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Fenton and Photo-Fenton Processes Coupled to UASB to Treat Coffee Pulping Wastewater

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One of the processes for pulping the coffee cherries can be obtained by using water. This process uses a great amount of water and its waste contains high concentration of organic matter and other compounds such as pesticides, which makes this wastewater potentially harmful to any receiving water system. The present work investigated the treatment of the pulping wastewater using two advanced oxidation processes (AOPs). The optimum molar concentration for the treatment was 6.3×10^{-2} mol L^{-1} for iron (II) and 2.5×10^{-1} mol L^{-1} of H_2O_2. The solar photo-Fenton system showed better results compared to the conventional Fenton, with a reduction of biological oxygen demand (BOD) up to 60%. The combination of chemical and biological treatment showed that the sequence of UASB followed by solar photo-Fenton treatment showed better BOD removal efficiency of 95%.

Keywords anaerobic UASB reactor; BOD; coffee; photo-Fenton

INTRODUCTION

Coffee is a much appreciated beverage around the world and Brazil is one of the major producers of this product (1). The coffee industry uses large amounts of water during the various stages of coffee production. The first step is the removal of the skin and pulp followed by removal of the pulp using water with a controlled fermentation that removes the remaining pulp to produce a better quality coffee. This process uses a great amount of water and the pulping wastewater contains high concentrations of suspended organic matter including fructose, glucose, proteins, polyphenols (caffeine, tannic acid), and small amounts of natural dyes (2). The chemical oxygen demand (COD) of these effluents is very high, in the order of 34,460 mg L^{-1} and 8% of the COD corresponding to phenol compounds (3). The coffee pulping wastewater is very harmful to the receiving aquatic system (4,5). Literature shows that very little work has been done concerning such effluents (6). Therefore, there is a need to develop a treatment process to reduce the organic load present in these effluents.

Upflow anaerobic sludge blanket process (UASB), a classical biological treatment, is being used to treat other food industry effluents such as from distilleries (7), poultry and livestock (8), and dairy products (9). The main problem is that those types of effluents are, in general, a complex mixture of high concentrations of natural organic matters and some other compounds including, in some cases, toxic ones. Therefore, other treatments are necessary and literature shows that a combination of biological treatment and advanced oxidation processes (AOPs) has been investigated as a potential alternative for the treatment of biologically recalcitrant pollutants, enhancing the biodegradability and lowering the treatment costs (10–13).

AOPs, in general, can destroy toxic organic or inorganic compounds and convert them to non-toxic ones (14,15). These processes involve the generation of hydroxyl radicals and due to their high redox potential of 2.730 V ($HO^\bullet$, H^+/H_2O) (16), $HO^\bullet$ can oxidize many classes of organic compounds, if not to CO_2, H_2O, and inorganic ions, at least to less harmful and biodegradable compounds (17–20).

The Fenton reaction (Eq. 1) is an example of AOPs. The reaction is a mixture of solutions of Fe(II) and hydrogen peroxide, that generates hydroxyl radicals in aqueous solutions (21).

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^\bullet + OH^- \quad (1)$$

The Fenton reaction efficiency can be enhanced in the presence of UV light, when it is known as photo-Fenton reaction (22). Fe(III) can be photoreduced to Fe(II) and this step is considered to enhance the oxidation effect. The regenerated Fe(II) can further react with H_2O_2 (Eq. 1), and generate additional hydroxyl radical (Eq. 2) (21).

$$Fe(OH)^{2+} + h\nu \rightarrow Fe^{2+} + HO^\bullet \quad (2)$$

Besides its simplicity, the photo-Fenton process has the possibility to use solar light, which can considerably reduce the operating costs (10,17,23).

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The objective of the present work was to investigate the possibility of diminishing the organic matter in terms of biological oxygen demand (BOD) of the coffee pulping water, by comparing two AOPs systems, namely, Fenton and solar photo-Fenton processes. Coffee farmers around our region are reporting problems concerning the safe environmental disposal of these effluents that are produced in large amount once a year. That was the reason why our group started to study POAs as an alternative treatment. In the present work it was also investigated that the coupling treatment of Fenton or solar photo-Fenton processes with an anaerobic biological treatment, using an up flow anaerobic sludge blanket (UASB) reactor in a laboratory prototype scale.

