



Chemical oxygen demand reduction in coffee wastewater through chemical flocculation and advanced oxidation processes

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Abstract

The removal of the natural organic matter present in coffee processing wastewater through chemical coagulation-flocculation and advanced oxidation processes (AOP) had been studied. The effectiveness of the removal of natural organic matter using commercial flocculants and UV/H₂O₂, UV/O₃ and UV/H₂O₂/O₃ processes was determined under acidic conditions. For each of these processes, different operational conditions were explored to optimize the treatment efficiency of the coffee wastewater. Coffee wastewater is characterized by a high chemical oxygen demand (COD) and low total suspended solids. The outcomes of coffee wastewater treatment using coagulation-flocculation and photodegradation processes were assessed in terms of reduction of COD, color, and turbidity. It was found that a reduction in COD of 67% could be realized when the coffee wastewater was treated by chemical coagulation-flocculation with lime and coagulant T-1. When coffee wastewater was treated by coagulation-flocculation in combination with UV/H₂O₂, a COD reduction of 86% was achieved, although only after prolonged UV irradiation. Of the three advanced oxidation processes considered, UV/H₂O₂, UV/O₃ and UV/H₂O₂/O₃, we found that the treatment with UV/H₂O₂/O₃ was the most effective, with an efficiency of color, turbidity and further COD removal of 87%, when applied to the flocculated coffee wastewater.

Key words: advanced oxidation processes; coagulation-flocculation; coffee wastewater; chemical oxygen demand (COD)

Introduction

The coffee industry uses large quantities of water during the various stages of the production process. Consequently, the amount of wastewater is high. It has been estimated that 40–45 L of wastewater are produced per kilogram of coffee (Rodríguez *et al.*, 2000). Coffee industry wastewater possesses a high polluting power as a result of its high organic load, pH and color. Such wastewater contains compounds such as caffeine, fat, and peptic substances, as well as many different macromolecules (Kirk-Othmer, 1985; Clarke and Macrae, 1985). The macromolecules are mainly lignins, tannins, humic acid, which are all highly structured compounds. Such macromolecules are difficult to degrade using conventional biological treatment processes and are responsible for the color of the wastewater. Therefore, to obtain a high efficiency in the removal of organic material, including recalcitrant organic compounds, a combination of various treatments, both physical and chemical, may be employed.

Mahesh *et al.* (1999) reported the study of tannin removal from coffee curing industrial effluents using adsorbent materials. They found that the process was pH dependent, with maximum adsorption between pH 3.0–4.5 for activated coconut shell (ACS) and 5.5 to neutral pH for industrial grade granular activated carbon

(IGGAC) respectively. Aguilera *et al.* (1997) evaluated the effect of ionizing radiation on coffee wastewater to decompose chemical organic refractory substances that cannot be degraded by biological treatment alone. One of the approaches used was chemical treatment followed by irradiation of the samples, since no nuclear changes of the coagulant solution or wastewater samples were expected. The method is safe, fast and effective and does not generate any pollution. Bejankiwar *et al.* (2003) studies the removal of color and organic compounds from biologically treated coffee curing wastewater by an electrochemical oxidation method. They showed that the steel anode was effective for the COD and color removal with anode efficiency of 0.118 kg COD/(h·A·m²).

In the present study, we used coagulation-flocculation in combination with advanced oxidation processes (AOP) to remove color and organic material from industrial coffee wastewater.

In the industrial coffee plant that supplied the crude wastewater used in the present work, a chemical coagulation-flocculation process (flocculant Ecofloc 6260; coagulant, T-1) was used to treat the wastewater. This process reduces the COD values from 4000–4600 mg/L for the crude wastewater to 1600–2000 mg/L.

Chemical coagulation-flocculation is widely employed in water treatment for the removal of waste materials in suspended or colloidal form, for reducing its COD content,

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and for controlling a wide range of contaminants. These include microorganisms, particulate matter that causes turbidity and color, some forms of natural organic matter, and inorganic substances. There have been a number of studies describing the primary treatment of industry wastewater, which generally use coagulants such as alum, ferric chloride, ferrous sulfate and polyelectrolytes in coagulation-flocculation approaches (Faust and Osman, 1983; Eckenfelder, 1989; Licsko, 1993; Bolto *et al.*, 1996; Aguilar *et al.*, 2002).

