Ç.Ü Fen Bilimleri Enstitüsü Yıl:2008 Cilt:17-6

DEGRADATION OF REACTIVE RED 195 (RR195) AZO DYE BY CATALYTIC OZONATION [*]

Reaktif Kırmızı 195 Azo Boyar Maddesinin Katalitik Ozonlama Tekniğiyle Parçalanması

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ABSTRACT

Reactive azo dyes are widely used in textile industry. Due their toxicity and recalcitrance, these dyes can be hazardous to the environment and resistant to destruction by biological treatment methods.

Catalytic ozonation is an innovative advanced oxidation process (AOP) and involves the generation of hydroxyl radicals which are higher electrochemical oxidation potential (EOP: 2.80 V) compared with molecular ozone (EOP: 2.07 V).

The purpose of the present study was to employ catalytic decolorization and oxidation of Reactive Red 195 azo dye by ozone combined GAC (granular activated carbon) catalyst.

Decolorization of Reactive Red 195 was monitored by light absorption at 532 nm while degradation of aromatic rings was monitored by UV absorption at 292 nm and 220 nm. Mineralization of the dye was monitored by determining the total organic carbon (TOC). A high degree of decolorization and dearomatization could be achieved by ozone combined GAC (granular activated carbon) catalyst. under the optimum conditions (pH:11, $C_{0\ azo\ dye}$:100 mg/l) but TOC removal efficiencies were not as high as the formers in 30 min.

Key Words: Catalytic ozonation, granular activated carbon, azo dyes, reactive red 195.

ÖZET

Reaktif boyalar tekstil endüstrisinde yaygın olarak kullanılmaktadır. Toksisiteleri ve parçalanmaya karşı dirençli olmaları nedeniyle bu boyalar çevre açısından riskli ve biyolojik arıtma metodlarıyla yok edilmeye karşı dirençlidirler.

Katalitik ozonlama son yıllarda gelişen bir ileri oksidasyon yöntemidir ve moleküler ozona (EOP: 2.07 V) kıyasla daha yüksek elektrokimyasal oksidasyon potansiyeline sahip (EOP: 2.80 V) hidroksil radikallerinin üretimini içermektedir.

Bu çalışmanın amacı granüler aktif karbon eklenmiş ozonla Reaktif Kırmızı 195 azo boyar maddesinin katalitik renk giderimini ve oksidasyonunu sağlamaktır.

Reaktif Kırmızı 195 azo boyar maddesinin UV absorpsiyonuyla 532 nm' de maksimum renk giderimi, 220 ve 292 nm' de aromatiklik giderimi gözlendi. Bu boyanın mineralizasyonu toplam organik karbon tayiniyle izlendi. Yüksek derecede renk ve aromatiklik giderimi optimum şartlar altında ((pH:11, $C_{0\ boyar\ madde}$:100 mg/l)

[*]Yüksek Lisans Tezi – MSc. Thesis

granüler aktif karbon eklenmiş ozonla 30 dakikada sağlandı, fakat toplam organik karbon giderimi renk ve aromatiklik giderimi kadar yüksek yeterlilikte olmadı.
Anahtar Kelimeler: Katalitik ozonlama, granüler aktif karbon, azo boyalar, reaktif kırmızı 195.

Introduction

Dyes are released into the environment mainly from textile and dyestuff industries, most of which are azo dyes (Chun and Yizhong, 1999). Azo dyes are an abundant class of synthetic, colored, organic compounds, which are characterized by the presence of one or more azo bonds (-N=N-) (Stylidi et al. 2003). It has been documented that some azo dyes are toxic and even mutagenic to living organisms in aquatic environments (So et al. 2002). The stability of their molecular structures renders them resistant to biological and even chemical degradation (Dai et al. 1996). Due to their toxicity and recalcitrance, these dyes can be hazardous to the environment though present at low concentrations.

Traditional physical techniques (adsorption an activated carbon, ultrafiltration, reverse osmosis, coagulation, ion exchange, etc) can be used efficiently for the removal of pollutants (Konstantinou and Albanis, 2004). Nevertheless, they are non-destructive. Due to large degree of aromatics present in dye molecules and stability of them, conventional biological treatment methods are ineffective for decolorization and degradation. Chlorination and ozonation can also used for the removal of certain dyes but they have high operating costs.

