3D printed lab-scale raceway ponds reactors applied to photo-Fenton processes

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Abstract

In this work, two different printable materials, PLA (polylactic acid) and Timberfill were evaluated in terms of chemical resistance to photo-Fenton reactants and viability for conducting the assays in raceway pond reactors (RPRs). The modeling and testing of chemical reactors, in particular their prototyping can benefit from additive manufacturing. However, the preparation of RPRs by 3D printing to study photo-Fenton reactions has not been investigated. First, these raw materials were exposed to H_2O_2/Fe(II) solutions at pH=3±0.2 under sunlight to simulate photo-Fenton environment. TOC analysis showed that PLA did not alter the concentration of TOC of the solution in the presence of H_2O_2 and iron. Furthermore, printed PLA and Timberfill lab-scale raceway ponds were examined under similar conditions in addition 30±0.5 mg·L^{-1} of caffeine as contaminant and involving the simultaneous exposition of the artificial UVA light. Through different assays in the PLA pond, TOC was not rised during operation, and no organic matter contaminated the solution from its container. However, in the case of Timberfill, the TOC of solution increased that represented the material destruction during contact time. This work shows the promising capability of PLA to be used as photo-Fenton reactor.

Keywords: Photo-Fenton, Wastewater treatment, PLA, Timberfill, 3D printing

1. Introduction

Water scarcity and its problem makes wastewater treatment an effective way to address water shortage issue. One of the most successful advanced oxidation processes (AOPs) in terms of effective micro pollutants degradation is the photo-Fenton process with the implementation of solar light to reduce the operating costs (Carra et al. 2014). Raceway pond reactors have been widely used in microalgae mass culture (Acien et al., 2013) and their application for micro pollutant removal in photo-Fenton processes has been recently assessed (Rivas et al., 2015). The main advantages of RPRs are being low cost, robust and flexible (Carra et al. 2014). In this regard, using additive manufacturing and computational modeling is increasing as digital tools for the design and fabrication of reactors in order to reduce cost and time of construction, in particular for prototyping steps. On the other hand, wide range of 3D printing materials with different characteristics are available which alter the thermal properties and durability life of the printed products. Most of the commercial 3D printing devices are used with PLA thermoplastic material because of its capability to use (Parra-Cabrera et al. 2018). Recently, further work has studied on Timberfill that is made of biodegradable material based on wood. Timberfill exhibits similar mechanical features PLA and models printed with this material have a genuine appearance of wood. In this work, the low cost and practical design of the raceway ponds was studied through additive manufacturing based on 3D printing of the two materials, PLA and Timberfill, from chemical point of view.

2. Methods and Results

All chemicals including hydrogen peroxide (33%), sulphuric acid (95–97%), iron sulphate heptahydrate (extra pure), and pure caffeine were supplied in analytical grade provided by Sigma–Aldrich. The water used was distilled grade. The concentration total organic carbon was measured by Shimadzu TOC-VCSH/CSN analyzer. A 10 W low pressure mercury lamp with main emission at 254 nm was used as a UV light source. In order to compare the chemical resistance of PLA and Timberfill contacting with Fenton's reagents, unprinted raw pieces of PLA and Timberfill were exposed to H_2O_2/Fe solutions in acidic pH under sunlight to simulate photo-Fenton environment. As TOC analysis showed, both Timberfill and PLA did not modify the concentration of TOC of the solution in the presence of H_2O_2 and iron. Afterwards, fused filament fabrication (FFF) was impelemented to print lab-scale raceway ponds by PLA and Timberfill with capacity of 500 mL.