EXPERIMENTAL

Reagents

All solutions were prepared using distilled water. $Fe_2SO_4 \cdot 7H_2O$ e H_2O_2 30% (w/w) were purchased from Synth. 1.0 mol L^{-1} solution of H_2SO_4 (Isofar) and NaOH (Impex) were prepared to adjust the pH value for the photodegradation experiments. KH_4PO_4 (Dinâmica); K_2HPO_4 (Nuclear); $Na_2HPO_4 \cdot 7H_2O$ (Nuclear), NH_4Cl (Isofar), $MgSO_4 \cdot 7H_2O$ (Ciro), $CaCl_2$ (Nuclear), $FeCl_3 \cdot 6H_2O$ (Vetec) were used to prepare the dilution water for BOD analysis according to the Standard Methods for the Examination of Water and Wastewaters (24).

Sample

Pulping water effluent was collected from a coffee farm located in Cachoeira de Minas, Minas Gerais state, Brazil. The photodegradation experiments were carried out in Itajubá city located at 21°47′S; 48°10′W, during spring and summer 2008. Parameters such as pH, total solid, and BOD were determined following the Standard Methods for the Examination of Water and Wastewaters (24). The suspended solids were previously removed and therefore only the supernatant fraction was used for the photodegradation experiments.

Fenton System

Samples (100 mL) were placed in a beaker and iron(II), as $FeSO_4 \cdot 7H_2O$, was added at a predetermined concentration. The pH value was adjusted between 2.5 and 3.0. Hydrogen peroxide was added and the resulted solution was mixed for 2 h. After this period, the pH of the solution was adjusted to 8.0 to stop the Fenton reaction by precipitation of iron hydroxide and then centrifuged. Aliquots were taken to monitor the BOD before and after the AOPs treatment. BOD analyses were also performed according to the Standard Methods for the Examination of Water and Wastewaters (24). Chemical oxygen demand was determined by means of a dichromate reflux method using a commercial kit, according to Standard Methods for the Examination of Water and Wastewaters (24). The mineralization of the compounds was monitored by TOC (TOC-5000A, Shimadzu). TOC analyses were determined for a few samples because this equipment was not available at our laboratory and samples were sent to be analyzed elsewhere (Univ. Estadual Paulista – UNESP).

Photo-Fenton System

The same procedure as for Fenton reaction was followed using the best ratio of Fe^{2+}/H_2O_2, to be able to compare data. However, the sample was placed in a shallow recipient and was maintained under sunlight radiation for 2 hours, always between 11:00 h until 13:00 h, in order to allow a comparison of the results. Irradiation energy accumulated during solar exposure was measured using a radiometer (Cole-Parmer 9811) in the 365 nm with the sensor placed horizontally. The average radiation intensity reaching the solution was 1.51 mW cm^{-2}.

Biological Treatment

UASB prototype was constructed at laboratory scale according to Kondo and Rosa (25), using recycled materials. In order to quantify the possible enhancement of the biodegradability of the pulping water after Fenton reaction, 10 L of a diluted sample (1:100 v/v), treated and untreated effluent, at pH near 6.0, were passed through the UASB reactor at a flow rate of 0.50 mL s^{-1}, and BOD was analyzed before and after the biological treatment.

RESULTS AND DISCUSSION

The pulping wastewater sample was analyzed. Table 1 presents the physical chemical parameter values of the wastewater sample. As it can be observed, the wastewater shows a high concentration of total solids, and due to this fact, it was chosen to perform all the experiments, including BOD and COD, using only the supernatant fraction of the effluent, which contains dissolved organic matters. The solid phase was separated by sedimentation. The

TABLE 1
Physical chemical parameters of the coffee pulping wastewater

Parameter	Value
pH	4.14
Total Solids	9.4 mg L^{-1}
Volatile Solids	6.8 mg L^{-1}
Fixed Solids	2.5 mg L^{-1}
COD	9650 mg O_2 L^{-1}
BOD	7294 mg O_2 L^{-1}

COD and BOD values show that the organic matter concentration was very high indicating that this effluent cannot be discharged without pre-treatment to the environment.