During the last two decades, advanced oxidation processes (AOPs) have been proposed as an alternative way of treating dyestuffs (Kusvuran et al. 2004, Kusvuran et al. 2005, Yildiz et al. 2005). Homogeneous systems without irradiation (O_3/H_2O_2, O_3/OH^-), homogeneous systems with irradiation (O_3/UV, O_3/H_2O_2/UV), heterogeneous systems with irradiation (TiO_2/O_2/UV, TiO_2/O_3/UV) are the main AOPs methods (Lachheb et al. 2002, Kasprzyk-Hordern et al. 2003) . AOPs were based on generation of very reactive hydroxyl radicals ($OH^{\bullet}$) that oxidize a broad range of pollutants non-selectively and very quickly.

Both ozonation and adsorption on activated carbon (AC) have proved to be efficient in removing color and some of the organic matter from highly colored effluents (Faria et al. 2005). The effect of AC on the ozone reaction must be promoting action in a hydroxide radical generation way (Jans and Hoigne, 1998, Legube and Leitner, 1999, Oh et al, 2004, Gul et al, 2006).

The objective of this study was to compare the performances of catalytic ozonation processes in degradation of RR195 azo dye in aqueous solutions. Optimization of the reaction pH and amount of catalyst was made in accordance with the absorbance values of treated aqueous solutions (absorbances at 532 nm), the absorbance of double bonds and aromatics (absorbances at 220 and 280 nm, respectively) and the TOC removal.

Material and Method

Material

Reactive Red 195 (RR195) azo dye was obtained from Eksoy Kimya Ltd., Adana, Turkey and used without further purification. The chemical structure of dye is given in Figure 1. The coal-based granular activated carbon (GAC) was purchased from Fluka.

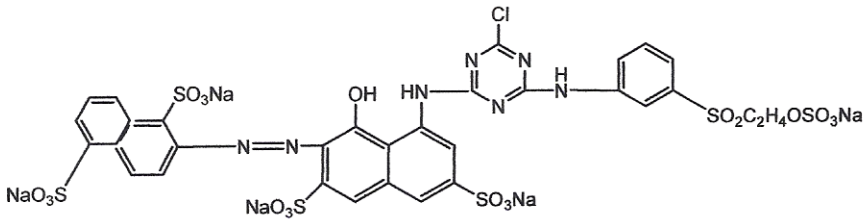

Figure 1. Molecular structure of Reactive Red 195

Method

The solution of RR195 was prepared by dissolving 100 mg/l in deionized water. The pH of dye solutions were adjusted to 3, 7 and 11 and each subjected to ozonation for 30 min to demonstrate the effect of pH on treatment efficiency. Following ozone treatment, the aqueous solutions were filtered through 0.45 µm Millipore syringe filter to remove GAC prior to analytic investigations (TOC and UV/VIS absorbance).

The color removal of the dye solution was determined with the absorbance value of the remaining dye at the maximum of the absorption spectrum by monitoring UV-VIS spectrum using Schimadzu UV-2101 PC double beam spectrophotometer. The absorption band at 532 nm was chosen to measure the color parameter, whereas the absorption bands at 292 nm and 220 nm were indicative for organic species having an aromatic structure and comprising –C=C- double bonds, respectively. TOC contents were determined by using Tekmar-Dohrmann Apollo 9000.

Ozonation reaction was carried out in a 1 liter stirred semi-batch lab scale glass reactor by passing ozone gas through the aqueous solution with a dose of 28 mg O_3/min. The reactor was filled with 1 liter of dye solution and 0.5, 1.0, 5.0 and 10 g/l of GAC were added. A magnetic stirrer was used to mix the reactor contents. Ozone was produced from pure oxygen in a Hermann firm ozone generator with a gas flow of 0.8 l/min. Two wash bottles full of 2% potassium iodide solution buffered with phosphate were connected in series in the exit of the reactor to quench the unreacted ozone gas passing through the reactor. Most of the test runs usually lasted in 30 minutes. Samples (ca.5 ml) were withdrawn at regular times for analysis.

Results and Discussion

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 alkali solution compared to neutral and acidic media (Figure 2 and Figure 3). As can be seen in Figure 2, a high degree of decolorization and dearomatization could be achieved by employing ozone under the stated conditions but TOC removal efficiencies were not as high as the formers (Figure 3).

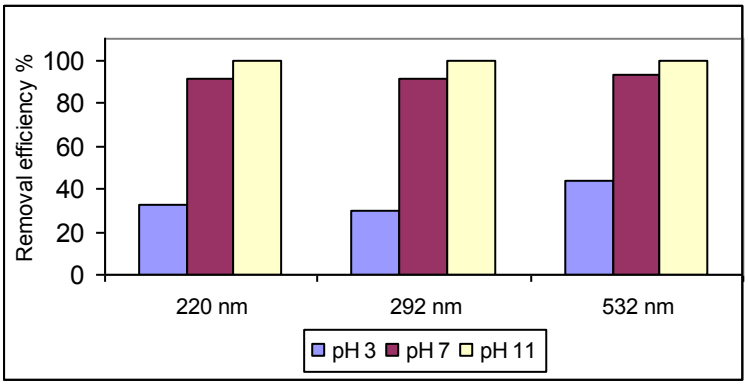

Figure 2. The effect of pH on the removal efficiency of RR195 by ozone.

