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Ozonation of C.I. Reactive Red 194 and C.I. Reactive Yellow 145 in aqueous solution in the presence of granular activated carbon

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Abstract

The purpose of this study was to investigate the catalytic role of granular activated carbon (GAC) on the degradation and mineralization of two reactive azo dyes (C.I. Reactive Red 194 (RR194) and C.I. Reactive Yellow 145 (RY145) in aqueous solution by treatment with ozone. Decolourization of the aqueous solution, disappearance of the parent compound, COD and TOC removal were the main parameters investigated for this purpose. Formation of inorganic ions Cl^-, SO_4^{2-}, NH_4^+, NO_3^- and pH changes were also followed throughout ozonation of various systems. It was determined that ozone by itself is strong enough to decolorize these aqueous solutions contaminated by azo dyes and almost all COD disappeared by these treatments but efficient mineralization had not been achieved. The extent of TOC removal was about 25% when no granular activated carbon (GAC) had been used and this value was doubled in the presence of GAC. While the reactive hydroxyl radicals were formed on the surface of GAC, it was deduced that the main reactions of the organic species with these reactive radicals took place in the bulk of the solution. One other observation was that the mass ratio of GAC to organic substrate in the aqueous solution should have an optimum value for effective degradation of the organic substrates; excess GAC inhibits degradation reactions probably due to the adsorption of the organic species on the surface of GAC.

Keywords: Catalytic ozonation; Granular activated carbon; Azo dyes; C.I. Reactive Red 194; C.I. Reactive Yellow 145

1. Introduction

Reactive dyes exhibit a wide range of different chemical structures, primarily based on substituted aromatic and heterocylic groups [1]. The release of these coloured waste waters in the environment is a considerable source of non-aesthetic pollution and eutrophication [2]. It is well known that some azo dyes and degradation products such as aromatic amines are highly carcinogenic [3]. Since reactive dyes are highly soluble in water, their removal from wastewater is difficult by conventional coagulation and activated sludge processes [4]. Recently, numerous studies on the application of advanced oxidation processes in aqueous solutions have been reported [5–7].

Both ozonation and adsorption on activated carbon (AC) have proved to be efficient in removing colour and some of the organic matter from highly coloured effluents [8]. The effect of AC on the ozone reaction must be promoting action in a hydroxyl radical generation way [9–11]. It is known that OH radical resulting from O_3 decomposition in water is more reactive than ozone itself [11–15].

The purpose of the present study was to study the effect of GAC on decolourisation and mineralization of aqueous solutions contaminated with Reactive Red 194 and Reactive Yellow 145 azo dyes during ozonation in the presence of activated carbon.

2. Experimental

2.1. Materials

C.I. Reactive Red 194 (RR194) and C.I. Reactive Yellow 145 (RY145) azo dyes were obtained commercially (Table 1) and used without further purification. The coal-based granular

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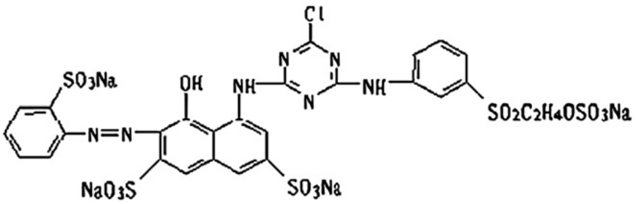
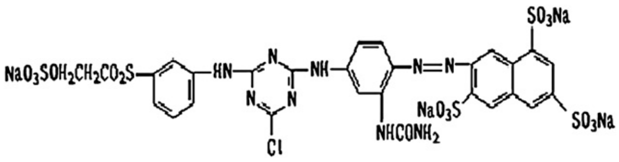
Table 1
The characteristics of the dyes used

C.I. Reactive Red 194 (RR194), MW: 984.21 g mol^{-1}, λ_{max}: 522 nm

C.I. Reactive Yellow 145 (RY145), MW: 1026.2 g mol^{-1}, λ_{max}: 419 nm


activated carbon (GAC) was purchased from Fluka. The GAC had an average diameter of 2.5 mm and a density of 2 g/cm^3. Its BET surface area was 1600 m^2/g. Desired amount of GAC (10–30 g/l) was added to reactor prior to ozonation.

The solutions of RR194 and RY145 were prepared by dissolving 100 mg/l in deionized water. The pH of the dye solutions were measured as 6.3 in RR194 and 5.9 in RY145 solutions. Following ozone treatment, the aqueous solutions were filtered through 0.45 μm Millipore syringe filter to remove GAC prior to analytic investigations (COD, TOC and UV–vis absorbance).

