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EFFECT OF HYDROGEN PEROXIDE IN PHOTOCATALYTIC TREATMENT AND ANAEROBIC DIGESTION OF POST-HYDROTHERMAL WASTEWATER

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ABSTRACT

Hydrothermal liquefaction can convert various types of biomass into bio-crude oil. However, post-hydrotermal wastewater (PHWW) may contain toxic compounds to several organisms. The aim of this study was to evaluate the use of H_2O_2 combined with photocatalysis and with anaerobic digestion for the treatment of PHWW. PHWW was generated through a S. plantesis conversion (300 °C, 30 min, 20 % of total solids). Photocatalytic experiments were carried out in the presence of TiO_2 (anatase) with H_2O_2/chemical oxygen demand (COD) ratio value (R_{HC}) ranging from 0 to 0.5 $gH_2O_2/gCOD$. The biomethane potential assays were performed as the only treatment and after H_2O_2 oxidation. As anaerobic digestion pre-treatment, the oxidation was performed with RHC value ranging from 0.25 to 0.75 $gH_2O_2/gCOD$. The efficiency of the photocatalysis combined with H_2O_2 was greater than that obtained when the process was applied isolated. The anaerobic digestion of pre-treated PHWW showed a greater CH_4 production and higher organic matter removal, compared to anaerobic digestion of raw PHWW.

Keywords: hydrogen peroxide; photocatalysis; anaerobic digestion; hydrothermal liquefaction.

1. INTRODUCTION

Hydrothermal liquefaction (HTL) is a thermochemical process that can transform several feedstock into bio-crude oil. This method is ideal for the conversion of wet biomass such as algae, because it

can cope with high water content. During the HTL process, an aqueous phase (PHWW) is produced with high organic content, nutrients (N, P) and also toxic compounds (Tommaso et al., 2015). To cope with this type of wastewater the use of physicochemical and biological treatments has been suggested. Anaerobic digestion involves microbiologically degradation and stabilization of organic compounds to biogas under anaerobic conditions. TiO_2 photocatalysis is an advanced oxidation process that has recently been used to remove organic and recalcitrant compounds of several wastewaters (Chatzisymeon et al., 2008). Nevertheless, the presence of toxic concentrations of N-heterocyclic compounds could reduce the efficiency of these processes. In this way, this work aimed to evaluate the effect of the application of H_2O_2 combined with photocatalysis and with anaerobic digestion of PHWW.

2. METHODS

Photocatalytic experiments were carried out as follows: 10 mL of PHWW and 2 g/L of TiO_2 (anatase, 21 nm particle size) were added to an appropriate amount of solution of 35 % (w/w) H_2O_2 to achieve the desirable final H_2O_2/chemical oxygen demand ratio value ($gH_2O_2/gCOD$) (R_{HC}= 0, 0.25, 0.375 and 0.5) in 120 mL flasks. PHWW was generated through a *S. plantesis* conversion (300 °C, 60 min, 20 % of total solids) and obtained through vacuum filtration (0.45 µm), which resulted in a COD of 144 g/L. The mixture was placed in the dark for 30 min at 100 rpm to ensure complete adsorption of organic compounds on the catalyst surface (Chatzisymeon et al., 2008). After that period, the UV lamp (Osram, HNS, 15W, 254nm) was turned on, while the mixture was continuously shaken. The experiments were conducted at atmospheric pressure at 37 ± 2 °C. Proper samples were collected and filtered (0.2 µm) to remove particles and then analyzed with respect to the color and COD reduction. Color was measured at λ = 538 nm on a spectrophotometer, which corresponded to the maximum absorbance in the visible region. Decoloration (%) was calculated relative to the initial absorbance. COD reduction (%) was calculated relative to the initial COD value.

The biomethane potential (BMP) assays were assembled according in 120 mL flasks containing 20 mL of biomass, 18.7 mL of basal medium, 1.3 mL of PHWW. Basal medium was prepared according to Angelidaki and Sanders (2004). Six conditions were tested, one using raw PHWW (R_{HC}= 0) and five using pre-treated PHWW with various R_{HC} values (0.25, 0.375, 0.5, 0.625 and 0.75). Granular sludge from an anaerobic reactor treating waste from poultry slaughterhouse was used. When necessary, pH values were adjusted with 0.2 mL of 10% HCl. Blank flasks, without any carbon source were also assembled. Methane production was measured through gas chromatography, with thermal conductivity detector (GC-TCD). Filtered (0.45 µm) samples before and after digestion were analyzed for COD reduction. The cumulative CH_4 production values were fitted by a modified Gompertz equation (Chen et al., 2006), using the Levemberg-Marquart method (Microsoft Origin 9.0).

3. RESULTS AND DISCUSSIONS

The extent of decoloration and COD reduction occurred during the photocatalytic treatment with H_2O_2 is showed in Figures 1 and 2. When the treatment was applied isolated, restricted values of color and COD reduction (17.8 % and 12.5 %) were obtained. On the other hand, the highest values of reduction (93.1 % and 23.5 %) were showed when a R_{HC} of 0.5 was applied. Thus indicating that the presence of H_2O_2 may enhance the production of radicals that can degrade organic compounds, and also, showing that PHWW is partly susceptible to bleaching (Chatzisymeon et al., 2008).

