

# Development of filler material in 3d printers supported by computer software for nitrogen removal

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Highlights:

Biological medias were produced with addictive manufacture by 3D printers.

The material used in the biological medias was PLA that is considered a biodegradable material.

The PLA material can be used to biolfilm supports and applied to sludge treatment to removal phosphorus and nitrogen.

Keywords: biological media, PLA, sludge treatment.

#### **INTRODUCTION**

Nutrients such as nitrogen and phosphorus naturally flow into rivers through processes such as surface runoff and through groundwater infiltration. In any case, human action has been increasing the concentration of these compounds in surface sources through the discharge of effluents, and these excesses of nutrients, brings some consequences such as artificial eutrophication (Akinnawo, 2023). In addition, this scenario poses risks to public health. Therefore, opting for the implementation of removal techniques during effluent treatment proves to be a more effective approach to mitigate such impacts. The Aerated Biological Filter Systems, which have the characteristic of immobilizing the biomass, promote an accentuated retention of solid particles, which stimulates the growth of nitrifying microorganisms in these reactors (Wang et al., 2024).

Another environmental problem is caused by traditional highly-durable plastics, whose degradation is very slow. The solution lies in the use of biodegradable products that do not persist in the environment (Walczak et al., 2015). As different materials can be used as support for biofilm formation in the biological treatment process, the application of biodegradable material is desirable; therefore, polylactic acid (PLA) was chosen. It is a polymer having a potential application, mainly in the field of disposables, packaging for food, bottles and films (Walczak et al., 2015). PLA is a biodegradable and biocompatible polymer widely used in biofilm formation and additive manufacturing. The 3D manufacturing allows the fabrication of different products with a range of geometries Among known structures, the Schoen Gyroid has been shown to display remarkable geometric and mechanical properties. The Gyroid surface possesses no reflection symmetry nor straight lines, and enables highly efficient mechanical properties compared to space-frame lattice structures (Yang et al., 2019). In this sense, the effectiveness of the removal of nitrogen compounds was investigated through the simulation of aeration in percolator filters, using filter media of PLA produced through 3D printing in gyroid geometric form.













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# **METHODOLOGY**

The effluent used in the treatment was collected at a sewage treatment plant (STP) located in the city of Maringá-Paraná. The samples were collected before anaerobic treatment.

A fixed bed reactor was built with a cylindrical acrylic tube with an internal diameter of 50mm and a useful volume of 1 L. The reactors were assembled with the support material produced in the 3D printer with the tested polymer, PLA. The following equipment were used for the system: aerator, peristaltic pump to feed the reactor with effluent, assembled according to the diagram shown in Figure 1.

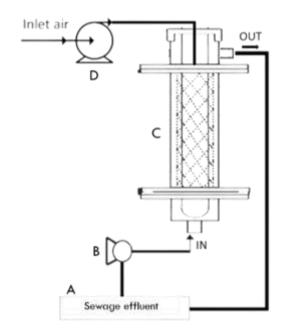


Figure 1: Schematic of bench-scale fixed-bed aerated reactor. Where: A - Container with raw effluent; B - Peristaltic pump; C - Acrylic tube with filling material; D - Air pump.

The modeling of gyroids geometries was performed using the Mathematica software, with the purpose of creating shapes that present a specific surface area.

During the experiments, analyzes were carried out to verify the following parameters: ammonia, nitrate, nitrite, total phosphorus and chemical oxygen demand (COD). The samples were collected and analyzed 2 to 3 times a week for 3 months and sent to the UEM Environmental Sanitation Laboratory for analysis.

Data represent the mean and standard error of the mean of triplicate analyses. Differences between treatments (PLA, ABS and PP filler material) and controls (raw effluent) were evaluated using analysis of variance (one-way ANOVA), followed by Tukey's test, and using the GraphPad Prism 5.0 software (GraphPad Software, Inc., San Diego, CA, USA). Statistical significance was considered when p<0.05.

## **RESULTS AND CONCLUSIONS**

The evaluation of the concentration of nitrogenous compounds is shown in Figure 2.



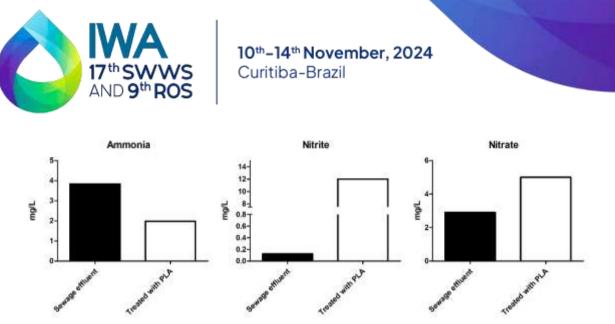


Figure 2: Analysis of the concentration of nitrogenous compounds ammonia (A), nitrate (B) and nitrite (C) in aerated fixed bed reactors with filling materials printed with PLA.

In general, it can be seen that the concentration of ammonia decreases after treatment (about 50%), while there is an increase in the concentration of nitrate and nitrite. It must be considered that when there is recent pollution, it is generally characterized by the predominance of nitrogen in organic and ammoniacal forms. In remote pollution, when under aerobic conditions, ammoniacal nitrogen passes into the less toxic forms of nitrite and nitrate, since the production of nitrate results from the bacterial oxidation of ammonium, with nitrite as an intermediate (VON SPERLING, 1996).

Generally, nitrate occurs in low concentrations in surface waters. In recent domestic effluents, the nitrate concentration is also low. In effluents from biological treatment plants with aeration tanks, nitrate is found at higher levels (VON SPERLING, 1996).

Nitrification is a key process in biological wastewater treatment and is essential for the removal of inorganic nutrients. During aerobic nitrification, ammonia is converted into nitrate, which is then removed through anoxic denitrification by producing nitrogen gas (N<sub>2</sub>). The first step of nitrification, known as nitritation, involves the conversion of ammonia to nitrite through two sequential oxidation reactions. Initially, ammonia (NH<sub>3</sub>) is oxidized to hydroxylamine (NH<sub>2</sub>OH) by the membrane-bound enzyme ammonia monooxygenase (AMO). The subsequent conversion of hydroxylamine to nitrite is catalyzed by the periplasmic enzyme hydroxylamine oxidoreductase (HOA). Bacteria responsible for this nitritation process belong to the genera *Nitrosomonas*, *Nitrosospira* ( $\beta$ -Proteobacteria), and *Nitrosococcus* ( $\gamma$ -Proteobacteria). The second step of nitrification, where nitrite is converted to nitrate, is catalyzed by the enzyme nitrite oxidoreductase (NOR), which is produced by the genera *Nitrobacter* ( $\alpha$ -Proteobacteria), *Nitrospina* ( $\delta$ -Proteobacteria), and *Nitrospira* (phylum Nitrospirae). In wastewater treatment plants, *Nitrosomonas* and *Nitrospira* are the dominant nitrifying organisms, while Archaea are predominant in environments with low nutrients, low pH, and high sulfide levels (Wang et al., 2015).

From the results, it is possible to verify the occurrence of the nitrification process, in which ammonia is oxidized and converted to nitrate in aeration treatments. Nitrate can be removed later by complementing biological treatment with the denitrification process, which is the second step in nitrogen removal by nitrification-denitrification. At this stage, the removal of nitrogen in the form of nitrate occurs by conversion to gaseous nitrogen carried out biologically under anoxic conditions (absence of oxygen) (Rahimi et al., 2020).













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