A comparison of different activated carbon performances on catalytic ozonation of a model azo reactive dye
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ABSTRACT
The objective of this study is to compare the performances of catalytic ozonation processes of two activated carbons prepared from olive stone (ACOS) and apricot stone (ACAS) with commercial ones (granular activated carbon-GAC and powder activated carbon-PAC) in degradation of reactive azo dye (Reactive Red 195). The optimum conditions (solution pH and amount of catalyst) were investigated by using absorbencies at 532, 220 and 280 nm wavelengths. Pore properties of the activated carbon (AC) such as BET surface area, pore volume, pore size distribution, and pore diameter were characterized by N₂ adsorption. The highest BET surface area carbon (1,275 m²/g) was obtained from ACOS with a particle size of 2.29 nm. After 2 min of catalytic ozonation, decolorization performances of ACOS and ACAS (90.4 and 91.3%, respectively) were better than that of GAC and PAC (84.6 and 81.2%, respectively). Experimental results showed that production of porous ACs with high surface area from olive and apricot stones is feasible in Turkey.

Key words | activated carbon, apricot stone, catalytic ozonation, olive stone, reactive azo dye, reactive red 195

INTRODUCTION
Dyes are released into the environment mainly from textile and dyestuff industries, most of which are azo dyes. Azo dyes released without proper treatment represent about 15% of the global production, which is 150 tons/day. Due to their toxicity and recalcitrance, these dyes can be hazardous to the environment although presented at low concentrations. The conventional chemical (coagulation–flocculation) and biological (activated sludge, sequential bed reactors, anaerobic/anoxic) based treatment methods are widely used for textile water treatment (Mishra & Tripathy 1993; Sarasa et al. 1998; Vandeviere et al. 1998; Selcuk 2005). However, the resulting effluent is still quite colored. In recent years, ozonation has been emerging as a potential process for color removal of dyes, as the chromophore groups with conjugated double bonds, which are responsible for color can be broken down by ozone either directly or indirectly forming smaller molecules (Sarayu et al. 2007; Gül & Özcan-Yildirim 2009; Yildirim et al. 2011). In spite of its high effectiveness, ozone decolorization is also an expensive process because of the high capital investment and operating costs (Lin & Lai 1999).

Both ozonation and adsorption on activated carbon (AC) have proven to be efficient in removing color and some of the organic matter from highly colored effluents (Güll et al. 2010). The effect of AC on the ozone reaction must be promoting hydroxide radical generation (Gül et al. 2007). It is considered that ACs obtained from agricultural by-products are in favor compared with other ACs used in industry with respect to their adsorptive properties, their catalytic efficiency and economic feasibility as a wastewater treatment process compared with other purification methods (Martinez et al. 2006; Önal 2006).

Olive and apricot stones are agricultural wastes predominantly produced in the Mediterranean countries. The commercial production of olive and apricot in Turkey are two important agricultural activities. The annual production of olive oil in Turkey is between 100,000 and 250,000 tons. Olive oil production generates a significant amount of solid waste (Uğurlu 2007). A total of 120,000 tons of apricots per year are harvested in Malatya (a city located in the south-east region of Turkey). Annual dried apricot production in this region is estimated to be 40,000 tons.

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(Sentorun-Shalaby et al. 2006). Therefore, it is important to evaluate olive and apricot stones, as AC resources and as local raw materials in Turkey.

The resulting products from carbonization of olive and apricot stones have been successfully used as sorbents for a wide variety of pollutants in aqueous solutions (Galiatsatou et al. 2002; Cimino et al. 2005; Martinez et al. 2006; Kula et al. 2008). In addition to its excellent adsorption capacity, AC also exhibits catalytic activity due its high surface area and surface chemical properties (Faria et al. 2005).

A prior work on chemically modified olive stone as a sorbent for basic dye (safranine) removal by Aziz et al. (2009) is available. Their results indicated that olive stones treated with concentrated sulfuric acid at room temperature exhibited a better efficiency in terms of sorption capacity towards the safranine, than those reported so far in the literature. Another work was performed with ZnCl₂ activated apricot stone (WA11Zn5) to remove three dyes, methylene blue (MB), malachite green (MG) and crystal violet (CV) by Akmil-Basar (Akmil-Basar 2006).

