Near-quantitative mineralization of two refractory triazines under hydrothermal-supercritical aqueous conditions assisted by ozone and UV/ozone

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Received (in Montpellier, France) 8th November 2002, Accepted 10th March 2003
First published as an Advance Article on the web 26th June 2003

Refractory atrazine and cyanuric acid were degraded under hydrothermal and supercritical aqueous media (HY-SC) conditions, as well as in the presence of ozone (HY-SC/O_3) and UV-illuminated ozone (HY-SC/UV/O_3) to assess whether the efficacy of the decomposition process could be enhanced using a single-pass flow-through treatment device under a constant pressure of 23 MPa. The progress of the degradation was evidenced by the extent of removal of total organic carbon (TOC) in solution, by UV absorption spectroscopy (opening of the atrazine and cyanuric acid heterorings), and by the extent of deamination (formation of NH_4^+) and dechlorination (release of Cl^- ions) of the two compounds. Loss of atrazine was confirmed by LC-MSD techniques in the positive ion mode. Formation of various intermediates from the degradation of atrazine was substantiated by positive and negative ion mode MSD analyses. Dechlorination of atrazine occurred around 100 °C under hydrothermal conditions for the HY-SC and HY-SC/O_3 processes but not for HY-SC/UV/O_3; it did increase rapidly at higher temperatures (beginning at *ca.* 220–230 °C) for all three methods: HY-SC through HY-SC/UV/O_3. Deamination, removal of TOC, and loss of atrazine mass spectral features began around 260–280 °C in hydrothermal aqueous media. Degradation of cyanuric acid showed a similar behavior. For the treated effluent solution in the collector reservoir, ozonation enhanced somewhat both dechlorination and mineralization, but had no significant effect on the deamination of either atrazine or cyanuric acid.

Introduction

Water pollutants originating from usage of agrochemicals, such as herbicides and pesticides, tend to resist bacteriological degradation. Accordingly, accumulation of these agrochemicals present at ppm (mg L^{-1}) levels in agricultural runoffs can cause considerable problems to aquatic ecosystems (the drinking water standard level for atrazine set by the U.S. Environmental Protection Agency is currently 3 ppb, *i.e.*, 3 μg L^{-1}). To the extent that most of these agrochemicals are classified as endocrine disruptors, treatment of their wastewaters poses substantial challenges in the remediation of the ecosystems involved. Degradation of these disruptors through usage of strong oxidizing agents necessitates the development of practical devices to achieve an acceptable treatment methodology for such waste chemical products. Disposal of refractory, non-biodegradable chemicals is an important aspect of green chemistry technologies.

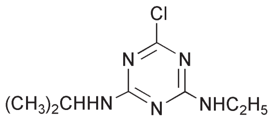
Pesticides bearing a triazine skeleton are widely used worldwide to treat soils for agriculture purposes. Consequently, triazines accumulate in nature for long periods of time without noticeable (bio)degradation. As an example of the damage such triazines cause, we need only note that the reproduction of alligators, plankton and fish is highly affected by the herbicide atrazine.[1–3] As a specific example, Hayes and coworkers[4] found that when male tadpoles were exposed to levels of atrazine greater than 0.1 ppb, this triazine induced *aromatase* and promoted the conversion of testosterone to estrogen, thereby effectively demasculinizing male frogs. It is not unlikely that other amphibian species exposed to such triazines are also at risk for impaired sexual development. Not surprisingly, seven European countries have banned the use of atrazine and any pesticide that tends to occur in drinking water at levels greater than 0.1 ppb.[5]

The degradation of triazine-type herbicides has been investigated by advanced oxidation technologies (AOTs) such as the photocatalytic method,[6,7] by Fenton chemistry,[8] by UV/ozone oxidation,[9] and by oxidation by $SO_4^{-\bullet}$ radicals produced by flash photolysis and radiolysis techniques.[10] The radiolytic method caused 76% of cyanuric acid to be decomposed after an applied dose of 18 kGy. Relevant studies have demonstrated that degradation of atrazine generates cyanuric acid as the final product.[11,12]Atrazine could not be mineralized further under the AOT conditions used,[6,7] even though the oxidative reactions involved the highly oxidizing $^{\bullet}OH$ radicals. Consequently, it is relevant to examine other treatment methodologies (*e.g.*, hydrothermal and supercritical water) to degrade the refractory atrazine and cyanuric acid. The degradation efficiency is remarkably enhanced by the cooperative combination of the photocatalytic method in hydrothermal and supercritical water media.[13]