Chemical oxidation technologies or advanced oxidation processes based on the use of UV radiation and oxidants such as hydrogen peroxide (H_2O_2) and ozone (O_3) have been successfully used in the remediation of water contaminated with a broad spectrum of substances. These processes rely on the formation of reactive oxidizing species that degrade the organic content of the wastewater stream. The oxidation of organic compounds in water can be increased by combining the UV/ H_2O_2 , $\text{O}_3/\text{H}_2\text{O}_2$, O_3/UV and UV/ $\text{H}_2\text{O}_2/\text{O}_3$ processes (Huang *et al.*, 1993; Legrini *et al.*, 1993; Prado *et al.*, 1994; Matthews, 1992; Domenech *et al.*, 2001). The combination of these processes has a synergistic effect because of the formation of very reactive hydroxyl radicals. The hydroxyl radicals attack organic pollutants and initiate a series of oxidation reactions that ultimately lead to their total mineralization (Lin and Lin, 1993). These processes can eliminate toxic substances and increase the biodegradability of organic pollutants. The main reason for combining chemical coagulation-flocculation and photo-oxidation processes is that these processes are usually insufficient when used on their own for the reduction of COD and color in industrial wastewater.

Therefore, the purpose of this study was to test the efficiency of the combination of the chemical coagulation-flocculation process with various advanced oxidation processes (UV/ H_2O_2 , UV/ O_3 , UV/ $\text{H}_2\text{O}_2/\text{O}_3$) in reducing the color, turbidity, and chemical oxygen demand in coffee industry wastewater.

1 Materials and methods

Firstly, we studied the coagulation-flocculation of industrial coffee wastewater with the aim of improving the efficiency reducing wastewater COD compared to the treatment technology applied in the industrial plant. We tested various chemical coagulation processes on coffee wastewater to optimize the dosages of the coagulant and flocculant, pH, sample volume and floc time with respect to effective removal of suspended solids. The commercial flocculants selected for our experiments were Ecofloc 6260, Ecofloc 6700, Ecofloc 6705, Ecofloc 5400, Ecofloc 6708; these flocculants and coagulant T-1 were obtained from Industry Chem Ecotec, and Sud flock K4 and Sud flock P-65 were purchased from Sd Chemie. Lime was also used as base precipitant.

Secondly, a series of experiments was carried out to test the effectiveness of the UV/ H_2O_2 , UV/ O_3 , or UV/ $\text{H}_2\text{O}_2/\text{O}_3$

photo-oxidation processes under acidic conditions. Hydrogen peroxide (50%, v/v) was used in these experiments. Ozone was produced using a King-ozone (model Hydrozon K-40) ozone generator, with a resulting ozone production of 40 mg/h. 2 mol/L H_2SO_4 and 2 mol/L NaOH were used to adjust the pH of the coffee wastewater samples, pH measurements were carried out using a Conductronic PC18 pH meter.

1.1 Chemical coagulation-flocculation treatment

The use of various coagulants and flocculants in the chemical coagulation-flocculation treatment of the coffee wastewater was assessed by measuring the separation of suspended solids from the wastewater as the coagulant and/or flocculants were added.

The tests were carried out with 1 L samples following the standard techniques generally used in the jar-test method (Eckenfelder, 1989), with a view to optimizing the variables that influence the flocculation process at initial pH (4.6) of the coffee wastewater samples: sample volume, coagulant dose, and flocculation time. The turbidity, COD, and pH were measured before and after chemical flocculation.

The tests were carried out by placing the filtered 1 L samples in glass jars. The pH was then adjusted using 2 mol/L sodium hydroxide solution or 2 mol/L sulfuric acid at room temperature. The flocculant or coagulant dosage was added and then the solution was briskly stirred for 1 min followed by slow-speed stirring for another 20 min. Turbidity and COD measurements were carried out on samples after 20 min sedimentation time using a Photometer SQ 118 (Merck). The tests were also carried out for various flocculant and coagulant dosages at constant pH.

