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Abstract: Ozonation was found to be effective for the decolorization of solutions, but has only a slight effect on TOC removal. On the other hand, adsorption on activated carbon improves the TOC removal, but the progressive uptake of the organic contaminants during the adsorption process decreases its removal efficiency. Decolorization, mineralization, and ozone consumption of colored solutions were evaluated under continuous operation in a column by three different processes: ozonation, adsorption on a fixed activated carbon bed, and ozonation in the presence of the activated carbon bed. The introduction of an ozone flow in a fixed activated carbon bed enhances both the decolorization of the solutions and mainly the mineralization of the organic matter, even when the activated carbon was previously partially saturated. Activated carbon acts both as an adsorbent and as a catalyst in the ozonation of colored solutions. The column configuration plays an important role in the performance of this system. The configurations in series and with activated carbon in the upper part of the column showed the highest colour and TOC removal for dye solutions.

The results obtained clearly show that the combination of ozone and activated carbon is a promising technique for the final treatment of colored effluents. Practical

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applicability of this process was validated by treating two industrial textile effluents, collected after two different biological treatments.

Keywords: Activated carbon, continuous operation, decolorization, dyes, ozonation, textile effluent

INTRODUCTION

Textile effluents can cause environmental problems if they are not controlled and treated conveniently. The textile industry is not only one of the biggest water consumers, but also a great user of chemical products. Therefore, the generation of large amounts of highly contaminated wastewaters is expected, which have to be treated before being discharged in the environment, in order to accomplish the legal limits (1).

The conventional treatment usually consists on physico-chemical and biological processes and, depending on the destination of the treated effluent, these processes can be completed with a tertiary treatment to remove color, detergents, and/or salinity. Taking into consideration that there is no individual technique able to remove color at affordable costs, the best solution can be more easily obtained through the combination of technologies, making possible the recovery and reutilization of water (1).

Ozonation is one of the most attractive alternatives for solving the problem of color in textile effluents. Ozone is an extremely strong oxidant ($E^o = 2.07$ V) and reacts rapidly with most of organic compounds. The ozone molecule is selective and attacks preferentially the unsaturated bonds of chromophores, which are often associated with color. Typically, ozonation rarely originates complete mineralization to carbon dioxide and water, but leads to partial oxidation sub-products such as organic acids, aldehydes, and ketones. Consequently, in order to provide higher efficiency in the ozonation process and to optimize the economic efficacy, several advanced oxidation processes (AOP) have been investigated (2, 3).

The combination of ozone and activated carbon into a single process has recently been proposed as a promising alternative to traditional advanced oxidation processes. For this reason several works studying the interaction between ozone and activated carbon have been done in the last years (3–13).

The decolorization of colored effluents by adsorption on activated carbon is effective and could lead to better results than ozonation in terms of TOC removal but the adsorbent can become saturated very easily, requiring regeneration or substitution. In addition to its excellent adsorption capacity, activated carbon also exhibits high catalytic activity for the oxidation with ozone via $HO^\bullet$ radicals, due to its high surface area and surface chemical properties. Combination of both methods into a single process could offer an attractive alternative to overcome their inherent specific disadvantages (4, 5, 9, 14, 15).

It has been shown that the combination of ozone and activated carbon processes can modify the chemical composition of the activated carbon surface groups. These reactions may determine the adsorption capacity of the activated carbon, its regeneration efficiency, and the economic feasibility of the process (16).

In a previous paper (17), the ozonation of different dye solutions in a bubble column under continuous operation was studied in order to optimize the operating parameters. It was shown that ozonation is highly efficient for the decolorization of the solutions, but considerably less efficient in terms of TOC removal. The aim of the present work is to overcome this limitation studying the catalytic ozonation in the presence of activated carbon. Decolorization and mineralization of colored solutions were compared under continuous operation in a column by three different processes: ozonation, adsorption on a fixed activated carbon bed and ozonation in the presence of the activated carbon bed. The performance of these processes on decolorization, TOC removal, and ozone consumption was analyzed. In order to evaluate the practical applicability of these processes, the decolorization and mineralization of two industrial textile effluents collected after different biological treatments were also studied.

