Investigation of 207 nm UV radiation for degradation of organic dye in water

Xiangfen Feng[1], Shaolong Zhu[1]* and Huiqi Hou[2]

[1] Institute for Electric Light Sources, Fudan University, Shanghai 200433, PR China

[2] Institute of Environmental Science, Fudan University, Shanghai 200433, PR China

Abstract

The photo-degradation of organic dye C.I. Acid Red 213 (AR-213) was achieved by 207 nm UV radiation emitted from a planar KrBr* excimer lamp without addition of oxidants at varying initial pH values. Precipitates were found to be generated when the irradiated solution of initial acid pH was adjusted to alkaline pH and they would disappear again when the solution was readjusted to acidic conditions. The efficiency of COD removal was greatly increased after the filtration of precipitates. Both the decolourisation rate and the COD removal rate reached the maximum in the initial pH 2.8 solution. The same phenomenon was also observed for other kinds of dyes. Direct photolysis was the only pathway in degrading dye molecules for both O_2-saturated and N_2-saturated solutions. The by-products formed for initial acidic solution were were identified by electro-spray ionisation (ESI) in positive mode and the influence of initial pH on the reaction mechanism of the dye under 207 nm radiation was analysed.

Keywords: 207 nm radiation, direct photolysis, dye, pH

Introduction

The removal of coloured substances from effluents is an important component of wastewater treatment and investigations on the decolourisation of textile dyes have been conducted for a long time. One method for removing organic pollutants is ultraviolet (UV) technologies (Munter, 2001). The most commonly used UV sources for the UV-treatment systems are low- or medium-pressure mercury lamps. However, most chemical bonds cannot be broken directly due to the limited available wavelengths not matching absorption bonds of the targeted organic material. Thus the UV degradation process must depend on oxidants such as H_2O_2 and ozone absorbing UV to generate active hydroxyl radicals to attack toxic organics (Neamtu et al., 2002; Shen and Wang, 2002; Koch et al., 2002; Choi and Wiesmann, 2004). However, an excess of oxidants added in the treated solution can interfere with the process (Chen et al., 2004).

Dielectric barrier discharge (DBD) driven excimer lamps are versatile lamps. Depending on the filling gas, they may emit radiation into narrow-band or quasi-monochromatic spectrum with desired specific wavelength (Mildren et al., 2001; Hirose et al., 2002; Falkenstein and Coogan, 1997; Zhang and Boyd, 1996). The entire UV spectral region can be covered with possible excimers (Xe_2^*, F_2^*, Cl_2^*, Br_2^*, I_2^*, $ArBr^*$, $ArCl^*$, ArF^*, KrI^*, $KrBr^*$, KrF^*, XeI^*, $XeCl^*$, $XeCl^*$, XeF^*) with wavelength from 172 nm to 317 nm (Kogelschatz, 2003). Since many photo-physical and photochemical processes are initiated by specific, narrow-band wavelength, DBD-driven excimer UV light sources could improve or solve specific photo-physical or photochemical processes without the addition of oxidants.

This study investigated the removal of dyes in water using the planar KrBr* excimer lamp that emits 207 nm radiation since most organic dyes and their aromatic and naphthalene intermediates exhibit strong absorption in the vicinity of 200 nm wavelength. The reaction mechanisms and by-products of direct photolysis of organic dye under 207 nm radiation were studied and the results are presented here.

Experimental

Excimer lamp

A planar lamp filled with 3.8×10^4 Pa Kr and Br_2 mixture gas was made from a quartz tube of 30 mm diameter with a height of 7 mm. The lamp was driven by a 20 kHz sinusoidal power supply. The lamp voltage was 4 000 V and the amperage was 11.6 mA. An Acton VM-505 vacuum-ultraviolet monochrometer was used in measuring the UV output. Figure 1 illustrates the UV emission spectrum from the KrBr*excimer lamp driven by DBD discharge. The peak of the emission from the KrBr* is observed around 207 nm. The full width half maximum (FWHM) of the 207 nm transition ($B_{1/2} \rightarrow X_{1/2}$) is approximately 2 nm. There is also weaker radiation at 222 nm ($C_{3/2} \rightarrow A_{3/2}$) and 228 nm ($B_{1/2} \rightarrow A_{1/2}$). The absolute radiance of the KrBr* UV source is obtained according to the following equation:

$$L_x = \int_{206}^{208} \frac{P_x(\lambda)}{P_D(\lambda)} \bullet L_D(\lambda) \bullet (\frac{D_D}{D_x})^2 \bullet d\lambda \tag{1}$$
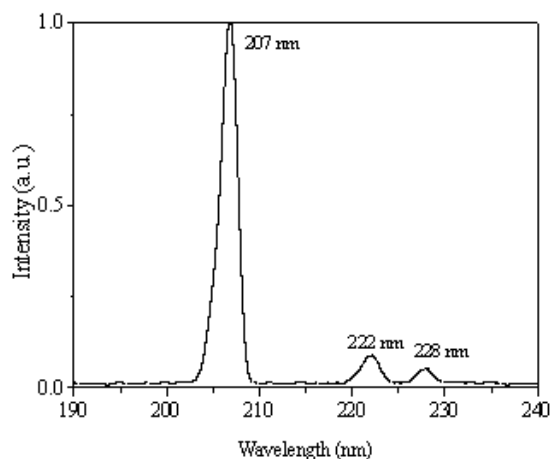
where:

L_x is the spectral radiance of the UV source (W m^{-2} Sr)

$L_D(\lambda)$ is the spectral radiance of a pre-calibrated standard deuterium lamp (W m^{-2} Sr)

$P_x(\lambda)$ and $P_D(\lambda)$ are respectively signals of the UV source and the deuterium lamp detected

D_D and D_x are respectively the diaphragm diameter of the UV source and the deuterium lamp.
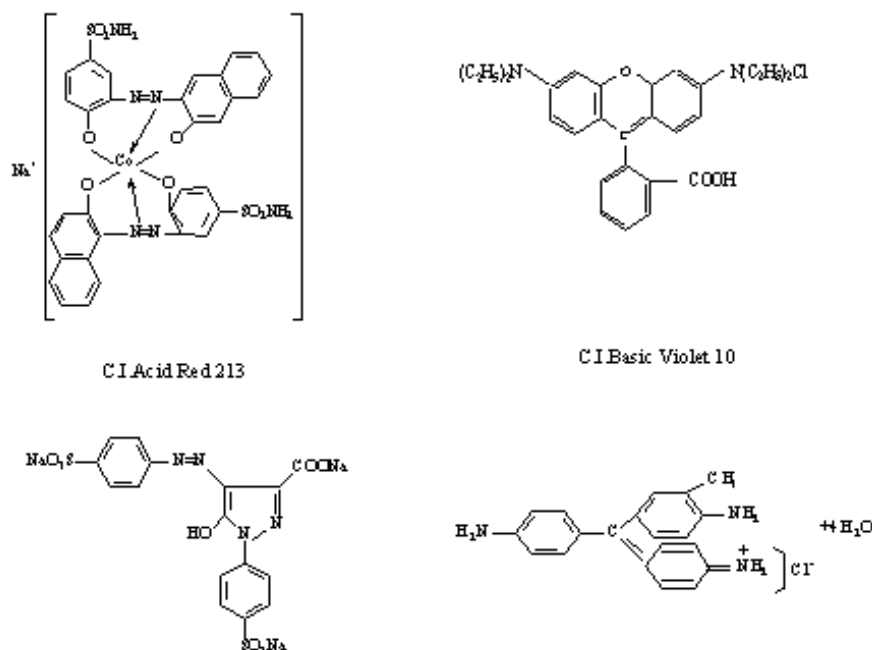
---

* To whom all correspondence should be addressed.

☎ +86-21-65642335; fax: +86-21-65646818;

e-mail: slzhu@fudan.edu.cn

Figure 1
UV emission spectrum from the KrBr excimer lamp*

CI Acid Red 213

CI Basic Violet 10

Figure 2
Structure of dyes

Figure 3
Schematic diagram of the experimental set-up

Assuming the planar excimer source is a Lambert radiator, the radiant emittance is $M = \pi L$ (W m^{-2}). The radiant power of the UV source is $P = \pi R^2 M$, R is the radius of the lamp window. Therefore the absolute radiant power of the KrBr* excimer source is 3 mW equalling an incident photon flow of 3.1×10^{-7} einst min^{-1}.