Fenton Treatment

Literature shows that different $Fe(II)/H_2O_2$ ratios have been used as optimum for the degradation of several organics, indicating that this ratio can vary with the compound to be degraded, due to different characteristics of each compound and effluent (17,26,27). Therefore, several experiments were conducted to obtain the optimum ratio between Fe^{2+} and hydrogen peroxide to treat the coffee pulping wastewater (Fig. 1). It can be observed that a constant H_2O_2 concentration of $4.7 \times 10^{-1}\,mol\,L^{-1}$ the efficiency of the process increased as Fe^{2+} concentration also increased, reaching a maximum of 30% using $1.5 \times 10^{-1}\,mol\,L^{-1}$ of Fe^{2+}. Decreasing the concentration of H_2O_2 from 4.7×10^{-1} to $2.5 \times 10^{-1}\,mol\,L^{-1}$ resulted in a significant increase in the treatment efficiency. These results can be explained due to the recombination of the hydroxyl radicals (Eq. 3) or the auto-decomposition of H_2O_2 (Eq. 4) when present in high concentration. Therefore competitive and/or inhibitory reactions could have been taking place at higher H_2O_2 concentration (26–28).

$$H_2O_2 + HO^{\bullet} \rightarrow H_2O + {}^{\bullet}O_2H \qquad (3)$$

$$2H_2O_2 \rightarrow 2H_2O + O_2 \qquad (4)$$

At this H_2O_2 concentration the best result was observed at a Fe^{2+} concentration of $6.3 \times 10^{-2}\,mol\,L^{-1}$. Higher Fe^{2+} concentration showed a decrease in the efficiency, probably due to the fact that Fe^{2+} now is acting as $HO^{\bullet}$ scavenger (Eq. 5) (29).

$$HO^{\bullet} + Fe^{2+} \rightarrow Fe^{3+} + OH^{-} \qquad (5)$$

Results shows yet that at an even lower H_2O_2 concentration ($1.25 \times 10^{-1}\,mol\,L^{-1}$) the efficiency of the process could be increased; however, in the present work it was chosen to use the $Fe(II):H_2O_2$ molar ratio of 6.3×10^{-2} to 4.7×10^{-1}, although any of the other two ratios could also be used. The choice for the intermediate value allows the use of this process in an effluent with higher organic load, because the process would have an additional, but not in excess, amount of H_2O_2.

Solar Photo-Fenton Treatment

The solar photo-Fenton treatment was investigated using the optimum ratio obtained for Fenton reaction, for the sake of comparison. It was observed that there was an enhancement in the BOD removal from 35%, using Fenton treatment, to more than 65% efficiency using the solar photo-Fenton system. This result indicates that with irradiation of the system it was possible to increase the biodegradability of the organic matter in the wastewater. The decolorization of a coffee solution, prepared by dissolving an instant coffee powder, showed an increase of efficiency from 38% using the Fenton process to 95% using solar photo-Fenton system (30). The irradiation can increase the hydrogen peroxide decomposition rate (Eq. 2), which will increase the amount of the hydroxyl radicals in the system, due to the photo reduction of Fe^{3+} to Fe^{2+} and consequently more organic matter can be degraded during the same period of time (22,31).