EXPERIMENTAL

Experimental Set-up

All the experiments were carried out continuously in an acrylic cylindrical column, perfectly isolated, with 2.5 cm internal diameter and 30 cm height. The height of the liquid inside the column was kept at 15 cm. All the experiments started with the column filled with distilled water.

Ozonation experiments were carried out at room temperature using the following operation conditions: liquid flow rate (Q_L) = 10 cm^3/min; residence time (τ) = 7.36 min; inlet dye concentration ($C_{dye,i}$) = 50 mg/L; gas flow rate (Q_G) = 10 Ncm^3/min; inlet ozone concentration ($C_{O3,i}$) = 50 g/Nm^3; pH = 7.

Adsorption on activated carbon bed experiments were performed in the same system using the following operation conditions: mass of activated carbon (m_{AC}) = 20 g; activated carbon particle diameter (d_{AC}) = 0.707–1.18 mm; Q_L = 5 cm^3/min; τ = 8.16 min; $C_{dye,i}$ = 50 mg/L; Q_G = 10 Ncm^3/min; pH = 7. For comparative purposes among the three processes (ozonation, adsorption on a fixed activated carbon bed and ozonation in the presence of the activated carbon bed), a nitrogen gas flow was continuously introduced into the column. Degasification of activated carbon was carried out in distilled water under vacuum before it was packed into the column to remove the air inside the pores.

Experiments of ozonation in the presence of an activated carbon bed were performed in the same operation conditions used in the adsorption experiments, changing the nitrogen flow for an oxygen/ozone mixture flow with 50 gO_3/Nm^3.

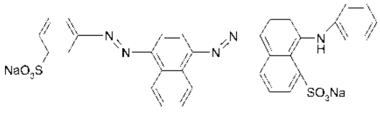
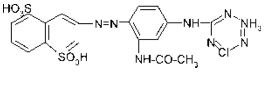
The oxygen/ozone mixture or nitrogen flow was continuously introduced into the column through a porous plate placed at the bottom. The liquid flow was continuously introduced using a peristaltic pump in a lateral entrance at the bottom of the column. Ozone was produced from pure oxygen, in a BMT 802X commercial ozone generator. Ozone in the gas phase leaving the generator was conducted by a system of three-way valves to one of the following options: bubble column; gas washing bottle, which is a by-pass to the column; BMT 964 commercial ozone analyzer, which allows the measurement of the ozone generated. After the column, there was a three-way valve which allows the gas flow to go to the ozone analyzer (to measure ozone that was not consumed in the column) or to a gas washing bottle. Ozone in the gas phase leaving the ozone analyzer was removed in a series of gas washing bottles filled with a 2% potassium iodide (KI) solution.

In all experiments, dye concentration, TOC, ozone concentration at the top of the column and pH were measured after different time periods. Decolorization of the effluent was evaluated at three different wavelengths: 436, 525, and 620 nm. In addition to TOC removal, the aromatic organic matter (roughly estimated by measuring the absorbance at 254 nm) was also measured.

Materials

An acid dye, C.I. Acid Blue 113, and a reactive dye, C.I. Reactive Yellow 3, were selected for this study. Some of the corresponding properties (18) are presented in Table 1. Dye solutions were prepared by dissolving each dye

Table 1. Selected dyes and main characteristics

Class	Commercial and generic name	Molecular structure	Chemical class	$\lambda_{máx}$ (nm)
Acid	Erionyl Navy R C.I. Acid Blue 113		Diazo	566
Reactive	Cibacron Yellow R C.I. Reactive Yellow 3		Monoazo	411

in distilled water and the initial pH of all solutions was adjusted to 7. The UV/Vis spectra for these dye solutions were previously obtained and the maximum absorbance wavelength determined.

The effluent to be treated by the processes studied in this work was previously submitted to two distinct types of biological treatments in order to remove most of the organic matter: TE1 – raw textile effluent treated in an airlift pilot plant reactor; TE2 – a blend of 50% of a raw textile effluent with 50% of a raw textile effluent previously treated in an anaerobic pilot digester, treated together in an airlift pilot plant reactor. The biological treatments substantially decreased the organic matter content, but the resultant liquids were still fairly colored. The properties of the samples collected after the biological treatments are shown in Table 2.