Materials

The organic dyes used in the experiments, namely C.I. Acid Red 213 (AR-213, $C_{32}H_{22}N_6O_8S_2CoNa$, MW = 765), C.I. Basic Violet 10 (BV-10, $C_{28}H_{31}N_2O_3Cl$, MW = 479), C.I. Food Yellow 4 (FY-4, $C_{16}H_9N_4O_9S_2Na_3$, MW = 534) and C.I. Basic Fuchsine 14 (BF-14, $C_{20}H_{20}N_3Cl$ = 338) were of commercially available reagent grade which were purified by precipitation. The chemical structures of the dyes are given in Fig. 2. All the dyes were dissolved in distilled deionised water with the concentrations of 1×10^{-4} M. NaOH and H_2SO_4 were of analytical grade (AR). Oxygen and nitrogen were of 99.999% purity.
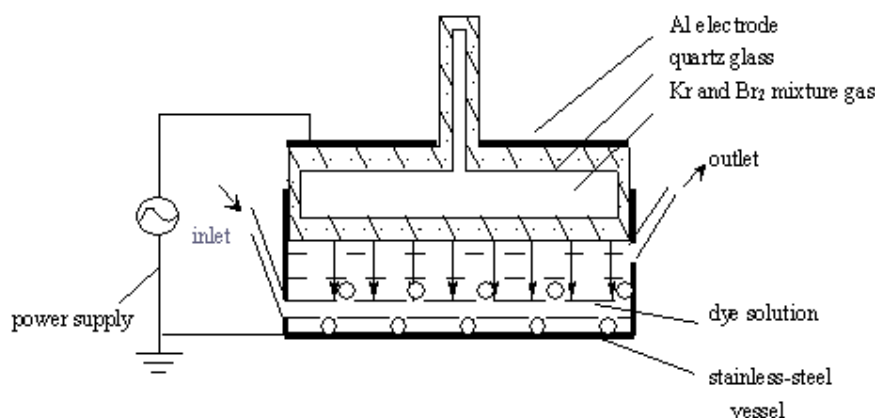
Set-up

Figure 3 shows a schematic diagram of the experimental set-up. The reaction solution was contained in a stainless-steel vessel of 30 mm internal diameter. Because of the low electrical power and small radiation area of the KrBr* excimer lamp, 10 mℓ dye solutions were treated each time. Thus the irradiation intensity in the reactor was 0.3 W·ℓ$^{-1}$. The irradiated solution served as one electrode of the lamp. In this way the UV radiation that came out of the lamp window directly entered the solution to minimise the UV losses. Oxygen or nitrogen was respectively bubbled into the solution through the inlet at the bottom of the reactor, which was maintained during the entire experiment to make the solution oxygen- or nitrogen-saturated.

Analysis

Since there was a linear relationship between dye concentration and absorbance, AR-213 dye concentration in the solution was determined by visible absorbance A at λ_{max} = 550 nm by a 721 spectrophotometer (Shanghai Third Analysis Apparatus Company). H_2SO_4 and NaOH were used to adjust the pH of the solution to desired values. All of the irradiated solution was readjusted to the initial pH 6.3 of AR-213 dye solution every time to detect its absorbance. The chemical oxygen demand (COD) was measured as a function of time using the standard potassium dichromate method. The change in pH was monitored by a PHS-2 pH-meter. The identification of by-products was performed with electro-spray ionisation (ESI, Esquire 3000, Bruker Daltonics) in positive mode.

Results and discussion

Effect of initial pH

The effect of pH on the rate of dye degradation was monitored at three different pH levels, namely 2.8, 6.3 and 11, adjusted by adding concentrated H_2SO_4 and NaOH. Because the pH value of the solution will be different after the irradiation and the absorption spectrum of the solution depends on the pH value, the absorbance measurement is always performed at a pH value readjusted to 6.3.

It was noted that precipitates were generated when the irradiated solution of initial pH 2.8 was readjusted to pH 6.3. Furthermore, the quantity of the formed precipitates increased with increasing pH values. These precipitates would disappear again when the solution was readjusted to acidic conditions. This was also the case for the solution of initial pH 6.3 after irradiation. There were no precipitates observed for the solution of initial pH 11 before and after irradiation. It was necessary to decide on the final pH at which the possible degraded intermediates could be completely transferred into precipitates since the quantity of precipitates changed with pH value. We adjusted the pH of the irradiated solution to different values, and then calculated the formed precipitates. The weight of precipitates couldn't be precisely obtained because of the low concentration of AR-213 solution. Therefore the pH value was determined at which the by-products could be totally converted to precipitates by measuring the COD change of the solution. Figure 4 is the change of COD of the filtered solution with the pH value for the N_2-saturated solution of initial pH 2.8, which was adjusted to different pH value after 30 min irradiation (the dye solution was mostly decolourised within 30 min). It could be seen that the COD of the solution would not reduce when the solution pH was adjusted to about 11. Thus it was established that the precipitates would not be further formed at pH of about 11. The pH of all of the treated solutions was therefore adjusted to 11 and then the precipitates were filtered. All the filtered solutions were then readjusted to pH 6.3 at which the absorbance was detected to obtain the dye concentration in the solution.