2.2. Analytical procedure

Colour removal of the dye solution was determined with the absorbance value of the remaining dye at the maximum of the absorption spectrum for every dye (Table 1) by monitoring UV–vis spectrum using Shimadzu UV-2101 PC double beam spectrophotometer. TOC contents were determined by using Tekmar-Dohrmann Apollo 9000. COD values were measured by the potassium dichromate standard method [15]. Anions and cations were analyzed by ion chromatographic system. The samples were filtered through a 0.20-μm membrane NC 20 filter (Schleicher & Schuell) and introduced directly into the HPLC injector port. Single column ion chromatographic (SCIC) equipment consisted of a Shimadzu model LC-10ADVP liquid chromatograph, a CDD-6A conductivity detector, a Shodex I-524A anion and Shimpack IC-C1 cation exchange columns.

Ozonation reaction was carried out in a 1 l 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 l of dye solution and 10, 20 and 30 g/l of GAC was 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. Ozone concentrations in the feed and in the reactor effluent were determined for each ozonation sequence using the iodometric procedure. Most of the test runs usually lasted for 30 min. Samples (ca. 5 ml) were withdrawn at regular times for analysis.

Ozone depletion is defined as the difference between the initial applied dose and sum of ozone residues in water and gas.

3. Results and discussion

The rate of ozone depletion increased when the amount of GAC increased in both dye solutions (Fig. 1). Ozone depletion was very low when GAC was not present in the solution. The reason for this observation was that GAC catalyzed the radical-type chain reaction in the solution consuming ozone while hydroxyl and other radicals were formed.

The effect of the amount of GAC on colour reduction is displayed in Fig. 2. Ozone consumption did not increase throughout the treatment of RY145 solution without using GAC (Fig. 1A). On the other hand, colour reduction

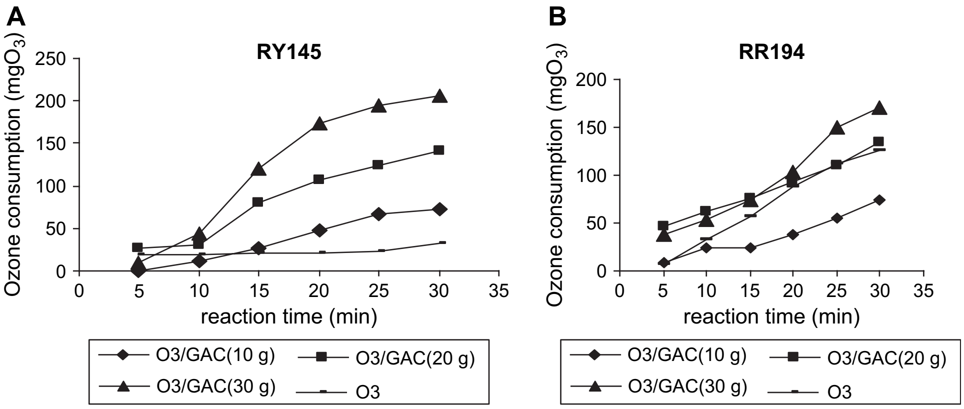


Fig. 1. Ozone depletion of RY145 (A) and RR194 (B) dyes.

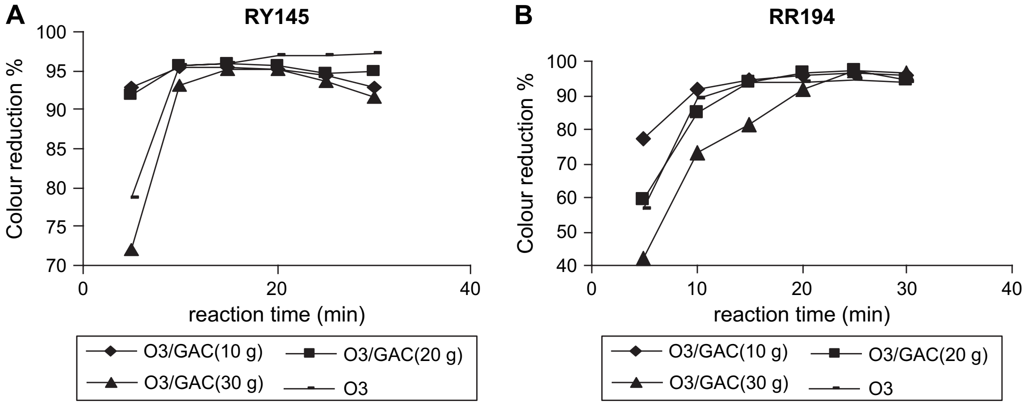


Fig. 2. Colour reduction of RY145 (A) and RR194 (B) dyes by ozone.