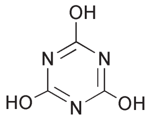
The goals of the present study were twofold. (1) Develop and establish a possible treatment methodology to degrade atrazine and cyanuric acid in a hydrothermal and supercritical water environment using a single-pass flow-through reactor system. Typically, cyanuric acid is converted to the acid anhydride (HONC) upon heating at 100 °C, followed by further conversion to cyanic acid after increasing the temperature to 300 °C. However, cyanic acid tends to polymerize back to cyanuric acid upon cooling. Accordingly, it was relevant to assess

DOI: 10.1039/b211046f

the degradation of atrazine and cyanuric acid by the methodologies herein examined. (2) Assess and improve the efficacy of the hydrothermal (HY) and supercritical (SC) water methodologies to decompose the two refractory products using the combination HY-SC, and also study combinations in which ozone is introduced (HY-SC/O_3) and is subsequently irradiated with UV radiation (HY-SC/UV/O_3) from a suitable light source.



Atrazine



Cyanuric acid

Experimental

Materials and procedures

The Hastelloy C276 single-pass flow-through reactor is illustrated in Fig. 1. It consists of a heated chamber fitted with quartz and sapphire windows for illuminating the solution with UV light (Hg lamp), a high-pressure pump, a cooling jacket, an ozone generator, and a backpressure regulator connected to a PC computer. An aqueous solution of either atrazine (0.1 mM; $C_8H_{14}ClN_5$) or cyanuric acid (0.1 mM; $C_3H_3N_3O_3$), supplied by Kanto Kagaku Co. and Wako Pure Chem. Industries Ltd., respectively, was introduced into the reactor using a JASCO high-pressure pump. The temperature of the solution was allowed to rise to *ca.* 400 °C at a rate of 2 °C min^{-1}. Control of the pressure at 23 MPa in the reactor was achieved with a JASCO backpressure regulator (BPR).

The temporal dependence of temperature and pressure on the time of flow of the solution is illustrated in Fig. 2. The flow rate of the pump was 0.5 mL min^{-1}; heating of the solution was begun simultaneously with the start of the pumping. Samples of the solution were collected from the reservoir after rapid cooling of the solution through the cooling jacket. The decomposition of atrazine and cyanuric acid was examined using the following three combined techniques: (a) hydrothermal and supercritical water method (HY-SC; note that water goes supercritical at 374 °C and 22 MPa), (b) an integrated HY-SC method in a solution that contained dissolved ozone (HY-SC/O_3), and (c) a combination in which the HY-SC/O_3 system was irradiated by UV light (HY-SC/UV/O_3). Ozone was introduced into the aqueous solution from the appropriate Tokyokaken OZM-01D ozone generator in which O_3 was generated from pure oxygen gas in about 60% yield, as stated in the manual supplied by Tokyokaken Co. Ltd. The concentration of ozone in the aqueous atrazine solution was monitored and maintained at *ca.* 0.2 ppm with a Lab-ozone detector (Asahi Technoglass Co. Ltd.). In the HY-SC/UV/O_3 combined method, a 250 W mercury lamp supplied the UV radiation impinging upon the solution through the quartz and sapphire windows. The light irradiance was *ca.* 6 mW cm^{-2} at 250 nm and *ca.* 7.2 mW cm^{-2} at 360 nm.

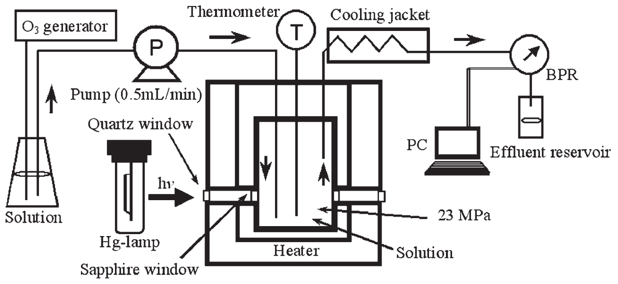


Fig. 1 Experimental setup of the single-pass flow-through reactor (60 mL) equipped with a pump and a backpressure regulator (BPR).

