recent, novel applications, modifications as well as 3D-printing fabrications of bio-carriers in order to improve wastewater treatment performance.

2. Novel applications of commercial and modified bio-carriers

Extensive research has been conducted regarding the modification and further enhancement of commercial bio-carriers or use of modified natural materials as bio-carriers, giving very promising results and advanced wastewater treatment performance (Chen et al. 2021; Gao et al. 2021; Lee et al. 2021; Li et al. 2021; Sun et al. 2021; Wang et al. 2021; Zhang et al. 2021a; Zhang et al. 2021b).

The bio-carriers RK 04Z098 (Sumitomo Bakelite, Japan) with specific gravity 0.98 g/cm^3, specific surface area 1500 m^2/m^3, and outside diameter and length equal to 4 mm (**Fig. 1 (a)**), was used effectively in a one-stage airlift internal circulation biofilm reactor (Chen et al. 2021). The biofilm that was growing, and refreshed as a result of the internal recirculation, on the surface of the bio-carriers, contributed to the domination of ammonia oxidation bacteria, suppressed nitrite oxidation bacteria, and controlled heterotrophic bacteria, resulting in its long term stable operation as well as achieved long term nitrogen removal equal to 70% for 668 days.

Except for the simple addition of bio-carriers, the use of bio-carriers enriched with various bacteria, such as anammox bacteria, has also been investigated (Gao et al. 2021). In a real wastewater treatment plant, where partial denitrification was coupled with anammox to treat municipal wastewater, it was found that the nitrogen removal increased to 78% and the effluent total inorganic nitrogen decreased to 11 mg/L when anammox bio-carriers were used compared to no bio-carriers addition.

Granule activated carbon bio-carriers (Filtrasorb 300, US) have also been used successfully combined with Kaldnes K3 plastic bio-carriers (China) modified by inserting a sponge cube (10 mm × 10 mm) (Lee et al. 2021). These bio-carriers facilitated a gravity-driven membrane reactor to treat municipal wastewater, revealing that also in this case the additional internal recirculation improved further the effluent quality, by increasing the nitrogen removal. Membrane filterability improved as well, by reducing the cake layer resistance.

Natural loofah sponge bio-carriers have also been applied in wastewater treatment giving a highly promising solution for the low removal problem of refractory pollutants that usually are treated with intimately coupled photocatalysis and biodegradation process (ICPB) (Li et al. 2021). Loofah sponge was selected from nature, coated with $Bi_{24}O_{31}Br_{10}$ photocatalyst (**Fig. 1 (b)**), and then immersed in activated sludge to cultivate biofilm. As a result, after employing loofah sponge in ICPB, the tetracycline hydrochloride removal rate was increased by 6.6%, the mineralization was increased by 9.2%, and almost all photocatalytic products were degraded.

Another interesting application case of bio-carriers is the enhancement of performance of an Orbal oxidation ditch after their addition. Their inclusion in a modified Orbal oxidation ditch, where internal nitrate recycling was, also, applied in a full-scale municipal wastewater treatment plant, increased the total nitrogen removal at 77% from 69% of the conventional Orbal oxidation ditch (Wang et al. 2021). In more details, suspended commercial K3 bio-carriers, with density ranging 0.96-0.98 g/cm^3 and specific surface area of 500 m^2/m^3 (**Fig. 1 (c)**), were added in the inner channel with a filling ratio of 15%, and achieved to increase the biomass and enrich the nitrifying bacteria, hence improving the ammonia nitrogen and total nitrogen removal.

Bio-carriers have also been applied in municipal wastewater treatment units that produce high-grade water, also known as NEWater. Sun et al. (2021) used K1 commercial carriers that were inoculated with activated sludge for fast attachment of microorganisms on their surface (**Fig. 1 (d)**). They applied in a single-stage ceramic membrane moving bed biofilm reactor (CMMBBR) for simultaneous COD and nitrogen removal, followed by a coupled reverse osmosis (RO) unit for ultra-clean water production. As a result, an effluent of excellent quality was obtained after the CMMBBR process and the membrane fouling of the ceramic membrane was reduced, a result attributed among others to the fluidized bio-carriers, as well. The excellent effluent quality led to a very low RO fouling rate, and finally, this process reduced energy consumption by 44% compared to the currently used NEWater production process.

Eco-friendly approaches of bio-carriers are always more attractive in wastewater treatment, such as the commercial basalt fibers (CBF13-1200, monofilament diameter 13 μm) that were modified with ferric citrate (**Fig. 1 (e)**), to improve their surface properties and their effectiveness in nitrogen removal (Zhang et al. 2021b). It was discovered that their surface roughness and hydrophilicity were increased, while their electronegativity was reduced. Moreover, their adhesion properties increased, and the attached bacteria presented high viability. Eventually, the total nitrogen removal performance, tested in hybrid sequencing batch reactors, increased by about 16% compared to the unmodified basalt fiber bio-carriers, and up to 95%.