A Norit GAC 1240 PLUS activated carbon was used for this study. According to the supplier specifications, it is an acid washed granular activated carbon produced by steam activation. It has a neutral pH and offers good adsorption properties for water applications. This activated carbon was previously characterized (19): micropore volume (V_{micro}) = 0.367 cm^3/g; mesopore surface area (S_{meso}) = 125 m^2/g; BET surface area (S_{BET}) = 972 m^2/g; Acidity = 149 $\mu eq/g_{AC}$; Basicity = 302 $\mu eq/g_{AC}$; pH_{pzc} = 9.7.

Analytical Methods

UV/Vis absorbances were determined in a Jasco V-560 UV/Vis spectrophotometer. TOC was measured in a Shimadzu TOC 5000A analyzer. Ozone concentration in the gas phase was determined using a BMT 964 ozone analyzer.

Table 2. Parameters of the industrial textile effluents after the biological treatments

	TE1	TE2
pH	7.7	8.4
Conductivity (mS/cm)	2.8	3.5
COD (mg/L)	258	204
TOC (mg/L)	91	64
α 254 (m^{-1})	1820	1414
α 436 (m^{-1})	175	121
α 525 (m^{-1})	1253	85
α 620 (m^{-1})	94	59

COD is the chemical oxygen demand; α (λ) is the spectral absorption coefficient (absorption per unit path length) and λ is the wavelength in nm.

RESULTS AND DISCUSSION

Ozonation, Adsorption on Activated Carbon Bed and Ozonation in the Presence of an Activated Carbon Bed

A Comparative Study for the Acid Dye

The color and TOC removal determine the possibility of effluent reutilization and the ozone consumption determines the economical advantage of the process. For that reason, these are the most important parameters to evaluate the performance of the continuous decolorization of textile effluents.

Decolorization and mineralization of the acid dye solution with an inlet concentration of 50 mg/L, at neutral pH, was carried out by ozonation, adsorption on a fixed activated carbon bed and ozonation in the presence of an activated carbon bed. Figure 1 shows the results of color, TOC removal, and ozone evolutions obtained for the three processes studied.

In the adsorption on a fixed activated carbon bed experiment, it can be observed that color and TOC removal decrease with time. The activated carbon bed is gradually saturated and under the experimental conditions of this work it was not possible to complete the breakthrough curve because the time required for that was too long. On the other hand, the mineralization obtained by ozonation alone is very low compared to color removal. This may be explained by the fast destruction of the chromophore groups responsible for the color, and by the fact that the resulting sub-products are very difficult to mineralize. When activated carbon is used alone there is no formation of sub-products and the color removal is similar to the decrease of organic matter. Taking into account that ozone by itself removes 96% of the color, the introduction of an ozone flow in the fixed activated carbon bed did not improve substantially the decolorization of the solution. However, this system increases the TOC removal, which is higher than that obtained by ozonation and slightly superior to that obtained in the adsorption on the fixed activated carbon bed. The TOC reduction in the experiment of ozonation in the presence of a fixed activated carbon bed is due not only to the oxidation of dye and sub-products but also to the adsorption of a fraction of these compounds on the activated carbon surface. In this experiment, a progressive saturation of the activated carbon in terms of TOC removal was observed but this effect is not visible in the colour removal due to the high efficiency of ozone for the decolorization.

Figure 1c shows the evolution of ozone consumption with time. In the beginning of the experiment of ozonation in the presence of a fixed activated carbon bed the fraction of ozone unused ($C_{O3,o}/C_{O3,i}$) is very low, but this fraction increases with time. This fact may be due to the catalytic activity of the activated carbon to decompose ozone. Several studies (7, 10, 16, 20, 21) have been carried out to investigate the effect of the combination of ozone and activated carbon. This combination has been shown to