efficiency was almost equivalent to the corresponding efficiencies in the runs done in the presence of GAC (Fig. 2A). This shows that ozone does not need GAC to decompose the original RY145 molecules and other daughter products giving colour to the aqueous solution. Conversely, ozone consumption in the absence of GAC in the treatment of RR194 solution increased with time (Fig. 1B) and colour reduction efficiency was similar to the corresponding efficiencies obtained in the presence of GAC. This implies that for decomposition of the starting material (RR194) and probably the colour giving daughter products, the catalytic effect of GAC is not necessary as in the case with RY145 but since ozone consumption increases throughout treatment time, which is not observed for the corresponding case with RY145, one can conclude that ozone by itself can decompose some more daughter ions compared to RY145 daughter products. Indeed, Fig. 3B shows that in RR194 system, ozone by itself is more effective in TOC removal than the corresponding case with RY145.

The decomposition extent of the dyes and their daughter products was followed by using two different techniques, i.e. the disappearance of the chemical oxygen demand (COD) and that of the total organic carbon (TOC). The latter indicated the mineralization level of the treatment (Fig. 3). Addition of GAC did not improve the COD decrease in the treatment of RY145 but there was a slight decrease (about 10%) in the corresponding cases with RR194 indicating that ozone by itself was strong enough in oxidizing those organics which were also not resistant to COD reagent for the case with RY145 but GAC helped a little for oxidizing those refractory daughter products in the case with RR194. On the other hand, when COD decrease during ozonations in the presence of 10 g and 30 g of GAC are compared, one can notice a difference of about 5–10% higher performance with the one having 30 g. It is interesting to note that there is no parallel observation in the TOC removal results. In this case, TOC removal performances by using 10 g GAC are much better than using 30 g in both RY145 and RR194 systems. It is obvious that, adsorption of various organic species on GAC will increase as the amount of GAC increases in the system, but since TOC removal decreases with increasing GAC, one can conclude that the main oxidation reactions of various organic species are taking place in the bulk of the solution rather than on the surface of the GAC. In other words, GAC catalyzes the formation of hydroxyl radicals but not the reactions of oxidants with the organic substrates. Conversely, it inhibits these oxidation reactions by adsorbing the organic species. 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.

According to the stoichiometry of the overall oxidation reactions listed in Table 2, the pH of the reaction medium is expected to decrease. Temporal variations are given in Fig. 4. pH

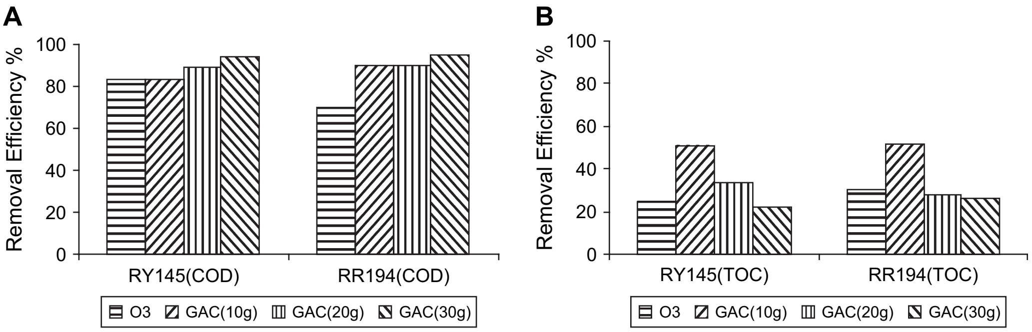


Fig. 3. COD (A) and TOC (B) removal efficiency in RY145 and RR194 dyes after 30 min of ozonation time.

Table 2
Stoichiometric equations of oxidation

RR194	$2C_{27}H_{18}ClN_7O_{16}S_5^{4-} + (163/2)O_2 \rightarrow 54CO_2 + 5H_2O + 26H^+ + 10SO_4^{2-} + 14NO_3^- + 4Cl^-$
RY145	$2C_{28}H_{20}ClN_9O_{16}S_5^{4-} + (179/2)O_2 \rightarrow 56CO_2 + 5H_2O + 30H^+ + 10SO_4^{2-} + 18NO_3^- + 4Cl^-$

decreased when ozone alone was used, but when GAC was added, the pH increased to almost neutral in all cases. It seems that GAC was effective in adsorbing acidic daughter products. Adsorption of the acidic protons would not be the reason for this neutral pH because such an adsorption would shift the pH to high values.