The aim of this work is to develop an efficient catalyst based on raw olive and apricot stone for the removal of reactive dyes by performing a cheaper and simple method compared with commercial AC production methods. In this study, the preparation of AC was carried out by impregnation of olive and apricot stones with KOH solution, followed by carbonization. The resulting materials were used to remove a reactive dye (Reactive Red 195) from aqueous solutions by catalytic ozonation.

**EXPERIMENTAL**

**Materials**

C.I. Reactive Red 195 was used in this study. The dye, C.I. RR195 (chemical formula = C₃₁H₁₉ClN₇Na₅O₁₉S₆, MW = 1,136.3 g/mol, λ<sub>max</sub> = 532 nm) was obtained from Eksoy Kimya Ltd., Adana, Turkey and used without further purification. The dye has both a vinylsulfone (VS) group and a monoclorotriazine (MCT) group. The chemical structure of the dye is given in Figure 1.

**Preparation of activated carbon samples from olive stone (OS) and apricot stone (AS)**

The olive and apricot stones were obtained from an olive oil producing plant (Adana) and apricot plant (Malatya). Olive and apricot stones were separated from the flesh of the fruit and air-dried for 2 weeks. This was followed by crushing and sieving the stones to obtain suitable particle size ranges (1.0–3.0 mm) using the same batches. Oil in the olive stone was removed by hexane extraction method by Soxhlet apparatus. Crushed raw materials were dried at 110 °C for 24 h and stored in plastic tubes.

In the first step of activation, the starting material was mixed with the reactant (KOH) at the reactant/starting material weight ratio of 4:1. This ratio was selected from previous works (Marsh & Rodriguez-Reinoso 2006; Martinez et al. 2006; Ubago-Peréz et al. 2006). High ratios of KOH to carbon result in the disintegration of the carbon granules to powder. The mixture was then dried at 110 °C to prepare the impregnated sample. In the second step, the impregnated sample was placed on a quartz dish, which was then inserted in a quartz tube (i.d. = 60 mm). The impregnated sample was heated up to activation temperature (800 °C) under N₂ flow (100 mL/min) at a rate of 10 °C/min and held at the activation temperature for 1 h. After activation, the sample was cooled down at room temperature under N₂ flow. Activated sample was washed by boiling with HCl for 1 h for residual KOH removal. The acidic washed samples were further washed with distilled water several times until neutral pH was attained. The final carbon products were dried at 110 °C for 24 h, for moisture removal.

**Instrumentation**

A Tri Star 3000 (Micromeritics, USA) surface analyzer was used to measure nitrogen adsorption isotherm at 77 K in the range of relative pressure 10⁻⁶ to 1. Before measurement, the sample was degassed at 300 °C for 2 h. The BET surface area (S_BET), total pore volume (V_total), micropore area (S_micro), mesopore area (S_meso), average pore diameter (D_p) results were obtained from the adsorption isotherms. Mesopore volume was determined by subtracting the micropore volume from the total pore volume.

The spectrophotometric determination of dye was performed on a Shimadzu UV–Vis spectrophotometer.
The morphological analysis of prepared and treated active carbons was carried out on a Philips SEM 505 electron microscope equipped with EDX analyzer.

**Analytical procedure**

The ozonation reaction was carried out in a 1 L stirred semibatch lab scale glass reactor by passing ozone gas through the aqueous solution with a dose of 8 g O₃/min. Sample contact times were 2–30 min. Samples (ca. 5 mL) were withdrawn at regular times for analysis.

The color removal of the dye solution was determined with the absorbance value of the remaining dye by monitoring the UV–VIS spectrum using a Schimadzu UV-2101 PC double beam spectrophotometer. The absorption band at 532 nm was chosen to measure the color parameter ($A_{532}$) associated with a long conjugated $\pi$ system, whereas the absorption bands at 292 nm and 220 nm (expressed in terms of $A_{292}$ and $A_{220}$) were indicative of benzene ring and naphthalene ring, respectively (Arslan et al. 2000).