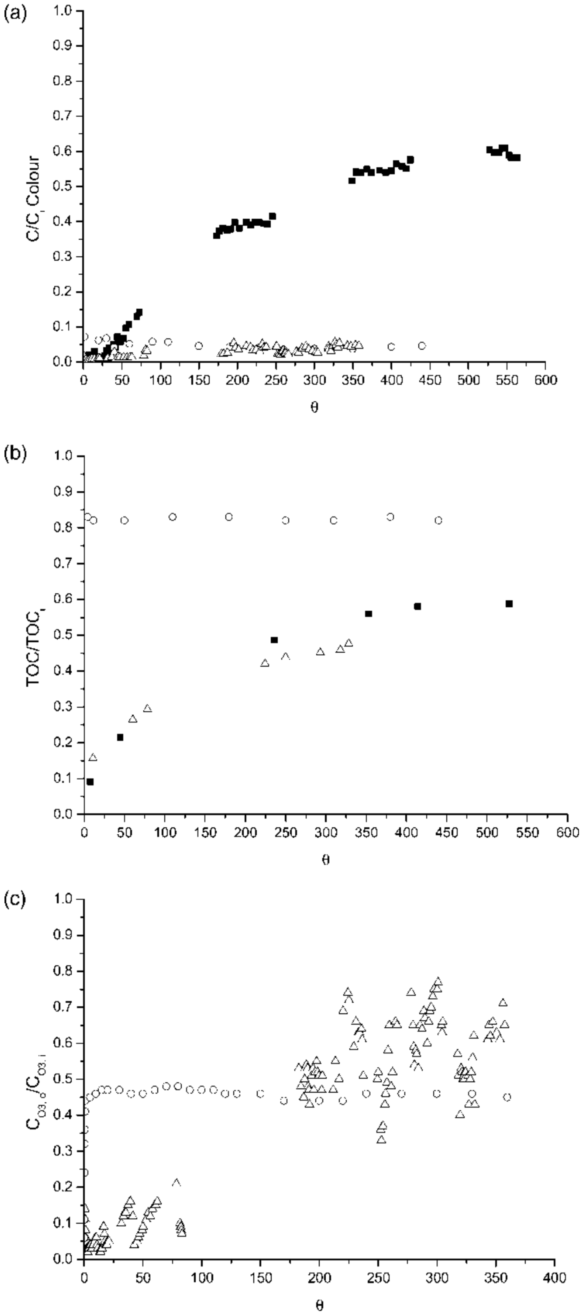


Figure 1. Evolution of (a) color removal, (b) TOC removal and (c) fraction of ozone unused by ozonation (○), adsorption on a fixed activated carbon bed (■) and ozonation in the presence of the activated carbon bed (Δ), for the experiments with the acid dye.

modify the chemical composition of the activated carbon surface groups. These studies demonstrated that the capacity of activated carbons to decompose ozone into highly oxidative species in aqueous medium is related to their surface chemistry. During the exposure of activated carbon to ozone its catalytic activity decreases, due to the increase of the number of oxygenated groups with acid characteristics on the carbon surface. This effect decreases its basic character and reductive properties and, consequently, the activity of the activated carbon towards promoting ozone decomposition. In addition, also the adsorption capacity of activated carbons for most of the organic molecules diminishes (19).

A Comparative Study for Effluent TE2

In order to evaluate the practical applicability of these processes, the decolorization and mineralization of a real textile effluent collected after biological treatments were studied, as a tertiary treatment. The textile effluent was previously submitted to biological treatments in order to remove most of the organic matter, but the resultant effluent (TE2) was still fairly colored.

Figure 2 shows the results of color and TOC removal and ozone evolution obtained for the three processes studied. The combination of ozone and activated carbon in a single process increases the decolorization efficiencies to practically 100%. Between 100 and 200 residence times an oscillation of the measured decolorization efficiencies can be observed, which probably results from a slight fluidization of the carbon bed, due to the gas flow. Until approximately 400 residence times, the adsorption on the fixed activated carbon bed presents higher decolorization efficiencies than ozone alone. However, after this period ozonation gives rise to higher decolorization efficiencies due to the progressive approach to saturation of activated carbon during the adsorption process. Nevertheless, ozonation in the presence of a fixed activated carbon has always the highest decolorization efficiencies.