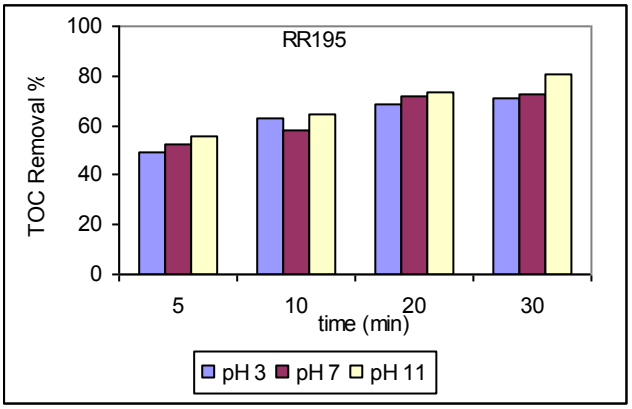

Figure 3. The effect of initial pH on per cent TOC removal of RR195 by ozone.

The effect of the amount of GAC on color reduction was displayed in Figure 4. The results demonstrated that the addition of GAC to an optimum amount of 1.0 g/l has beneficial improvement of on color removal in RR195 solution. Thus, an optimum amount of GAC will be beneficial for catalyzing the oxidation of refractory organics via creating oxidative radical species but if the amount exceeds a certain quantity, then its role will be reverted.

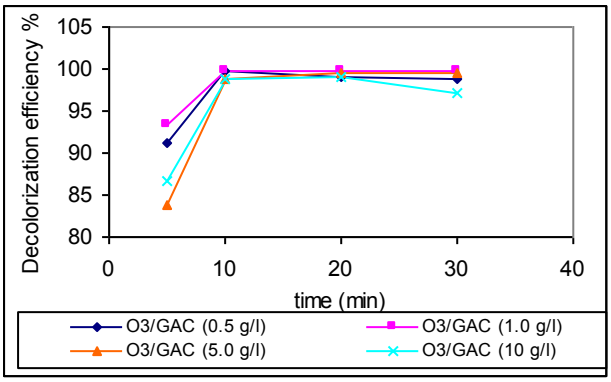

Figure 4. The effect of GAC amount on decolorization of RR195.

The comparison of ozone oxidation, GAC adsorption and ozone/GAC oxidation for the degradation of RR 195 is illustrated in Figure 5. At ambient temperature and pH 11, the decolorization efficiency of ozone oxidation within 30 min was 99.61%. Adsorption capacity of 1.0 g/l GAC was only 1.12% when the contact time of RR195 was 30 min and the concentration of RR195 was 100 mg/l. While under the same conditions, the decolorization efficiency of GAC catalytic ozonation process reached 99.71%.

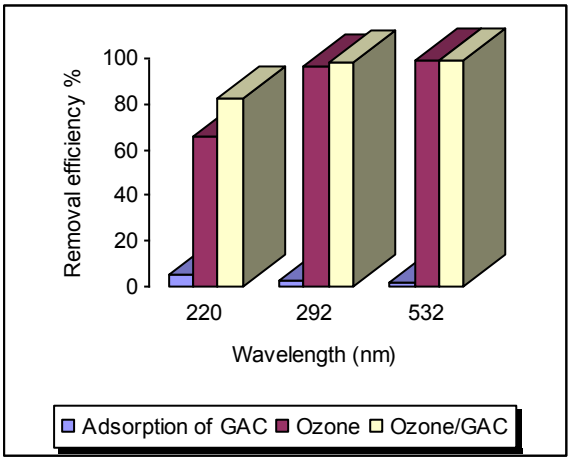

Figure 5. Comparison of ozone/GAC oxidation, ozone oxidation and the adsorption of GAC for the decolorization and dearomatization of RR 195.

Conclusion

The results of this study showed that decolourization and mineralization of aqueous solutions contaminated by the monoazo dye (RR195) can be achieved by

treating the solutions with ozone only. On the other hand, the presence of an optimum amount of granulated activated carbon catalyzes the cleavage of aromatic rings due to the formation of active hydroxyl radicals, thus enhancing mineralization of the contaminated aqueous solutions.

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