(a) (b) (c) (d) (e)

Figure 1. Commercial and modified bio-carriers, (a) RK 04Z098 (Chen et al., 2021), (b) Loofah sponge coated with $Bi_{24}O_{31}Br_{10}$ photocatalyst (Li et al., 2021), (c) K3 (Wang et al., 2021), (d) K1 with biofilm growth (Sun et al., 2021), (e) Basalt fibers modified with ferric citrate (Zhang et al., 2021).

3. Novel applications of 3D-printed bio-carriers

3D printing is an additive manufacturing process with great flexibility in design and very strong prospects. During the last years, research has been directed to the application of 3D-printing in fabricating bio-carriers to further enhance MBBR performance and to improve wastewater treatment efficiency and long-term stability (Dong et al. 2015; Kardel et al. 2015; Carrano et al.

2016; Elliott et al. 2017; Tang et al. 2017a; Tang et al. 2018; Proano-Pena et al. 2020).

The main target when fabricating 3D-printed bio-carriers is to increase their specific surface area (SSA), to create an optimal void size that prevents clogging, and a topographical design that will protect biofilm from premature detachment. Several gyroid 3D-printed bio-carriers with specific surface area far beyond 2300 m^2/m^3 were investigated by Elliott et al. (2017) (**Fig. 2 (a)**) and it was found that an optimal SSA is determined at 1168 m^2/m^3 that is 133% larger than the commercial K1 Kaldnes bio-carriers. 3D-printed gyroid bio-carriers of small SSA of 523.8 m^2/m^3, medium SSA equal to 1013 m^2/m^3 and large SSA of 1981 m^2/m^3, presented in **Fig. 2 (b)**), fabricated with acrylic polymer and applied in batch reactors (Proano-Pena et al. 2020). It was found that the ammonia conversion performance was correlated with the SSA of the bio-carriers reaching 99% for the gyroid bio-carriers with the largest SSA of 1981 m^2/m^3. Spindle-shaped 3D-printed bio-carriers, shown in **Fig. 2 (c)**, were also manufactured and tested (Tang et al. 2017a). The materials used were Polyols:Isocyanate = 2:1 with an SSA of 10.5 m^2/m^3. It was found that the bio-carriers cause three different mass transfer zones in the bioreactor: the zone of bulking solution, the boundary layer, and the zone inside the biofilm. The experimental results also indicated that the shape and structure of the bio-carrier, as well as the shearing force caused by the aeration, are crucial parameters and essential to create micro-habitats in a bioreactor and expand the biodiversity (Tang et al. 2017b).

One extra advantage of 3D-printers technology is the possibility to utilize the desirable materials to create bio-carriers aiming to improve the wastewater unit performance. A highly promising approach is the fabrication of zeolite bio-carriers from zeolite-embedded polymer monoliths consisting of poly(amide-imide) (Torlon) polymer and zeolites 13X and 5A (**Fig. 2 (d)**) (Thakkar et al. 2018). It was demonstrated that these bio-carriers presented robust structures with mechanical integrity and great adsorption capacity at least for the gas separation processes where they examined.

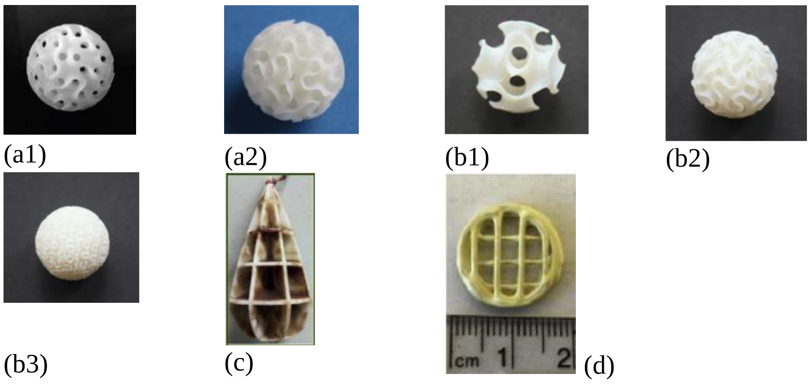

Figure 2. 3D-printed (a1) gyroid bio-carriers with orientation aligned with internal channels, (a2) with random orientation (Elliott et al., 2017), (b1) gyroid bio-carriers with small SSA, (b2) medium SSA, (b3) large SSA (Proano-Pena et al., 2020), (c) spindle-shaped bio-carrier (Tang et al., 2017), (d) zeolite bio-carrier (Thakkar et al., 2018).

4. Conclusions

Bio-carriers have extensively been used during the last decades to improve wastewater treatment efficiency through the Moving Bed Biofilm Reactors technology, a compact wastewater treatment process with increased treatment capacity. The special characteristic of the bio-carriers is that they allow the immobilization of microorganisms on their surface, improving the efficiency of biological processes. According to this work, an overview of the most innovative applications of several kinds of bio-carriers was summarized that have been used to improve wastewater treatment processes. Furthermore, almost all the research regarding the design and application of 3D-printed bio-carriers in wastewater treatment, which is still in an early stage, is presented in this mini-review work. These efforts have been made to date are opening up new opportunities for many relevant applications, from new applications of bio-carriers in wastewater treatment processes to new shapes and materials of 3D-printed bio-carriers and will benefit future research in this field.