TOC removal obtained in the experiment of ozonation in the presence of a fixed activated carbon bed is higher than that corresponding to ozonation alone, but is lower than that observed in the adsorption experiment. This result may be explained by the fact that for this effluent the sub-products of oxidation by ozone may have a lower affinity than the original contaminants towards adsorption on the activated carbon. However, it was observed that the removal of aromatic organic matter (Fig. 2e), measured by the absorbance at 254 nm, in the adsorption on a fixed activated carbon bed is similar to that obtained during ozonation in the presence of a fixed activated carbon bed, both decreasing with time and higher than that observed using ozone alone.

As was already discussed for the acid dye, a progressive saturation of the activated carbon in terms of TOC removal was also observed in this experiment. Nevertheless, this effect was not visible in terms of color removal probably due to the high efficiency of ozone to decolorize the effluent. An oscillation on the fraction of ozone unused was observed (Fig. 2d) and, as

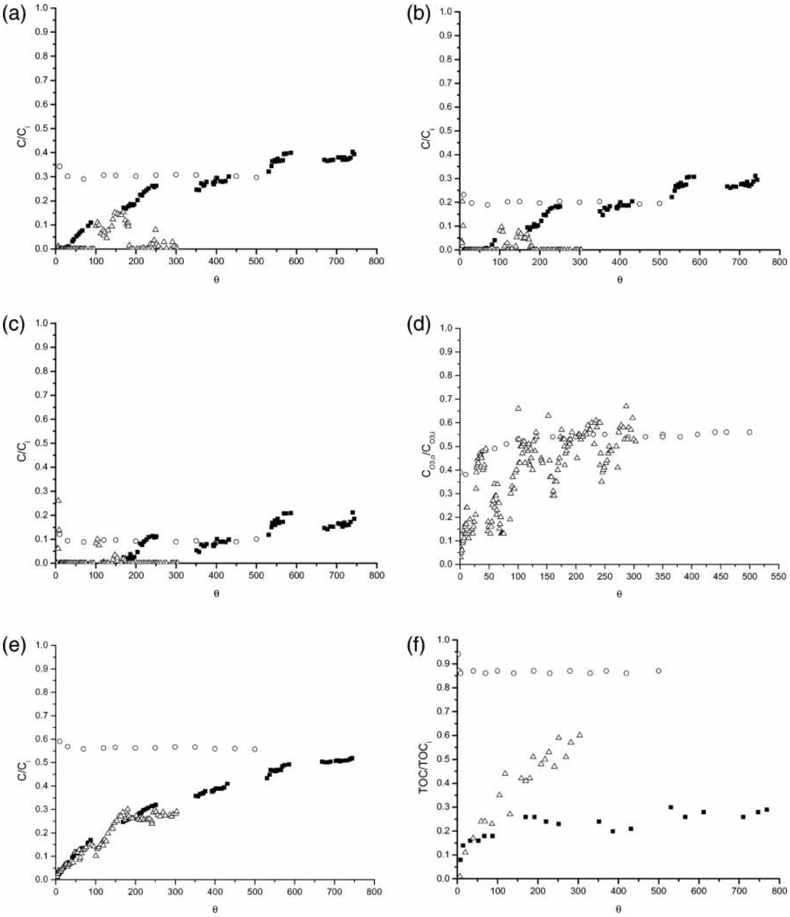
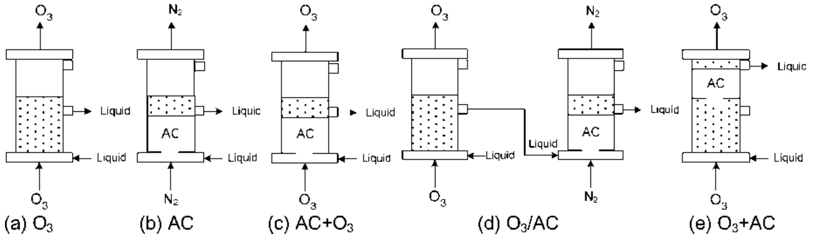


Figure 2. Evolution of color removal at λ = (a) 436, (b) 525 and (c) 620 nm, (d) fraction of ozone unused, (e) removal of aromatic organic matter at 254 nm and f) TOC removal by ozonation (○), adsorption on a fixed activated carbon bed (■) and ozonation in the presence of the activated carbon bed (Δ), for the experiments with effluent TE2.

already explained for the acid dye experiment, this may be due to a progressive alteration of the activated carbon surface properties, which decreases the ozone decomposition rate.