Next, the ponds were tested using as contaminant 30 ±0.5 mg·L^{-1} of caffeine. PhotoFenton process results more efficient adjusted at pH around 3 ± 0.2. Fenton reagent was selected in concordance with literature 300 ±10 mg·L^{-1} H_2O_2, 10 ±0.1 mg·L^{-1} Fe(II), (Rozas et al., 2010). In order to compare with a blank container experiments have been also conducted inside a Pyrex rector. Evolution of Fenton reaction in dark and under

UV light was monitored after 20,120, 240 min and 8 days. Results from PLA raceway pond were consistent with the ones obtained from the reference pyrex reactor. Unlike PLA, the TOC of solution in Timberfill pond changed over time in two steps. First, the TOC of Timberfill pond decreased gradualy by a same trend with PLA one which involved the attack of ·OH radicals to the organic matters during first 240 min of reaction time. Afterwards, the TOC of solution went up sharply due to lack of H_2O_2 and subsequently ·OH radicals after 8 days. Fig. 1 a illustrates the evolution of TOC trends without UV lamp (dark condition) which confirms the promising capability of PLA to be used as a material for Fenton reactor. Finally, the experiments were repeated at the same conditions with UV light for testing photo-Fenton environment in the reactors during 2 days. In Fig. 1 b) is possible to observe similar trends than the ones reported in Fig.1 a). That analysis indicated that PLA material satisfies the requierements for conducting Fenton and photo-Fenton processes. Unfortunately, Timberfill material interferes in the system, probably it is partly degraded during the contacting time causing a TOC increase.

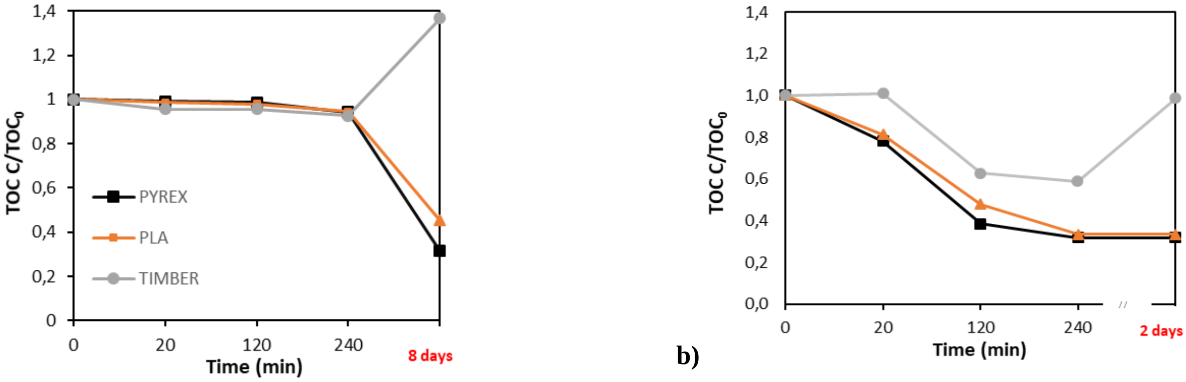

Figure 1. Evolution of TOC (30 ±0.5 mg·L^{-1} caffeine solutions, TOC_0= 17.2 ± 1 mg·L^{-1}) in PLA, Timberfill, and pyrex reactors. Experimental conditions: pH=3 ± 0.2, H_2O_2=300 ±10 mg·L^{-1}, Fe(II)=10 ±0.1 mg·L^{-1}. a) without UV light b) with UV light.

3. Conclusion

This study took advantage of 3D printing which is a promising low-cost and low-time spending methodology to build prototyping photo-Fenton reactors by PLA and Timberfill. Result from the first step, expose materials to H_2O_2 / Iron solutions at pH=3 and to sunlight to simulate photo-Fenton environment showed that both PLA and Timberfill did not alter the concentration of TOC. The printed PLA and Timberfill lab-scale RPR were tested for holding a photo-Fenton process and compared with a standard pyrex reactor under similar conditions (artificial UVA light, Fenton reagents and contaminant). The results of different assays, with and without contaminant confirm that no organic matter from the container contaminated the solution when the material tested was PLA even for longer experimental time. Thus, this work shows the promising capability of PLA to be used as a RPR reactor. On contrary, in Timberfill reactor organic matter from the container contaminated the solution and consequently TOC mesures increase.

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