References

Carrano A.L., Blersch D.M., Kardel K. and Khoshkhoo A. (2016), Understanding attachment preferences of benthic algae through controlled surface topographies on 3D-printed substrata. 5th International Conference on Surface Metrology, 4-7 April.

Chen H., Wang H., Yu G., Xiong Y., Wu H., Yang M., Chen R., Yang E., Jiang C. and Li Y.Y. (2021), Key factors governing the performance and microbial community of one-stage partial nitritation and anammox system with bio-carriers and airlift circulation, B*ioresource Technology*, **324,** 124668.

Dong Y., Fan S.Q., Shen Y., Yang J.X., Yan P., Chen Y.P., Li J., Guo J.S., Duan X.M., Fang F. and Liu S.Y. (2015), A Novel Bio-carrier Fabricated Using 3D Printing Technique for Wastewater Treatment, *Scientific Reports,* **5**.

Elliott O., Gray S., McClay M., Nassief B., Nunnelley A., Vogt E., Ekong J., Kardel K., Khoshkhoo A., Proaño G., Blersch D.M. and Carrano A.L. (2017), Design and Manufacturing of High Surface Area 3D-Printed Media for Moving Bed Bioreactors for Wastewater Treatment, *Journal of Contemporary Water Research & Education*, **160** (1), 144–156.

Gao R., Peng Y., Li J., Du R., Yang L., Wang M. and Deng L. (2021), Nitrogen removal from low COD/TIN real municipal sewage by coupling partial denitrification with anammox in mainstream, *Chemical Engineering Journal*, **410**, 128221.

Kardel K., Carrano A.L., Blersch D.M. and Kaur M. (2015), Preliminary development of 3D-printed custom substrata for benthic algal biofilms, *3D Printing and Additive Manufacturing*, **2**(1), 12–19.

Lee S., Badoux G.O., Wu B. and Chong T.H. (2021), Enhancing performance of biocarriers facilitated gravity-driven membrane (GDM) reactor for decentralized wastewater treatment: Effect of internal recirculation and membrane packing density, *Science of the Total Environment*, **762**, 144104.

Li F., Lan X., Shi J. and Wang L. (2021), Loofah sponge as an environment-friendly biocarrier for intimately coupled photocatalysis and biodegradation (ICPB), *Journal of Water Process Engineering*, **40**, 101965.

Proano-Pena G., Carrano A.L. and Blersch D.M. (2020), Analysis of very-high surface area 3D-printed media in a moving bed biofilm reactor for wastewater treatment. *PLoS ONE*, **15**, 1–17.

Sun H., Liu H., Zhang M. and Liu Y. (2021), A novel single-stage ceramic membrane moving bed biofilm reactor coupled with reverse osmosis for reclamation of municipal wastewater to NEWater-like product water, *Chemosphere*, **268**, 128836.

Tang B., Chen Q., Bin L., Huang S., Zhang W., Fu F. and Li P. (2018), Insight into the microbial community and its succession of a coupling anaerobic-aerobic biofilm on semi-suspended bio-carriers, *Bioresource Technology*, **247**(100), 591–598.

Tang B., Song H., Bin L., Huang S., Zhang W., Fu F., Zhao Y. and Chen Q. (2017a), Determination of the profile of DO and its mass transferring coefficient in a biofilm reactor packed with semi-suspended bio-carriers, *Bioresource Technology*, **241**, 54–62.

Tang B., Zhao Y., Bin L., Huang S. and Fu F. (2017b), Variation of the characteristics of biofilm on the semi-suspended bio-carrier produced by a 3D printing technique: Investigation of a whole growing cycle. *Bioresource Technology*, **244**(100), 40–47.

Thakkar H., Lawson S., Rownaghi A.A. and Rezaei F. (2018), Development of 3D-printed polymer-zeolite composite monoliths for gas separation, *Chemical Engineering Journal*, **348**, 109–116.

Wang X., Gao C., Jin P., Zhang Y., Xie Y., Chen T. and Zhang A. (2021), Nitrogen removal performance and bacterial community in a full-scale modified Orbal oxidation ditch with internal nitrate recycle and biocarriers, *Journal of Water Process Engineering*, **40**, 101791.

Zhang H., Zhou W., Zhan X., Chi Z., Li W., He B. and Tan S. (2021a), Biodegradation performance and biofouling control of a halophilic biocarriers-MBR in saline pharmaceutical (ampicillin-containing) wastewater treatment, *Chemosphere*, **263**, 127949.

Zhang X., Ding J., Gao F., Zhou X., Wei J., Liang Z., Liu Z., Xiao X. and Wu Z. (2021b), Enhancement of nitrogen removal in hybrid wastewater treatment system using ferric citrate modified basalt fiber biocarrier, *Environmental Science and Pollution Research*.

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