Influence of Column Configuration with Partially Saturated GAC

After demonstrating the practical applicability of the combination of ozone and activated carbon under continuous operation, experiments with different



(a) O_3 (b) AC (c) AC+O_3 (d) O_3/AC (e) O_3+AC

Figure 3. Scheme of the experimental column configurations.

column configurations were carried out with the aim of selecting the best one in terms of an efficient color and organic matter removal and ozone utilization. The following configurations were studied: a fixed activated carbon bed was placed in the lower part of the column and an ozone flow was introduced at the bottom of the column (Fig. 3c) AC + O_3; sequential experiment where ozonation was carried out in the first column and, after that, the collected effluent was introduced in a fixed activated carbon bed, (Fig. 3d) O_3/AC); a fixed activated carbon bed was placed in the upper part of column and ozone was introduced at the bottom (Fig. 3e) O_3 + AC). For comparative purposes, ozonation experiments (Fig. 3a) O_3) and adsorption on a fixed activated carbon bed (Fig. 3b) AC) were also performed.

The operating conditions were selected in order to guarantee a residence time in the fixed activated carbon bed ($\approx$ 10 min) and an applied ozone dose per volume of solution ($\approx$94 gO_3/m^3solution) identical for all the different configurations studied. In the ozonation experiment a residence time ($\approx$18 min) identical to that expected in the lower part of the column in the experiment O_3 + AC was used.

In order to guarantee that the results obtained by adsorption remain almost constant during the experiments, about 10 g of a partially saturated carbon bed was used. For this purpose, the activated carbon was previously put in contact with the same solutions used in the experiments until at least 60% of saturation was reached. After this value the removal by adsorption changes very slowly (cf. Fig. 1). A hydrodynamic study of the bubble column reactor was previously performed. The residence time distribution curves obtained under these operation conditions showed that the bubble column can be described as approximately one continuous stirred tank reactor and the steady state is reached after a period of 3–4 residence times. These experiments were carried out with acid and reactive dye solutions and with a textile effluent (TE1) collected after biological treatment. The results obtained at steady state are presented in Fig. 4.

Dye Solutions

Figures 4a and 4b show the effect of the column configurations on color and TOC removal for dye solutions. It is obvious that the column configuration plays an