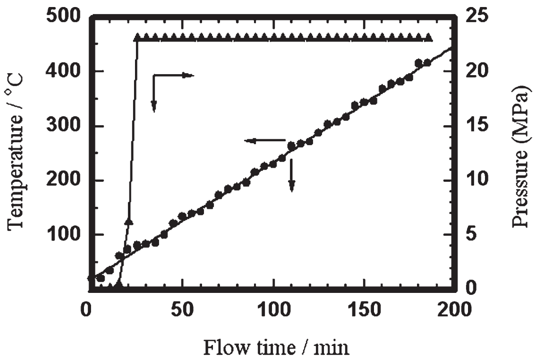


Fig. 2 Temperature rise of the solution and variation of pressure against flow time.

The quantity of TOC remaining in solution (reservoir; see Fig. 1) was determined by a Shimadzu TOC-5000A analyzer. Temporal variations in the concentrations of both refractory products were monitored though UV absorption spectroscopy utilizing a JASCO UV/VIS/NIR V-560V spectrophotometer. Formation of Cl^-, NH_4^+ and NO_3^- ions was assayed with a JASCO HPLC chromatograph, equipped with a CD-5 conductivity detector using either a Y-521 cationic column or an I-524 anionic column. Decrease of the quantities of atrazine was also followed using an Agilent Technologies HP1100 LC-MSD apparatus (liquid chromatograph coupled to an electrospray mass spectral detector operated in both negative and positive ion modes). The eluent was a solution of methanol and water {1:1 v/v; the ion-exchanged water used throughout was ultrapure to < 5 μg L^{-1}. TOC and electrical conductivity was < 0.1 μS cm^{-1}). The LC-MSD system was equipped with an Agilent Eclipse XDB-C_8 column. The mass spectra from the API-ES ionization mode were recorded under conditions whereby the fragmenter was set at 100 V, the capillary voltage was 2200 V and the dry gas temperature was 300 °C. The intermediates generated from the degradation of atrazine were also identified with the HP1100 LC-MSD using direct injection into the mass spectral detector with methanol–water as the eluent. The settings of the mass spectral detector were identical to those used for atrazine.

Ozone under UV radiation

Formation of $^\bullet$OH radicals from UV-irradiated ozone takes place through the processes summarized by eqns. (1)–(4).[14]

$$O_3 + H_2O + h\nu \rightarrow \{2\ HO^\bullet\} \rightarrow H_2O_2 \quad (1)$$

$$H_2O_2 \equiv HO_2^- + H^+ \quad (2a)$$

$$HO_2^- + O_3 + h\nu \rightarrow HOO^\bullet + O_3^{-\bullet} \quad (2b)$$

$$O_3^{-\bullet} + H^+ \rightarrow HO_3^\bullet \rightarrow HO^\bullet + O_2 \quad (3)$$

$$O_3^{-\bullet} + H_2O \rightarrow HO^\bullet + HO^- + O_2 \quad (4)$$

They typically involve degradation of ozone. Detection of the $^\bullet$OH radicals by electron spin resonance (ESR) methods tends to be somewhat difficult because of the rather short lifetime of these radicals (a few microseconds). Accordingly, when needed ESR measurements were conducted at liquid nitrogen temperatures or at ambient temperatures using the DMPO (5,5-dimethyl-1-pyrroline-*N*-oxide) spin trap agent. It was not possible to detect formation of $^\bullet$OH radicals at temperatures much above ambient because of the thermal decomposition of DMPO. Substantiation of the formation of $O_3^{-\bullet}$ radicals (see Fig. 3) was achieved in the presence of DMPO under ambient conditions with a JEOL JES-TE200 ESR

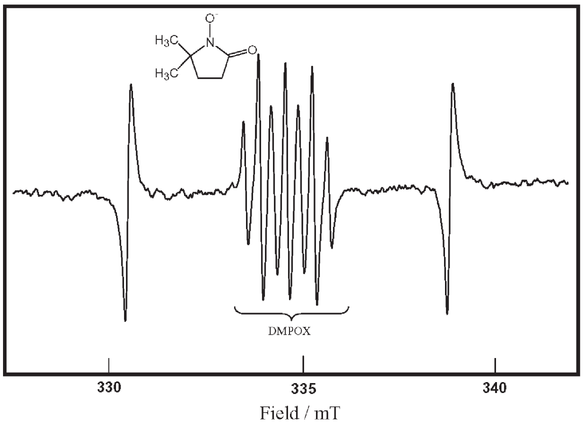


Fig. 3 ESR spectrum of 5,5-dimethyl-2-ketopyrrolidone-*N*-oxyl (DMPOX) for the O_3-containing aqueous solution under UV irradiation (ambient temperature and pressure).

spectrometer. The ESR spectrum accorded with the spectrum obtained from the JEOL-supplied database for 5,5-dimethyl-2-pyrrolidone-*N*-oxyl (DMPOX).