**RESULTS AND DISCUSSION**

**Characterization of the activated carbon samples**

The BET analysis results of the two commercial ACs (Granular activated carbon-GAC, powder activated carbon-PAC) and activated carbon prepared from olive stone (ACOS) and activated carbon from prepared apricot stone (ACAS) are given in Table 1.

From Table 1, it can be concluded that the surface area of the ACOS and ACAS were higher than that of the commercial carbons (GAC and PAC). The specific surface area of the ACOS had the highest value (1,275 m²/g) compared with other ACs. The highly active surface properties of ACOS and ACAS were attributed to their chemically modified surfaces. The porosity is dependent on the starting material (Byrne & Marsh 1995; Yeganeh et al. 2006). Pore volume analysis showed that more than 90% of the total pore volume of the ACAS is micropore volume. During KOH activation of ACOS, pore volumes are evolving by generation of micropores (13%) and the originally narrow micropores collapse to mesopores (87%).

Surface morphology plays a significant role in determining the surface availability. These enormous BET surface areas are created by a distinct KOH activation mechanism. Potassium hydroxide is reactive above 700 °C. After the formation of the char and in this sense the activation initially consists of a redox reaction, in which carbon is oxidized to CO or CO₂, thus, incidentally, creating some porosity and K₂CO₃ as a by-product. As a result, KOH is reduced to metallic potassium. As potassium is intercalated between the graphite layers of structure the carbon particles break down and disintegrate into powders (Moreno-Castilla et al. 2001; Stavropoulos & Zabaniotou 2005).

The scanning electron microscope (SEM) images presented in Figure 2 show a highly porous morphology of the KOH treated ACs with pores of different sizes and shapes. The micrographs reveal that the external surfaces are full of cavities which suggest that ACOS and ACAS exhibit high surface area.

For the PAC sample, the surface topography was found to be irregular with some occasional crevices. The GAC did not have a homogeneous structure with a predominance of macropores. It had a rougher texture with a heterogeneous surface and greater variety of randomly distributed pore size.

**Effect of the initial pH value of the dye solution**

As the reaction pH is an important parameter influencing the performance of the ozonation, the pH of the dye solution was adjusted to 3, 7 and 11 and each solution subjected to ozonation for 30 min to demonstrate the effect of pH on the treatment efficiency.

Decolorization (degradation of diazo linkage between aromatic structures, decrease in $A_{532}$) and dearomatization (decrease in $A_{220}$ and $A_{292}$) took place more effectively in alkaline solution compared with neutral and acidic media (Figure 3).

![Table 1](https://iwa.silverchair.com/wst/article-pdf/66/1/179/442850/179.pdf)

**Table 1** Porous structure parameters of the activated carbons

<table>
<thead>
<tr>
<th>Sample</th>
<th>$S_{BET}$ (m²/g)</th>
<th>$S_{micro}$ (m²/g)</th>
<th>$S_{meso}$ (m³/g)</th>
<th>$V_{total}$ (cm³/g)</th>
<th>$V_{micro}$ (cm³/g)</th>
<th>$V_{meso}$ (cm³/g)</th>
<th>$D_p$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACAS</td>
<td>968</td>
<td>863</td>
<td>106</td>
<td>0.50</td>
<td>0.45</td>
<td>0.05</td>
<td>2.07</td>
</tr>
<tr>
<td>ACOS</td>
<td>1,275</td>
<td>185</td>
<td>1,091</td>
<td>0.73</td>
<td>0.094</td>
<td>0.064</td>
<td>2.29</td>
</tr>
<tr>
<td>GAC</td>
<td>841</td>
<td>757</td>
<td>84</td>
<td>0.43</td>
<td>0.39</td>
<td>0.046</td>
<td>2.07</td>
</tr>
<tr>
<td>PAC</td>
<td>851</td>
<td>570</td>
<td>281</td>
<td>0.53</td>
<td>0.29</td>
<td>0.235</td>
<td>2.49</td>
</tr>
</tbody>
</table>
The increase of pH value has a positive influence on the generation of hydroxyl radicals due according to the following reaction (Ma et al. 2004):

\[ 3O_3 + OH^- \rightarrow 2OH^+ + 4O_2 \]

Therefore, as shown in Figure 3, removal efficiency of RR195 by ozone was improved with the increase of pH.