Figure 5 shows the decolourisation efficiency of AR-213 vs. the UV energy consumed during the irradiation process. As can be seen, the decolourisation efficiency is much greater in acidic solutions than in neutral and alkaline conditions; in O_2-saturated solution than in N_2-saturated solution. The efficiencies of photochemical reactions are hardly to be compared between different experimental conditions due to the complexity of the reaction mixture. But considering the low UV intensity (0.3 $W \cdot \ell^{-1}$) in the experiment, the degradation of AR-213 dye is in fact very effective since the energy dose necessary for the completely decomposition of AR-213 is very low.
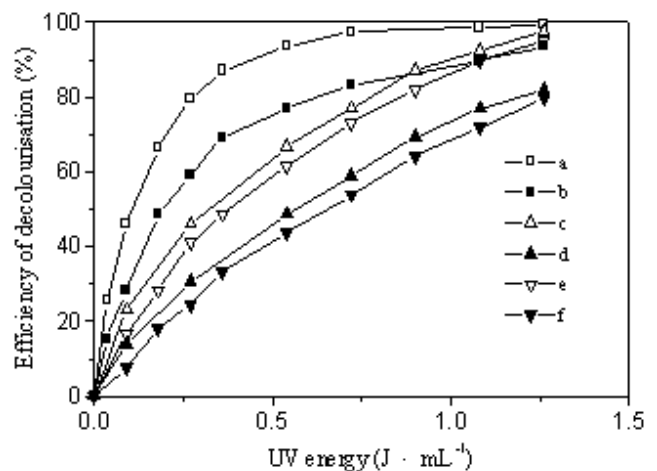
COD removal

Figure 6 is the efficiency of COD removal of the initial pH 2.8 solution with and without filtration of precipitates after the irradiated solution was adjusted to pH 11. It can be seen that the efficiency of COD removal is greatly increased after the filtration of precipitates. For the filtered solution, the COD removal increases during the initial irradiation stage, which is different from that of the solution without filtration. This was because during the initial stage, the UV photon mainly attacked the parent substrates, which were decomposed to intermediates that would be converted into precipitates under alkaline conditions. With the increase in irradiation time, more AR-213 molecules
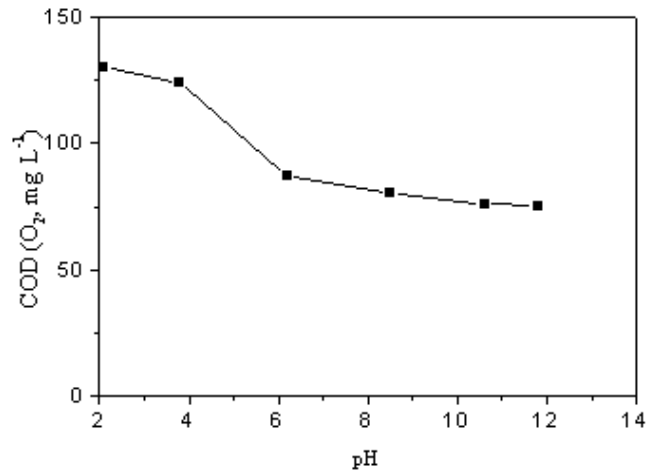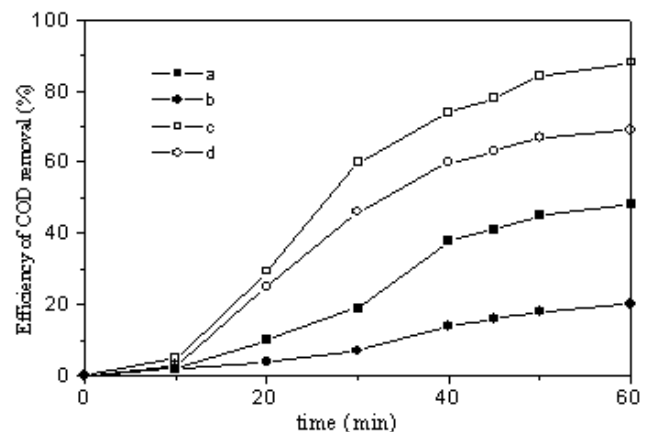