1.2 Chemical photo-oxidation process

The photo-oxidative treatments were carried out on 850 ml coffee wastewater samples placed in a photoreactor batch of 1 L capacity and equipped with a 1000-W medium pressure mercury lamp. The pH of each sample was initially adjusted using sulfuric acid and/or sodium hydroxide. The photo-oxidation processes were carried out in the presence of H_2O_2 (50% v/v) or O_3 , or combined H_2O_2 and O_3 . Ozone was continually bubbled through the reaction vessel at a concentration of 40 mg/h. Samples were taken at regular intervals to determine the concentrations of the pollutants (COD) as a function of exposure time to UV irradiation. Residual H_2O_2 was eliminated after the photo-oxidative treatment by ebullition to avoid disturbing the determinations of the COD. At the end of each experimental run, the treated wastewaters were subjected to COD, color, and turbidity measurements.

The chemical oxygen demand of the samples was measured using COD vials (COD 300–3500 mg/L from Merck, Germany). The digestion process of 2 ml aliquots was carried out in the COD vials for 2 h at 148°C. The absorbances of the digested samples were then measured with a photometer (SQ118; Merck). The color and turbidity of the samples were also measured with this photometer.

2 Results and discussion

The results obtained in the present work can be divided into two sections: (1) treatment of crude industrial coffee wastewater using coagulation-flocculation alone; and (2) photooxidative treatment of coffee wastewater that has previously been subjected to coagulation-flocculation treatment.

The coagulation-flocculation process was employed to remove waste materials in suspended or colloidal form and to reduce the COD content of the wastewater. The photooxidation of the organic compounds in the wastewater samples was then carried out to further reduce the COD. This photo-oxidative step was carried out using UV/H₂O₂, UV/O₃ or UV/H₂O₂/O₃ processes.

2.1 Chemical coagulation-flocculation treatment

The raw wastewater produced by the industrial coffee plant had a COD of 4000–4600 mg/L. In the plant, this raw wastewater is treated using a chemical coagulation-flocculation process with the commercial flocculant Ecoflot 6260 and coagulant T-1. This treatment reduces the COD by 55%–60%.

In order to enhance the efficiency of the removal of color, turbidity and COD from the wastewater samples, the optimal conditions were determined for the use of each flocculant alone and in combination with coagulant T-1.

Table 1 lists the results obtained by applying chemical coagulation-flocculation to the raw coffee wastewater, using Ecoflot 6260, 6705, or 6708 as the flocculant, either with or without the coagulant T-1. Compared to the raw wastewater, which is characterized by a COD of 4300 mg/L and pH 4.6, the presence of the flocculant reduces the COD for all of the flocculants tested. The optimal doses of flocculant are indicated in Table 1. The reduction in COD is on the order of 11% and 19% for Ecoflot 6705 and 6708, respectively. Moreover, the presence of both the coagulant and flocculant at the optimal dose produces a larger reduction in COD. In the case of the flocculant 6705 with coagulant T-1, the COD is reduced by approximately 33%, while use of flocculant 6708 with coagulant T-1 reduced the COD by approximately 34%. The greatest reduction in COD, 58%, was obtained using the flocculant 6260 with coagulant T-1, which is the combination used in the coagulation-flocculation process used in the industrial

coffee plant.

Experiments were also carried out using other commercial flocculants, namely Ecofloc 5400, Ecofloc 6700, Sud flock K4, and Sud flock P-65. However, these flocculants did not significantly modify the COD value and hence were deemed unsuitable for the treatment of coffee wastewater (data not shown).

Interesting results were also obtained when coagulation-flocculation of the raw coffee wastewater was carried out using a combination of lime with the coagulant T-1. The use of lime in combination with coagulant T-1 is the most effective approach for the removal of the organic compounds in coffee wastewater. A COD reduction between 65%–70% was achieved using 1.0 g of lime and 8.0 ml of coagulant T-1 in 1 L of wastewater at pH 4.6. Orozco (1973) showed that calcium oxide in coffee wastewater with a high content of mucilage pectin precipitates as calcium pectate.