The dye is in hydrolyzated form at pH 11. As a result, degradation of RR195 increases with increasing pH of solution.

### Catalytic effect of activated carbon

Figure 4 compares the decolorization efficiency of RR195 for the selected processes: ozone alone, adsorption on the AC catalyst in absence of ozone and catalytic ozonation. Under the studied conditions (ozone dosage: 8 g/min, solution pH: 11.0, dye concentration: 100 mg/L, treatment time: 2 min), the removal efficiency of RR195 by ozone alone was about 86%. Adsorption of RR195 on the ACOS and ACAS catalysts was found to have no effect on the azo dye decolorization. The catalytic ozonation was found to be really effective for an optimum amount of catalyst applied. The addition of an
optimum amount of ACOS (1.0 g/L) and ACAS (3.0 g/L) during catalytic ozonation considerably increases color removal from 86% by ozone alone, to 90.4 and 91.3% by catalytic ozonation with ACOS and ACAS, respectively.

Effect of the amount of catalyst used

The effect of the amount of AC used on color reduction is shown in Figure 5. The results demonstrate that the addition of ACOS to an optimum amount of 1.0 g/L has beneficial improvement on color removal of 90.4% in RR195 solution by ozonation while under the same conditions, the decolorization efficiency of the O$_3$/ACAS process reached up to 91.3% with the use of 3.0 g/L. Adding 0.5 g/L ACs caused a negative effect on removal efficiencies, as seen in Figure 5. It can be concluded that ozone by itself can decompose some daughter ions (O$_3^-$, O$_2^-$) compared with RR195 daughter products (Guiza et al. 2004; Gül et al. 2007) in the presence of ACs. Thus, an optimum amount of AC will be beneficial for catalyzing the oxidation of refractory organic compounds via the creation of oxidative radical species (OH$^-$), however if the amount exceeds a certain quantity, then its role is reverted. In other words, AC catalyzes the formation of hydroxyl radicals but not the reaction of oxidants with the organic substrates. Conversely, it inhibits these oxidation reactions by adsorbing the organic species.

Comparison of performances of ACs

The performances of catalytic ozonation processes using ACOS, ACAS, GAC and PAC in degradation of RR195 azo dye were evaluated in terms of color and absorbencies at 220 and 280 nm (Figure 6).

As shown in Figure 6, it was obvious that catalytic ozonation had much higher decolorization than deaeromatization. For all of the catalytic treatments studied herein, the removal efficiency of color was over 80% and the reaction time was very short (2 min). The UV bands at 220 nm and 292 nm disappeared less efficiently than did the visible band. The hydroxyl radicals initially attack azo groups and opened the N=N bonds which are more easily destroyed than aromatic structures. After 2 min catalytic ozonation, performances of ACOS and ACAS were better than GAC and PAC. Experimental data indicated that the difference in RR195 decolorization efficiency between ACOS and ACAS was insignificant.

CONCLUSIONS

The experimental results indicated that the preparations of ACs were both efficiently and economically promising. The BET surface area and the pore volume of the produced ACs are much higher than that of the commercially available ACs. Chemical activation with KOH of olive and apricot stone had proved to be effective in producing good-quality ACs, while micro and mesoporosity are enhanced. The ACOS had a higher $S_{\text{BET}}$ and mesoporosity than the ACAS. However, it was very soft due to the breaking of the olive stone particles after their impregnation with KOH solution. This was due to the fragmentation of lignin and hemicelluloses produced by the attack of strongly nucleophilic hydroxyl ions. The agricultural wastes (olive and apricot stones) can be utilized for the production of ACOS and ACAS and achieve wastewater treatment at a reasonable cost.

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