Figure 4
Change of COD of the filtered solution with the pH value for the N_2-saturated solution of initial pH 2.8 after 30 min irradiation

Figure 5
Decolourisation efficiency of AR-213 vs. UV energy consumed
(a), (c), (e) O_2-saturated solution of initial pH = 2.8,6.3,11;
(b), (d), (f) N_2-saturated solution of initial pH = 2.8,6.3,11

Figure 6
Efficiency of COD removal of the initial pH 2.8 solution with and without filtration of precipitates after the irradiated solution was adjusted to pH 11
(a), (b) O_2-saturated and N_2-saturated solution without filtration of precipitates
(c), (d) O_2-saturated and N_2-saturated solution with filtration of precipitates
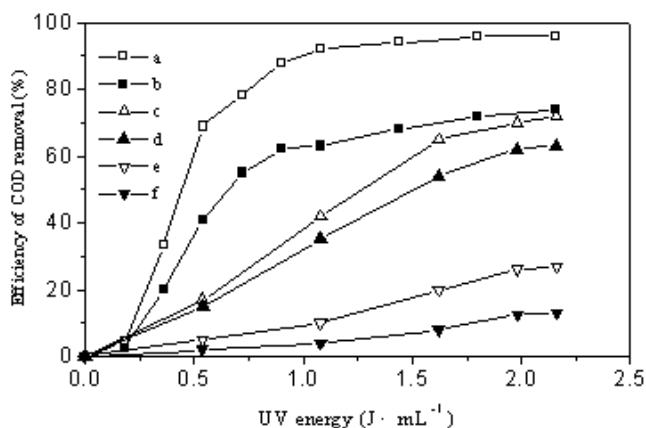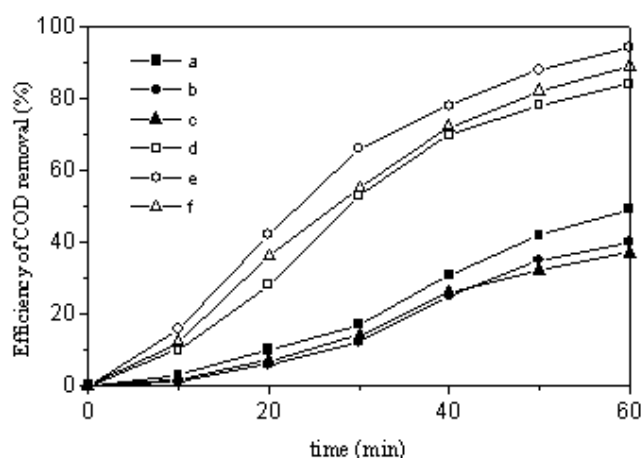
Figure 7
Efficiency of COD removal for the solution of initial pH 2.8, 6.3, 11
with the filtration of precipitates
(a), (c), (e) O_2-saturated solution of initial pH = 2.8, 6.3, 11
(b), (d), (f) N_2-saturated solution of initial pH = 2.8, 6.3, 11

Figure 8
Efficiency of COD removal of other dyes
(a), (b), (c) Solution of BV-10, FY-4 and BF-14 without filtration
of precipitates
(d), (e), (f) Solution of BV-10, FY-4 and BF-14 with filtration
of precipitates

were decomposed. Thus more precipitates were formed when the solution was adjusted to alkaline pH. After most of the AR-213 molecules had been destroyed, the COD removal of the filtered solution did not increase much.

Figure 7 is the efficiency of COD removal for the solution of initial pH 2.8, 6.3 and 11 with the filtration of precipitates after the irradiated solution had been adjusted to 11. It can be seen that under initial acidic conditions not only the decolourisation rate but also COD removal rate is fastest. The efficiency of COD removal was very low for the initial alkaline solution because most of the degraded by-products still remained in the solution due to no precipitates formed. It was thus established that the optimal pH region for the AR-213 degradation was acidic during the experiment.

Degradation of other dyes by 207 nm radiation

It is found that using 207 nm UV radiation AR-213 dye degradation is pH dependent so it is interesting to determine whether there are similar phenomena for other kinds of organic dyes by 207 nm radiation. BV-10, FY-4 and BF-14 were chosen to be

studied. The experimental conditions were the same as those of AR-213 and their concentration was also 1×10^{-4} M. Considering the practical industry application, instead of oxygen and nitrogen, air was bubbled into the solution during the process of irradiation. The dyes were irradiated at initial pH 2.8. It was also found that precipitates were generated when the treated solution was adjusted to alkaline pH for all these dyes. These precipitates again dissolved under acidic conditions. Figure 8 shows the efficiency of COD removal for the solution with and without filtration of precipitates after the irradiated solution was adjusted to pH 11. It is shown that the COD removal is markedly increased after the precipitates were filtered. Such phenomenon was not observed using the traditional AOPs and it supplied an alternative way to treat the dye wastewater.