2.2 Chemical coagulation and degradation using UV/H₂O₂

Raw wastewater samples were treated with the following coagulation-flocculation processes: (1) flocculant Ecoflot 6260 + coagulant T-1; or (2) lime + coagulant T-1. That is, the wastewater samples were treated using the combinations that gave the best results in the coagulation-flocculation experiments described in Section 2.1. After coagulation-flocculation treatment, the wastewater samples were subjected to UV/H₂O₂ (0.05% v/v) photooxidation treatment at pH 4.6 for 60 and 120 min. The results are summarized in Table 2.

In both of the systems considered, the presence of the flocculant and coagulant caused a reduction in the COD, with the combination of lime and the coagulant T-1 giving a greater reduction (67%). Subsequent photooxidation treatment caused a further decrease in COD. After irradiation for 60 min, the COD had been reduced to 1398 and 1335 mg/L for the systems treated with Ecoflot 6260+T-1 and lime+T-1, respectively. After 120 min of irradiation, the COD had further decreased to 655 and 612 mg/L, respectively, which correspond to COD reductions on the order of 85% and 86%. However, the long UV irradiation time required to achieve this reduction makes this treatment approach costly.

Table 1 Flocculation with various flocculants at pH 4.6 for COD of 4300 mg/L*

Commercial flocculant	Without coagulant		With coagulant T-1 (1.5 ml)		
	6705 (15 ml)	6708 (10 ml)	6705 (15 ml)	6708 (10 ml)	6260 (6 ml)
Ecofloc (dissolution 1%)	6705 (15 ml)	6708 (10 ml)	6705 (15 ml)	6708 (10 ml)	6260 (6 ml)
COD (mg/L)	3812	3496	2884	2820	1820
COD removal (%)	11	19	33	34	58

*Sample volume was 1 L.

Table 2 Effect of combining coagulation-flocculation and photodegradation with UV/H₂O₂ on COD reduction*

Flocculants	COD (mg/L)	COD (mg/L) ^a	COD (mg/L) ^b	Reduction of COD (%)
Ecofloc 6260 + coagulant T-1	2012	1398	655	85
Lime (1.0 g) + coagulant T-1(8 ml)	1491	1335	612	86

*Initial COD conc. was 4300 mg/L; ^aafter UV irradiation for 60 min; ^bafter UV irradiation for 120 min.

2.3 Degradation using UV/H₂O₂, UV/O₃, and UV/H₂O₂/O₃ radiation processes

In order to determine the optimal conditions for the UV/H₂O₂, UV/O₃, and UV/H₂O₂/O₃ photo-oxidation treatments, several runs were performed using these photo-oxidative treatments after treatment by chemical coagulation carried out by coffee industry.

Oxidative photodegradation processes are known to be affected by pH (Weavers *et al.*, 1997; Prado and Esplugas, 1999; Azbar *et al.*, 2004), so the oxidative photodegradation processes were carried out at the initial pH of the coffee wastewater (4.0–4.6) and repeated at various other pH values (both acidic and alkaline). According to the experimental data obtained for the three processes (UV/H₂O₂, UV/O₃, and UV/H₂O₂/O₃), the best results were obtained at pH 2.0. The samples were analyzed in duplicate to get reproducible results. The results are presented in the following sections.

2.3.1 UV/H₂O₂ and UV/O₃ radiation processes

Oxidation of organic pollutants by a combination of ultraviolet light and oxidants (H₂O₂, O₃, etc.) are characterized by the generation and subsequent reaction of hydroxyl radicals. These processes involve simple reactions including the UV photolysis of H₂O₂, O₃, and the formation of other photoactive oxidants. The result of our experiments focused on the reduction of the COD of the coffee wastewater by oxidative UV/H₂O₂ and UV/O₃ photodegradation processes are showed in Tables 3 and 4, respectively.

Table 3 Reduction of COD by UV/H₂O₂ photodegradation at pH 2.0

Experiment	H ₂ O ₂ concentration (% v/v)	COD (mg/L)	Color (m ⁻¹)	Turbidity (UNF)
1	0.013	1073	27.2	101
2	0.020	986	24.3	88
3	0.040	793	13	25
4	0.080	695	1.4	6

Initial COD conc. was 4300 mg/L; UV irradiation time 35 min.