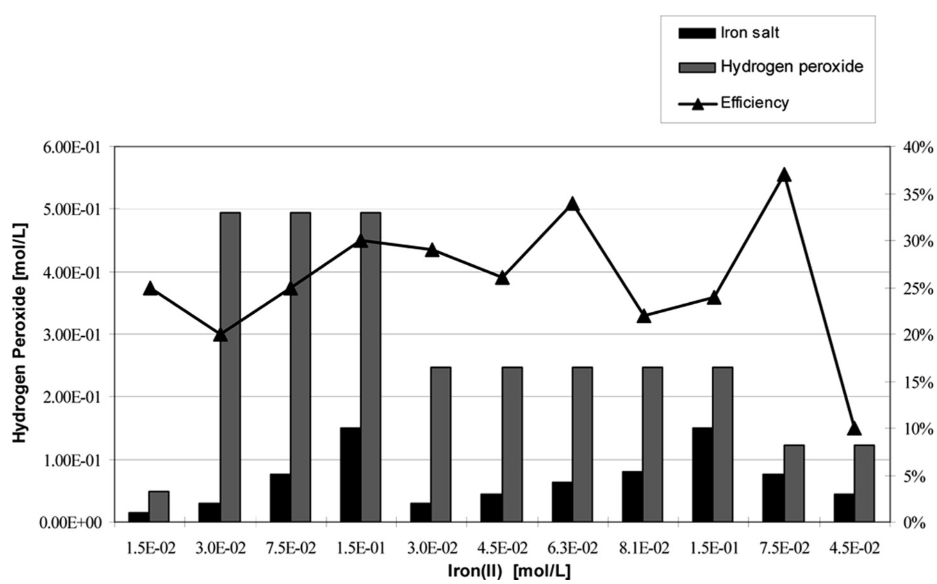

FIG. 1. BOD reduction efficiency of coffee pulping wastewater at different Fe^{2+}/H_2O_2 ratio after 2 h of reaction.

Solar Photo-Fenton Coupled to UASB Treatment

Studies using the solar photo-Fenton reaction followed by UASB treatment were also performed, to investigate the possible enhancement of the BOD removal efficiency. Some researchers have been also investigating a combination of POAs with conventional biological treatments as an alternative proposal to enhance the efficiency of the organics removal and lower the budget of the entire process (12,13,32).

For comparison, a small amount of the pulping wastewater (150 mL) was treated with solar photo-Fenton system using the same Fe(II):H_2O_2 molar ratio of reagents. After 2 h of sunlight irradiation, the pH was adjusted to 8.0 to stop the Fenton reaction. This effluent was centrifuged and the remaining solution was diluted in a 1:100 ratio with distilled water. Samples of this treated solution were withdrawn for the analysis of residual BOD. The results show that the BOD of the effluent using only the solar photo-Fenton process was reduced at 60%, which corresponded to 4380 mg L^{-1} of organic load removal, compared to the initial value (Fig. 2).

Qualitative analysis, using a procedure described by Oliveira et al. (33), when hydrogen peroxide react with VO_3^- ions which produces a red-orange color peroxovanadium cation (VO_3^+), showed that these samples were also H_2O_2 free. The absence of hydrogen peroxide is an important aspect to avoid toxic effects toward microorganisms during UASB treatment. Literature shows that hydrogen peroxide can oxidize and even dissolve sludge particles into soluble organic compounds (34). The diluted and treated effluent from solar photo-Fenton process was then passed through the UASB reactor. It can be observed in Fig. 2 that a coupled system enhanced only 5% more of the BOD removal in comparison with the remaining BOD after the solar photo-Fenton process. Probably this small efficiency of the UASB after solar photo-Fenton treatment, even though AOPs had removed high concentration of the organic load, was due to the formation of some organic intermediates during AOPs that are more bio-resistant than the initial ones. Although some researchers have observed similar results (12,35), literature shows that for wastewater containing toxic and non-biodegradable compounds, the combination of photo-Fenton and biological oxidation was more effective to remove these compounds (10,11,36,37).

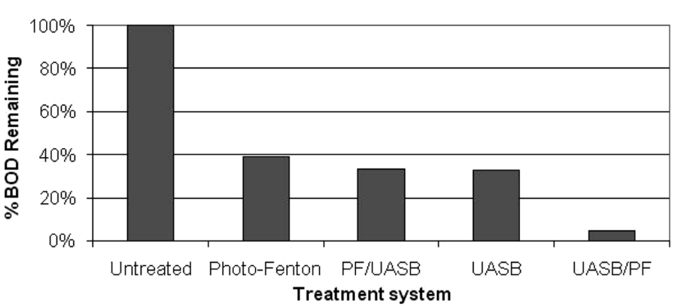

FIG. 2. Comparison of BOD reduction efficiency using coupling system with solar photo-Fenton (PF) and UASB treatment. $[Fe^{2+}] = 1.25 \times 10^{-2}$ mol L^{-1}, $[H_2O_2] = 4.7 \times 10^{-1}$ mol L^{-1}, solar irradiation (11:00 h – 13:00 h).