The ions nitrate, ammonium, chloride and sulphate were determined by using ion chromatography and are described in Fig. 5. Sharp increases in Cl^- concentration in the initial stages of ozonation in the presence of GAC show that the C—Cl bond on the 1,3,5-triazine ring (Fig. 5A and B) is the weakest bond and the easy cleavage of this bond in the presence of GAC indicates that C—Cl bond on the triazine ring is very susceptible to the hydroxyl radical attack [16]. The slight decrease in Cl^- concentration following the initial stages of the ozonation may be due to further oxidation of Cl^- to OCl^- and Cl_2 species [17].

Sulphur heteroatoms were converted into innocuous SO_4^{2-} ions. The temporal evolution of SO_4^{2-} ions is presented in Fig. 5C and D for the dyes containing five S atoms in sulphonyl groups per molecule. The rate of formation of sulphate ions are relatively slow compared to the rate of formation of both chloride and ammonium ions which should be the expected consequence of successive oxygenation of sulphur up to the +6 oxidation state. The increase in sulphate concentration then followed by a decline in RY145 is due to production of sulphate radical ($SO_4^{\bullet-}$) when pH exceeds 6 as reported by Muthukumar and Selvakumar [18].

Nitrogen atoms in the −3 oxidation state, such as in amino groups, retained their oxidation states and produced NH_4^+ cations. The central —N=N— azo-group should have been converted into gaseous dinitrogen. In diazonium group, each nitrogen atom is in its +1 oxidation degree and therefore may convert to gaseous nitrogen easier than the other forms of nitrogen in the dye molecules. The formation of NH_4^+ and NO_3^- are rather controversial, i.e. no ammonium had been produced during catalytic ozonation (Fig. 5E and F). The formation of nitrate ions took place only ozonation alone in both of the dyes (Fig. 5G). Since the protonation of amine groups are needed for the formation of ammonium ions, one can conclude that formation of acidic groups should be more favourable in the presence of GAC. The reason behind this behaviour should be the effective degradation of aromatic rings by successive hydroxylation due to the attacks of OH radicals [19] that are formed by the catalytic effect of GAC, thus forming acidic carboxyl groups. On the other hand, in the absence of GAC, there will not be effective hydroxyl radical formation and therefore aromatic rings will resist cleavage during which the cleaved amine bridges by ozone are oxidized-up to the nitrate ions.

4. Conclusions

The decolourization of aqueous solutions contaminated by the two diazo dyes under investigation was achieved by treating the solutions with ozone only. However, such treatment could not mineralize the aqueous solutions due to the resistance of the aromatic structures to cleavage. On the other hand, the presence of an optimum amount of granulated activated carbon catalyzed the cleavage of aromatic rings due to the formation of active hydroxyl radicals, thus enhancing mineralization of the contaminated aqueous solutions. One should be cautious about the ratio of the GAC to the organic substrates as excess GAC inhibits the degradation of the organic dyes probably because of adsorption of reactive species. It was concluded that, although the formation of hydroxyl radicals took place on the surface of GAC, the main oxidative reactions towards degradation of organic structures took place in the bulk of the solution.

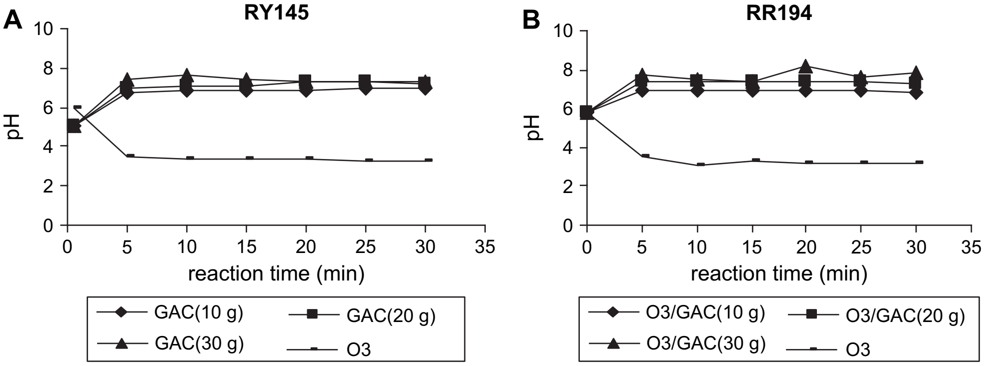


Fig. 4. pH changes of both dyes during catalytic ozonation.