Table 4 Reduction of COD by UV/O₃ photodegradation in function of pH

Experiment	pH	COD (mg/L)	Color (m ⁻¹)	Turbidity (UNF)
1	9.0	1000	12	19
2	8.0	1230	27.5	65
3	7.0	1140	5.2	14
4	4.6	1432	29	122
5	2.0	695	1.2	4.0

Initial characteristics of coffee wastewater after the coagulation/flocculation treatment applied in the industry: COD=1898 mg/L, color 32.5 m⁻¹, turbidity 139 UNF; conditions: irradiation time 35 min, O₃ flow rate 40 mg/h.

Table 3 shows the effect of varying the concentration of H₂O₂ on the reduction of COD, while maintaining the pH constant at 2.0 and the UV irradiation time at 35 min. The results show that the COD, color and turbidity all decrease as increasing the concentration of H₂O₂ between

0.013%–0.080% v/v. The highest reduction of COD in coffee wastewater was 84% (with respect to the COD of the raw wastewater, 4300 mg/L), which was achieved for UV/H₂O₂ photooxidation treatment using 0.080% v/v of H₂O₂.

In the oxidative photodegradation processes, pH is an important parameter. For this reason, the determination of optimal pH values is necessary. We studied five different pH levels (2, 4.6, 7, 8, 9) to observe the effect of pH on COD, color and turbidity removal, the results are in Table 4. The lowest COD value, color and turbidity were obtained at pH 2.0. The COD value at this pH, 695 mg/L, is equivalent to an 84% reduction, similar to that obtained for the UV/H₂O₂ system (Table 3). The oxidations of organic pollutants in both treatments were incomplete. It is interesting to observe that for pH>2 the COD was higher. This result is apparently opposed with the expected, since under neuter or alkaline conditions the UV/O₃ process accelerates the formation of radical OH· and therefore, it should increase the degradation of organic contaminants. Nevertheless, Martin *et al.* (2003, 2005), found that the ozonation of vinasse in acid media was more effective to remove polyphenols than that in alkaline media. So some macromolecular compounds presents in coffee wastewater, must be degraded with more facility under acid conditions.

2.3.2 UV/H₂O₂/O₃ irradiation process

Various experiments were carried out using ultraviolet irradiation in the presence of H₂O₂ and O₃. This combination is effective in the degradation of organic compounds. Some researchers have concluded that the simultaneous introduction of ozone and hydrogen peroxide at specific ratios gives better results (Prado *et al.*, 1994; Huang *et al.*, 1993). Table 5 shows the results when the UV/H₂O₂/O₃ irradiation process was applied to coffee wastewater that had previously been treated by a coagulation-flocculation process in the industrial plant.

Table 5 Reduction of COD by UV/H₂O₂/O₃ photodegradation

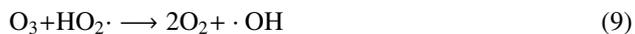
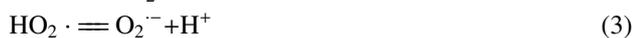
Experiment	H ₂ O ₂ (% v/v)	COD (mg/L)	Color (m ⁻¹)	Turbidity (UNF)
1	0.023	780	5.5	16
2	0.030	540	4.0	0.9
3	0.038	580	3.0	0.7
4	0.047	670	9.0	1.8

Conditions: pH 2.0; a fixed ozone flow rate 40 mg/h; UV irradiation time: 35 min.

The experiments were performed at pH 2.0 with various concentrations of H₂O₂ while maintaining the ozone flow rate constant. Varying the H₂O₂/O₃ composition used in the irradiation process affects the removal of COD, color and turbidity from the wastewater samples. The greatest reduction of COD in the coffee wastewater was achieved with the UV/H₂O₂/O₃ process under the following conditions: pH 2.0, fixed flow of ozone of 40 mg/h and 0.030% (v/v) of H₂O₂. Under these conditions, 87% of the COD was removed within 35 min of irradiation. The results in Table 5 clearly show that H₂O₂ concentrations greater than or less than 0.030% (v/v) with constant flow of

ozone (40 mg/h) produce higher COD values. This can be attributed to the formation of much less powerful $\cdot\text{OH}_2$ radicals, which are formed by the reaction between hydroxyl radicals and excess hydrogenperoxide, as discussed by Azbar *et al.* (2004). Control experiments confirm that the combination of UV, H_2O_2 and O_3 is slightly more efficient than the UV/ H_2O_2 and UV/ O_3 treatments. Additionally, it was observed a completed disappearance of the original color of the coffee wastewater.