An inverse coupling system was also studied, treating the wastewater first with a UASB reactor and then with solar photo-Fenton (PF) reaction. It is important to mention that the original effluent was first diluted in a 1:100 ratio with distilled water, prior to the UASB treatment. This precaution was taken because the BOD of the initial effluent was too high, in order of 7300 mg O_2 L^{-1}, for the microbiological treatment without any dilution. Figure 2 also shows the results of this study. BOD removal of 70% was obtained after UASB treatment. This is an expected BOD percentage removal for a domestic wastewater effluent, using this laboratory prototype UASB treatment (25). The effluent from UASB was then treated with solar photo-Fenton reaction. After the UASB/solar photo-Fenton coupled treatment, the BOD removal reached 95%.

Although the coupling treatment using UASB/solar photo-Fenton systems was performed using the diluted effluent, the final efficiency showed to be much higher than using an inverse treatment system, solar photo-Fenton/UASB treatment. Data from TOC analysis showed similar results. After the solar photo-Fenton treatment, 20% TOC removal was observed, which can indicate that this process may be producing intermediates, which were not identified in this work, instead of degrading all the organics to total mineralization. After UASB treatment, the TOC removal reached only 14%, and this value can be explained considering that the effluent could be composed of biodegradable and non-biodegradable compounds. Therefore the values of BOD have been reduced, while the TOC values still remain high. Values of TOC after UASB/PF coupling treatment showed 80% removal. Similar results were obtained by Nam et al. [13]. The authors suggested that easily biodegradable compounds were removed by biodegradation and photo-Fenton reaction can then target the remaining organics. Since a more detailed monitoring of organics was not studied in the present work, further investigations must be done to try to identify some of these compounds.

An ideal process is the one in which a non-diluted effluent can be efficiently treated in site, in other words, at the coffee farm. Results of the present work show that it was not possible to treat a non-diluted effluent by UASB and therefore further studies need to be performed in order to optimize the process. One alternative is to enhance the period of solar radiation exposure of the photo-Fenton process that probably could increase the organic load removal, consequently decreasing the TOC value. The decrease in the organic load can probably turn possible the biological treatment without any dilution. Furthermore, not all coffee farms can afford a biological treatment facility at location, since these effluents are being produced in large amounts only once a year during the harvest season.

CONCLUSIONS

It was observed that for the present effluent the optimum concentration of iron (II) and H_2O_2 were $6.3 \times 10^{-2}\,mol\,L^{-1}$ and $4.7 \times 10^{-1}\,mol\,L^{-1}$, respectively. Among the two AOPs studied, Fenton and solar photo-Fenton reactions, the latest showed better efficiency to remove BOD of a non-diluted effluent. Solar photo-Fenton alone removed more than 60% of BOD after 2 h of irradiation. In comparison, UASB alone removed almost 70% of the BOD. However, it is important to note that for the UASB treatment, the effluent was diluted in 1:100 ratio with distilled water. Coupling systems using photo-Fenton and UASB treatments showed that the use of the sequence UASB and then solar photo-Fenton reaction resulted in BOD removal of 95%, and the inverse sequence resulted in 70% BOD removal. Probably some intermediates that are more bio-resistant where generated during solar photo-Fenton reaction which makes the coupling treatment more difficult. The sequence UASB/solar photo-Fenton treatment showed the best results to remove BOD and TOC from a coffee pulping wastewater, reaching 95% and 80% removal, respectively. These results are promising for a further step study in pilot scale due to the fact that for the coffee production the farmers would be able to implement the proposed alternative treatment with low budget, since it uses solar radiation. This study will also help the industry to achieve a sustainable coffee production, with the generation of less harmful wastewater.

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