Degradation mechanism

During the photolytic process of AR-213 dye using 207 nm radiation, it was suggested that AR-213 degradation was attributable to direct photolysis rather than oxidative degradation by active radicals. The reasons were the following: First, H_2O was not a source for HO˙radicals since photon absorption by H_2O at wavelength ≥193 nm could be negligible (Thomas Jr, 1995). The oxidative degradation by HO˙ radicals was excluded in the case as there were no other additional oxidants. Then, the number of photons absorbed by AR-213 dye and oxygen for O_2-saturated solution were compared. The absorbance A at 207 nm wavelength was determined from the UV-Vis curve of AR-213. Thus the absorption coefficient of AR-213 was obtained as $\varepsilon_{207} = 5.5 \times 10^4 \cdot M^{-1} \cdot cm^{-1}$ according to the Beer-Lambert law $A = \varepsilon \, l \, c$. The concentration of dissolved O_2 molecules is $1.29 \times 10^{-3} \cdot M^{-1}$ at 25ºC in water (Weast et al., 1982) and the absorption coefficient of O_2 for 207 nm radiation is about $2.4 \times 10^{-3} \cdot M^{-1} \cdot cm^{-1}$ (Okabe, 1978). The ratio of the number of photons absorbed by AR-213 and oxygen can be calculated by using Eq. (2) shown below:

$$\frac{n_{(dye,abs)}}{n_{(O_2,abs)}} = \frac{\varepsilon_{dye} M_{dye}}{\varepsilon_{O_2} M_{O_2}} = \frac{5.5 \times 10^4 \times 1 \times 10^{-4}}{1.29 \times 10^{-3} \times 2.4 \times 10^{-3}} = 1.78 \times 10^6 \gg 1\% \quad (2)$$

Therefore the photons absorbed by oxygen can be disregarded. Thus direct photolysis was the only pathway to degrade AR-213 for both O_2-saturated solution and N_2-saturated solution.

Some of the possible reactions of AR-213 dye under 207 nm radiation are shown below:

$$R_1 N = NR_2 \xrightarrow{h\nu} R_1 NH_2 + R_2 NH_2 \quad (3)$$

$$R_1 N = NR_2 \xrightarrow{h\nu} R^\bullet + \text{fragments} \quad (4)$$

$$R^\bullet \xrightarrow{h\nu} \text{product} \quad (5)$$

$$R^\bullet + O_2 \longrightarrow RO_2{}^\bullet \longrightarrow ... \quad (6)$$

$$R^\bullet + R^\bullet \longrightarrow R - R \quad (7)$$

The intermediates formed by the break-up of AR-213 molecules would absorb photons and continue to be decomposed (Eq. (5)). In the O_2-saturated solution, these intermediates might be oxidised by oxygen (Eq. (6)), thus reducing the competition for photons with the parent dye molecules. In absence of dissolved molecular oxygen, the organic radicals R˙ may recombine to form oligomers and polymers which may cover the surface of the lamp, hence, reducing the incident photon number, which would ultimately reduce the decolourisation rate. The decolourisation rate and the COD removal rate of AR-213 were therefore faster in O_2-saturated solution than those in N_2-saturated solution.

The experiments revealed that the AR-213 degradation rate was much faster under acidic conditions than in a neutral and alkaline environment due to the influence of pH on the dye structure. The dye would be protonated or deprotonated respectively in acidic or in alkaline media, which resulted in the change of the electron distribution around the chromophore group (Rodriques et al., 1999; Mosquera et al., 1997). UV photons attacking the chromophore initiated the first step of dye degradation while the degree to which a dye azo group was reduced depended on the electron density around the –N=N– bond. The protonation of AR-213 decreased the electron density around the chromophore group, which then became vulnerable to attack by UV photon. The degradation rate was inhibited under alkaline pH conditions due to the increase in electronic conjunction between groups by the deprotonation of the dye molecule (He et al., 1999).