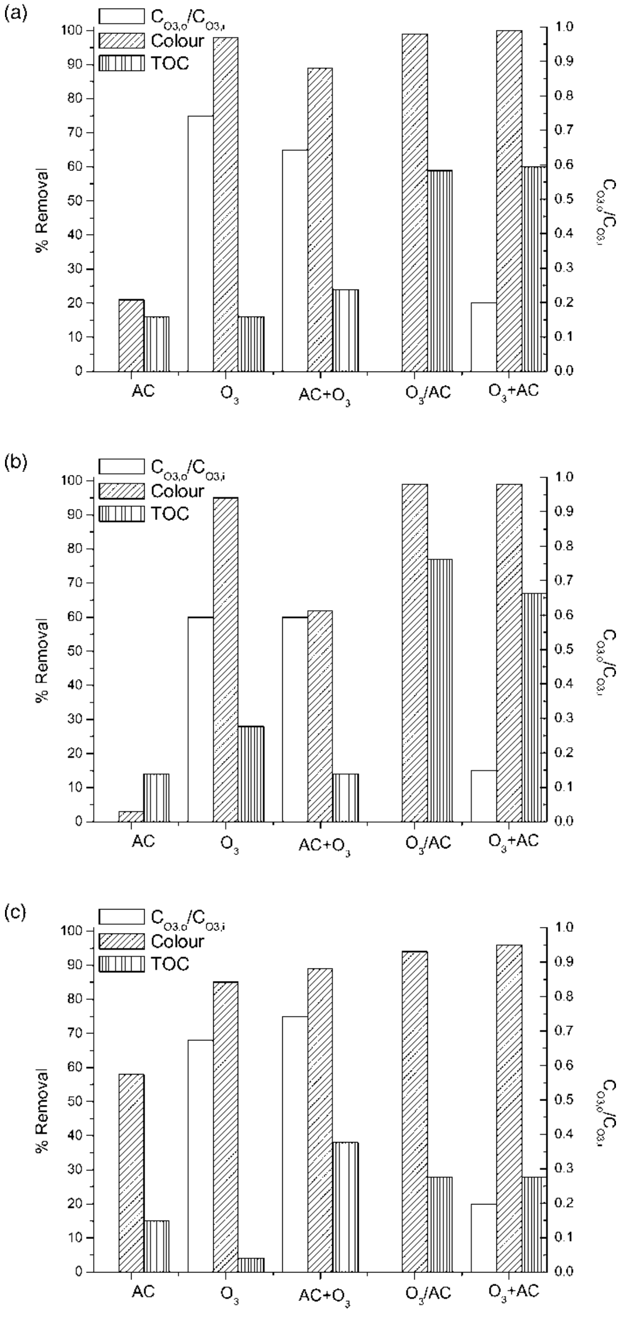


Figure 4. Steady state color and TOC removal and fraction of ozone unused for the (a) acid and (b) reactive dye solutions ($C_{dye,i} = 50$ mg/L) and (c) effluent TE1 in the experiments with different configurations.

important role in the performance of the system. For both dyes, O_3 experiment presents higher decolorization efficiency than $AC + O_3$ experiment. This difference is related to the mass transfer coefficient of ozone from the gas to the liquid phase. In preliminary studies (not included in this paper) it was found that the configuration $AC + O_3$ presented the lowest rate of mass transfer ($K_La = 0.098\ min^{-1}$ compared with $K_La = 0.131\ min^{-1}$ for O_3 configuration). In this configuration there is no uniform distribution of the gas bubbles, leading to a less efficient contact between the ozone and dye molecules and a lower color removal than that obtained with ozone alone. This effect is more pronounced for the reactive dye. However, for the acid dye this configuration ($AC + O_3$) presents higher TOC removal than O_3 and AC alone. This fact may be due to the oxidation of dye and primary sub-products and probably to the adsorption on the activated carbon surface of a fraction of those sub-products. On the other hand, the activated carbon can enhance the decomposition of ozone into hydroxyl radicals which are less selective for decolorization but increase the mineralization of the organic compounds. Looking at the results obtained for the reactive dye, it is obvious that this dye presents a different behavior. TOC removal by ozone alone is higher than that observed for the AC and $AC + O_3$ experiments. This might be due to the weak affinity of the activated carbon for this dye. Also for this dye, color removal in AC experiment is lower than TOC removal. This is related to the fact that this is a commercial dye, which usually has other additives that may be colorless but contribute to the TOC of the solution.

For the acid dye solution, color removal in O_3, O_3/AC, and $O_3 + AC$ experiments are practically coincident: 98, 99, and 100%, respectively. These findings indicate that the effect of the presence of the fixed activated carbon bed is covered up by the high efficiency of ozone for color elimination, although the same did not occur concerning TOC removal. For the reactive dye solution, the presence of activated carbon increases the color removal, since the color removal in O_3/AC and $O_3 + AC$ experiments is similar (99%), while ozone alone presents 95%. For both dyes, the results corresponding to TOC removal in O_3/AC and $O_3 + AC$ experiments correspond to the highest values. Although the activated carbon was partially saturated with dye molecules, it still presents high adsorption capacity for the sub-products resulting from dye oxidation. This fact can be explained by the large size of the dye molecules, responsible for high diffusional limitations, while the sub-products molecules are smaller, contributing to the increase of TOC removal in the solution. On the other hand, according to literature studies (7, 10, 21) activated carbon catalyses ozone decomposition in aqueous phase in highly oxidative species increasing the removal of organic matter. Thus, the increase of TOC removal is due to the activated carbon that acts not only as an adsorbent but also as a catalyst during ozonation. According to Figs. 4a and 4b, the lower ozone consumption is obtained for the O_3 experiment and the highest is obtained for the $O_3 + AC$ experiment. As already explained, this difference is related to the catalytic activity of activated carbon to decompose ozone.