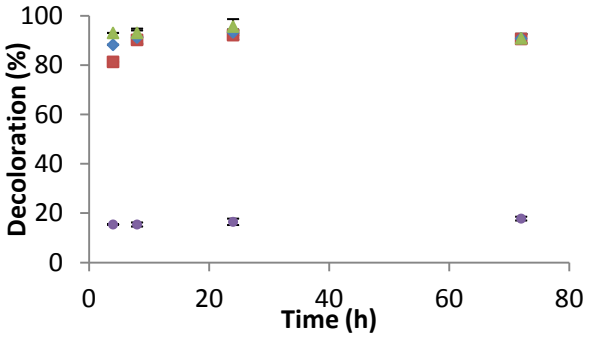

Figure 1. Decoloration vs time for R_{HC}: 0 (●), 0.25 (■), 0.375 (♦) and 0.5 (▲)

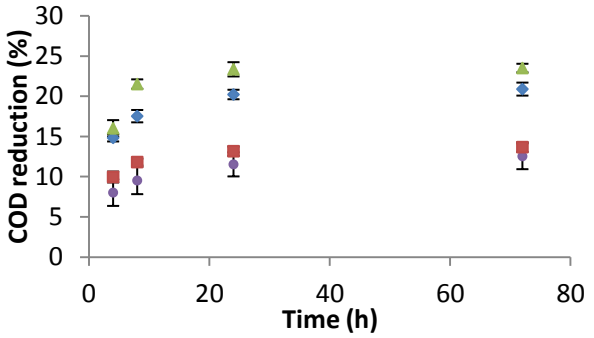

Figure 2. COD reduction vs time for R_{HC}: 0 (●), 0.25 (■), 0.375 (♦) and 0.5 (▲)

Figure 3 shows cumulative CH_4 production from both raw (4.47 mmol) and pre-treated PHWW (4.68 - 5.25 mmol) for the 912 h BMP test performed. This improvement may have happened due to the presence of radicals from H_2O_2, which can partly convert the organic and recalcitrant compounds into low-weigh molecules that can be easily biodegraded (Siciliano et al., 2016).

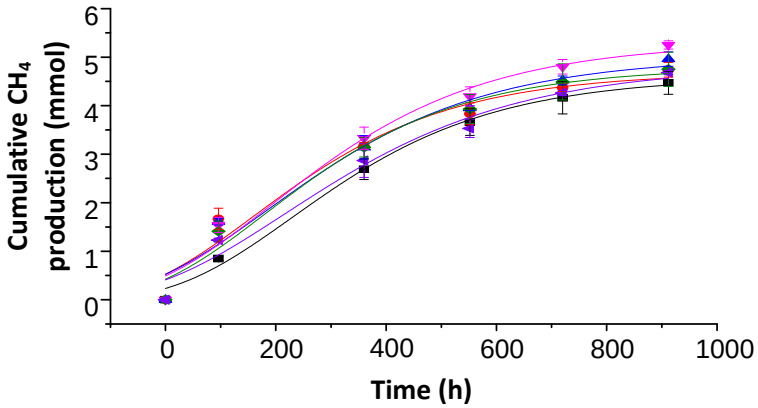

Figure 3. CH_4 production for R_{HC}: 0 (■), 0.25 (●), 0.375 (▲), 0.5 (▼), 0.625 (♦), 0.75 (◄) and model (-)

The restricted value obtained when raw samples were digested confirms the presence of toxic compounds that can inhibit anaerobic consortium. This is confirmed by the kinetic adjustment, which resulted in the longest lag phase observed when raw samples were digested. Table 1 shows the values of the duration of lag phases and the values of the specific CH_4 production rate estimated by the model, as well as COD reduction measured in the tests. Higher COD reduction values were obtained when H_2O_2 was applied. However, for R_{HC} greater than 0.375 COD reduction showed no difference or diminution, with R_{HC} = 0.75 presenting the lowest value of COD reduction.

Table 1. COD reduction and values predicted by the modified Gompertz model

R_{HC}	P_{CH_4} (mmol)	λ (h)	k ($\text{mmol} \times \text{h}^{-1} \times 10^{-3}$)	COD reduction (%)
0	4.60	229.3	8.06	53
0.25	4.64	159.87	8.41	59
0.375	5.01	183.84	8.15	58.8
0.5	5.31	191.63	8.80	57.2
0.625	4.79	179.62	8.67	53.8
0.75	4.83	216.96	7.36	49.6

4. CONCLUSIONS

The addition of H_2O_2 to the photocatalysis and anaerobic digestion are promising alternatives for the treatment of PHWW. In the photocatalysis, the efficiencies of color and COD reduction were higher that the obtained when the process was applied isolated. In the anaerobic digestion, CH_4 productions were higher when pre-treated PHWW was used.

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