AR-213 is a kind of water-soluble dye because of the –SO_2NH_2 group in the side-chain. Dyes were photolysed into organic radials and some fragment products and –SO_2NH_2 group were removed from the phenyl ring by UV photons. These photo-degraded intermediates would be deprotonated by hydrogen loss under alkaline conditions, thus maybe forming high molecular-mass hydrophobic oligomers by linking up with each other. The solubility would be further reduced if these oligomers contained amidocyanogen group. These oligomers were hydrolysed into low-mass fragments again due to the protonation when the solution was readjusted to acid pH. The oligomerisation and protonation processes could be represented by the following equilibrium:

$$\text{dye} \xrightarrow{h\nu} \text{products} \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} \text{oligomers} \qquad (8)$$
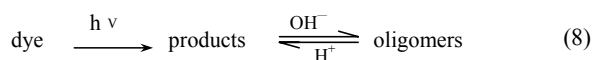
In initial alkaline solution organic radicals may react with OH^- ion to form product-OH adducts with hydrophilic characteristics so the photoproducts can dissolve in the solution. In photo-oxidative methods, dyes are decomposed by the attack of $HO\cdot$ radicals. $HO\cdot$ radicals could add to the aromatic ring or –N=N– group, resulting in dye-OH adducts, which are easily oxidised by O_2 in solution to become hydrophilic (Krapfenbauer et al., 2000).

Therefore, it may be concluded that the pH dependence of the dye degradation under direct photolysis is a key factor influencing the reaction mechanism. Further studies are still needed to detail the reaction mechanism.

Photoproduct analysis

For N_2-saturated solutions, both the parent dye molecule and its intermediates were decomposed by the direct attack of photons. So it was necessary to detect its photoproducts. LC-MS analysis was performed for the irradiated N_2-saturated solution of initial acid pH. The major molecule ion peaks of photoproducts identified by ESI in positive mode and their proposed structures are listed in Table 1.

The fragment ion peak at m/z = 344 ($[M+H]^+$) corresponded to the loss of one of the two ligands making up the dye (photoproduct A), but only low quantities were observed, which indicated that they were not stable and soon decomposed further by photon attack. Breaking the azo bond could result in two moiety radicals that may recombine with themselves and by picking up a hydrogen atom from the water solution, could form a photoproduct B, which contains an –NH_2 group in the side chain. Breaking the N–C bond of the –N=N–C moiety and cracking the aromatic ring could form photoproduct C. The side-chain of photoproduct C could be removed by the attack of photons to produce photoproduct D. The continuous ring opening of aromatic intermediates resulted in the aliphatic adducts such as CH_3-$(CH_2)_5$-NH_2

TABLE 1
Proposed chemical structures, $[M+H]^+$ ions and molecule formulas of the principal identified by-products by ESI

By-product number	Chemical structure	$[M+H]^+$	Formula
A	SO_2NH_2 ... –N=N– ... OH HO	344	$C_{16}SO_4N_3H_{13}$
B	H_2N ... NH_2	235	$C_{16}N_2H_{14}$
C	HN=N ... $CH_2CH_2CH_3$	199	$C_{13}N_2H_{14}$
D	...–$CH_2CH_2CH_3$	121	C_9H_{12}
E	$CH_3(CH_2)_5$-NH_2	102	C_6NH_{15}

(photoproduct E), which could not be easily decomposed by UV radiation. These aliphatic adducts might recombine to become hydrophobic characteristics when adjusting the irradiated solution to alkaline pH due to the lack of a hydrophilic group. No hydroxyl derivatives would be formed in N2-saturated solution since the intermediates were degraded by direct photolysis.

The presence of these intermediate species is likely to have clarified the mechanism of direct photolysis, which involves breaking of the azo bond, cracking of the ring, and a combination of organic radicals and the formation of an adduct, but no oxidation by active radicals.

Conclusions

Photo-degradation of organic dye was achieved without addition of oxidants by 207 nm UV radiation emitted from the planar KrBr* excimer lamp. The results indicated that the degradation of dye using 207 nm radiation was by direct photolysis, which was different from other traditional photo-oxidative methods. A strong pH dependence of the dye degradation under direct photolysis was a key factor influencing the reaction mechanism. Precipitates would appear when the irradiated solution of initial acid pH was adjusted to alkaline pH and they would disappear again when the solution was readjusted to acidic conditions. The same phenomenon was also observed for other kinds of dyes. Precipitates generated at alkaline conditions may be a consequence of deprotonation of the photo-degraded intermediates by hydrogen loss, thus forming high molecular-mass hydrophobic oligomers by linking up with each other. These oligomers were hydrolysed into low molecular-mass fragments again due to the protonation when the solution had to be readjusted to a lower pH. But further studies are still needed to detail the reaction mechanism. The efficiency of COD removal was greatly increased after the precipitates were filtered. Considering that the UV energy dose necessary for the complete decomposition of AR-213 was very low, the degradation of AR-213 dye was in fact very effective, providing another alternative way to photodegrade organic compounds.