These results show that the best results are obtained for the configurations O_3/AC and $O_3 + AC$. This last configuration not only allows high color and TOC removal, but also presents the lowest ozone concentration leaving the column. This means that ozone utilization is high, minimizing the operational costs of the process.

According to some studies (4, 9), the existence of significant synergistic effects between ozone and activated carbon was expected. However, under the experimental conditions of this work, there are practically no synergistic effects when ozonation is carried out in the presence of activated carbon for these dye solutions, since the removal efficiencies in configuration O_3/AC (results obtained by the addition of ozonation and adsorption contributions) are practically the same as those obtained in $O_3 + AC$ configuration. Nevertheless, the results obtained in the experiments with ozone and activated carbon are better than those obtained when theses processes are used alone.

Effluent TE1

For the wavelengths studied, color removal curves present similar behavior with time, the highest removal efficiency being obtained at 620 nm. For this reason, only the results for this wavelength will be presented. As was already observed for the dye solutions, the removal efficiencies for the effluent TE1 depend on the configurations used (Fig. 4c). Color removal in $AC + O_3$ experiment is higher than that obtained in the O_3 experiment (89 and 85%, respectively), although the mass transfer coefficient of ozone is superior in the O_3 experiment. It is also verified that this configuration presents higher TOC removal efficiency than the ozonation and adsorption experiments alone.

Decolorization efficiencies obtained in the O_3/AC and $O_3 + AC$ configurations (94 and 96%, respectively) are superior to those obtained in the remaining configurations. These results show that, for this type of effluent, the presence of activated carbon enhances both color and TOC removal. TOC removal in O_3/AC and $O_3 + AC$ configurations are higher than to those obtained in the O_3 and AC experiments, but are lower than that obtained in $AC + O_3$ experiment. This might be explained by the existence of some catalytic effect when the configuration $AC + O_3$ is used to treat effluent TE1.

Once again, it is obvious that $O_3 + AC$ configuration presents the higher ozone consumption. As was already mentioned, this difference is related to the catalytic activity of the activated carbon for ozone decomposition. On the other hand, $AC + O_3$ experiment presents the lower consumption of ozone; this fact is probably related to the lower mass transfer coefficient of ozone in this case.

As was already observed for the dye solutions, it can be concluded that for this effluent the simultaneous use of ozone and activated carbon in the configurations O_3/AC and $O_3 + AC$ practically did not show a synergistic effect, under the operation conditions used. Nevertheless, the $AC + O_3$ configuration seems to have some catalytic effect for TOC removal.

CONCLUSIONS

According to the experimental results, the following conclusions can be drawn:

1. Ozonation is highly efficient in the decolorization of the solutions, but considerably less efficient in terms of TOC removal.
2. Adsorption is efficient for the decolorization of colored solutions, but due to the progressive uptake of contaminants on the activated carbon surface the removal efficiency decreases drastically during operation.
3. The combination of ozonation and activated carbon in a single process enhances the decolorization of the solutions and especially the mineralization of the organic matter, even when the activated carbon was previously partially saturated. Activated carbon acts both as an adsorbent and as a catalyst in the ozonation of colored solutions.
4. Column configuration plays an important role in the process performance. When activated carbon is placed in the lower part of the column, its presence did not improve significantly the decolorization of dye solutions, being its effect more evident in the mineralization of organic matter. O_3/AC and $O_3 + AC$ configurations present the highest values of color and TOC removal. Nevertheless, there are practically no synergistic effects, since the removal efficiencies in configuration O_3/AC are practically the same as those obtained in $O_3 + AC$ configuration.
5. The practical applicability of this process was validated by treating two industrial textile effluents. In this case, some catalytic effect for TOC removal was noticed for the configuration $AC + O_3$.
6. The results clearly show that ozonation in the presence of a fixed activated carbon bed is a promising technique for the final treatment of colored effluents, overcoming the inherent specific disadvantages of the individual process (ozonation, adsorption on activated carbon).

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