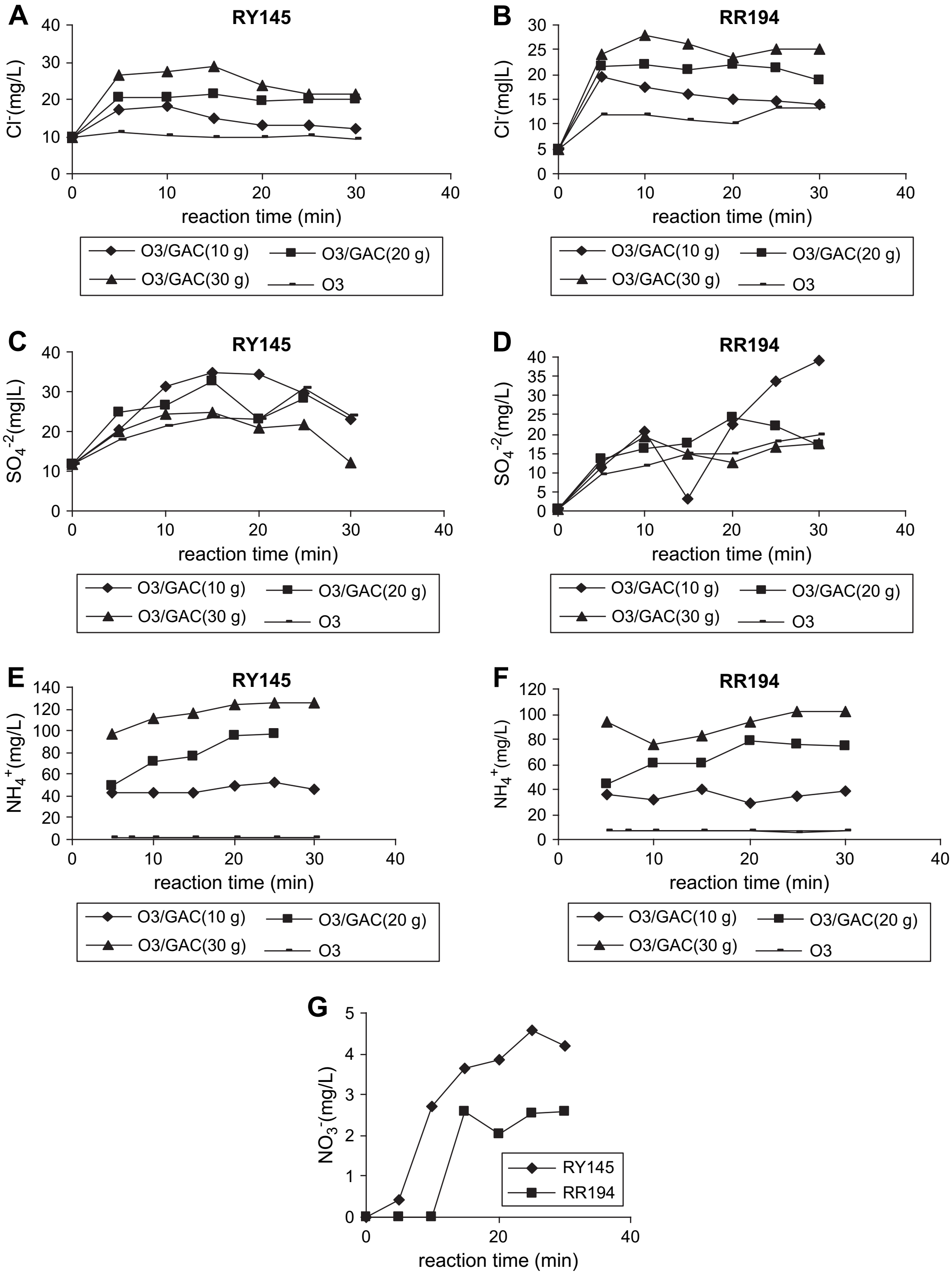


Fig. 5. Formation of inorganic ions. (A) Cl^- ion evolution of RY145, (B) Cl^- ion evolution of RR194, (C) SO_4^{2-} ion evolution of RY145, (D) SO_4^{2-} ion evolution of RR194, (E) NH_4^+ ion evolution of RY145, (F) NH_4^+ ion evolution of RR194, (G) NO_3^- ion evolution of RY145 and RR194 ozonation alone.

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