References

CHEN QM, YANG C, GOH NK, TEO KC and CHEN B (2004) Photochemical degradation of 1,3-dinitrobenzene in aqueous solution in the presence of hydrogen peroxide. *Chemosphere* **55** 339-344.

CHOI IS and WIESMANN U (2004) Influence of mass transfer and chemical reaction on ozonation of azo dyes. *Water Sci. Technol.* **49** (4) 37-43.

FALKENSTEIN Z and COOGAN JJ (1997) The development of a silent discharge-driven XeBr* excimer UV light source. *J. Phys. D: Appl. Phys.* **30** 2704-2710.

HE YY, AN JY and JIANG LJ (1999) pH effect on the spectroscopic behavior and photo induced generation of semiquinone anion radical of hypocrellin B. *Dyes Pigm.* **41** 79-87.

HIROSE K, SUGAHARA H and MATSUNO H (2002) Basic performance of VUV exposure systems using head-on type Ar_2^* and Kr_2^* DBD excimer lamps. *J. Light & Vi. Env.* **26** (1) 35-41.

KOCH M, YEDILER A, LIENERT D, INSEL G and KETTRUP A (2002) Ozonation of hydrolyzed azo dye reactive yellow 84 (CI). *Chemosphere* **46** 109-113.

KOGELSCHATZ U (2003) Dielectric-barrier discharges: their history, discharge physics, and industrial applications. *Plasma Chem. Plasma Process* **23** (1) 1-46.

KRAPFENBAUER K, WOLFGER H, GETOFF N, HAMBLETT I and NAVARATNAM S (2000) Pulse radiolysis and chemical analysis of azo dyes in aqueous solution I. *p*-phenylazoaniline. *Radiat. Phys. Chem.* **58** 21-27.

MILDREN RP and CARMAN RJ (2001) Enhanced performance of a dielectric barrier discharge lamp using short-pulsed excitation. *J. Phys. D: Appl. Phys.* **34** L1-L6.

MOSQUERA M, RODRÍ GUEZ MCR and RODRÍ GUEZ-PRIETO F (1997) Competition between protonation and deprotonation in the first excited singlet state of 2-(3'-hydroxy-2'-pyricly benzimidazole in acidic solutions. *J. Phys. Chem. A* **101** 2766-2772.

MUNTER R (2001) Advanced oxidation process-current status and prospects. *Proc. Estonian Acad. Sci. Chem.* **50** (2) 59-80.

NEAMTU M, SIMINICEAU I, YEDILER A and KETTRUP A (2002) Kinetics of decolorization and mineralization of reactive azo dyes in aqueous solution by the UV/H_2O_2 oxidation. *Dyes Pigm.* **53** 93-99.

OKABE H (1978) *Photochemistry of Small Molecules*. New York, Wiley. 178 pp.

RODRIQUES MA, BROCHSZTAIN S, BARROS T, BOPTISTA M and POLITI MJ (1999) pH-dependent excited-state properties of N, N'-di (2-phosphoethyl)-1,4,5,8-naphthalenediimide. *Photochem. Photobiol.* **70** (1) 35-39

SHEN YS and WANG DK (2002) Development of photoreactor design equation for the treatment of dye wastewater by UV/H_2O_2 process. *J. Hazard. Mater.* **B89** 267-277.

THOMAS JR VR, SCHREINER AF, XIE TY, CHEN CL and GRATZL JS (1995) Photolyltic dechlorination of 4-chlorophenol in O_2-saturated aqueous solutions in the absence of photocatalysts or additives using ArF* (193 nm) and KrF* (248 nm) excimer lasers. *J. Photochem. Photobiol A: Chem.* **90** 183-191.

WEAST RC and ASTLE MJ (1982) *CRC Handbook of Chemistry and Physics*. CRC Press, Boca Raton, FL. B-126 pp.

ZHANG JY and BOYD IW (1996) Efficient excimer ultraviolet sources form a dielectric barrier discharge in rare-gas/halogen mixtures. *J. Appl. Phys.* **80** (2) 633-638.