The photooxidation and mineralization of organic pollutants with hydroxyl radicals created from a mixture of oxidants such as hydrogen peroxide and ozone in the presence of UV radiation is a well-known process. H_2O_2 can initiate the decomposition of O_3 by electron transfer (Huang *et al.*, 1993) and the resulting reaction generates $\cdot\text{OH}$ radicals, consuming H_2O_2 and O_3 as in Equation (1), and producing a chain mechanism, as shown in Equations (2) to (9) (Domenech *et al.*, 2001).



It is known that the use of ozone at high pH increased levels of hydroxyl radicals and, as a consequence, increased degradation of organic contaminants. Moreover, it has been reported (Legrini *et al.*, 1993) that this process can treat organic contaminants present at pH values between 7 and 8; the optimal molar ratio of $\text{O}_3/\text{H}_2\text{O}_2$ is 2:1 and the process is faster at alkaline pH values, as can be deduced from the pre-equilibria (2) and (3), (Glaze *et al.*, 1987). In particular, for coffee wastewater samples, UV/ H_2O_2 , UV/ O_3 , and UV/ $\text{H}_2\text{O}_2/\text{O}_3$ treatments are most effective in the degradation of contaminants at very acidic conditions (pH = 2). This behavior probably can be explained if we take into account the fact that some macromolecular compounds present in wastewater, such as lignins, celluloses, hemicelluloses, and peptic substances, are degraded in acidic conditions. It has been reported that strong acids can break down and partially dissolve lignocellulose compounds, in addition to dissolving hemicelluloses and peptic substances, (Giger and Pochet, 1987; Derregibus, 1997). On the other hand, the UV/ H_2O_2 , UV/ O_3 , and UV/ $\text{H}_2\text{O}_2/\text{O}_3$ treatments of coffee wastewater does not require a long irradiation time. The required irradiation time is sufficiently low for UV/ $\text{H}_2\text{O}_2/\text{O}_3$ treatment to be an economically attractive solution. Nevertheless, COD cannot be totally eliminated from coffee wastewater. The residual COD probably is due to the presence of macromolecules in the coffee wastewater that are very difficult to break down.

3 Conclusions

The removal of the natural organic matter present in coffee processing wastewater through chemical coagulation-flocculation and advanced oxidation processes (AOP) has been studied under acidic conditions. The results obtained when coagulation-flocculation alone was applied to the raw coffee wastewater showed that at pH 4.6, the system with Ecofloc 6260 as the flocculent in combination with the coagulant T-1 gave the greatest reduction in COD (55%–60%). In addition, we found that the combination of lime (1.0 g) and coagulant T-1 (8 ml) at pH 4.6 gave an even greater reduction in COD (about 67%). The use of chemical coagulation-flocculation treatment in conjunction with UV/ H_2O_2 photooxidation achieved an 86% reduction in COD, but required a long irradiation time of 120 min.

Among the advanced oxidation process schemes tested, we found that the UV/ $\text{H}_2\text{O}_2/\text{O}_3$ process was the most effective in reducing the COD, color and turbidity of coffee wastewater. The UV/ $\text{H}_2\text{O}_2/\text{O}_3$ process is capable of reducing the COD content of the wastewater by 87% in 35 min at pH 2.0. By comparison, the UV/ H_2O_2 and UV/ O_3 treatments under the same conditions reduced the COD by approximately 84%. Thus, the present results indicate that applying UV photooxidation in the presence of $\text{H}_2\text{O}_2/\text{O}_3$ to industrial coffee wastewaters is the most efficient approach for reducing COD, and consequently the amount of organic material.

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