Results and discussion

Degradation of atrazine

The thermally dependent decrease of the concentration of atrazine occurring during its decomposition by the HY-SC method and monitored by LC-MSD techniques is summarized in Fig. 4. Decomposition was slow at first from ambient to about 259 °C, following which further heating caused rapid degradation of the atrazine up to about 364 °C, at which point the LC-MSD signal of atrazine (molecular weight of 217), seen at the mass/charge ratio (*m*/*z*) of 216 in the positive ion mode, was no longer observable at near-supercritical conditions. The data of Fig. 4 were obtained from the water-soluble samples collected from the reservoir. It is worth noting that under supercritical conditions water behaves like an organic solvent, since both its dielectric constant and the ion-product of water decrease above the critical points of temperature and pressure.[15] Evidently, the solubility of atrazine and of the degradation intermediates in supercritical water is different from the solubility of these products usually encountered at ambient temperatures and atmospheric pressure. In addition, the degradation of this triazine is most efficient in supercritical water (see results from *ca.* 370 °C to 400 °C) than under low temperature hydrothermal conditions (temperature range: ambient to 259 °C), however, hydrothermal degradation in the temperature range 260–370 °C is evidently fast at the higher temperatures. Reaction times for complete conversion of atrazine under the low-temperature HY conditions are much longer.

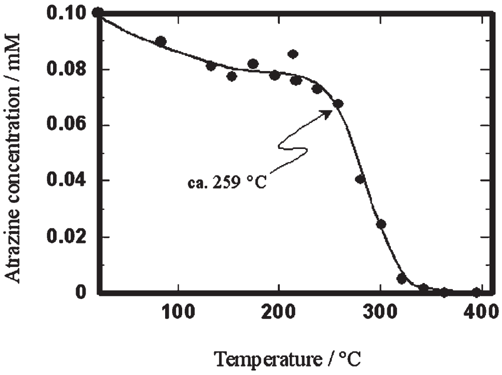


Fig. 4 Decrease in atrazine concentration under hydrothermal (HY) and supercritical (SC) aqueous conditions as evidenced by LC-MSD detection.

The relevant UV absorption spectral patterns are displayed in Fig. 5, whereas Fig. 6 displays the decreases in the concentration of atrazine monitored by UV absorption (wavelength, 222 nm) during decomposition by the HY-SC, HY-SC/O_3, and HY-SC/UV/O_3 methods. We note that the quantity of atrazine, and thus its UV absorption band, during its degradation by the HY-SC method decreased rapidly at *ca.* 259 °C; that is, at the same temperature as the temperature of disappearance of atrazine monitored by the LC-MSD technique (see below). These observations suggest, at least in part, that the initial degradation of atrazine takes place through ring opening in competition with formation of aromatic intermediates.

The corresponding temperatures for the loss of UV absorption of atrazine at 222 nm during its decomposition by the HY-SC/O_3 and HY-SC/O_3/UV methods are very similar to those of the HY-SC method. Nonetheless, there is a perceptible difference, however slight, in the temperature region of 250–300 °C. Moreover, we observed no new UV absorption features and no band shifts in the UV absorption spectra of atrazine at 222 nm (Fig. 5). Also, we were unable to observe UV absorption features of cyanuric acid (expected absorption band at 193 nm) in the entire temperature range of 22–400 °C.

The temperature-dependent evolutions of the NH_4^+ and Cl^- ions formed during the decomposition of atrazine are depicted in Fig. 7(a) and Fig. 7(b), respectively. Under supercritical conditions, the mineralization yield of the five nitrogen atoms in the atrazine structure was 100% for degradation by all three HY-SC, HY-SC/O_3 and HY-SC/UV/O_3 methods. The onset temperature at which we observed the initial formation of NH_4^+ ions was 225 ± 10 °C for the HY-SC and HY-SC/UV/O_3 methods. In contrast, the onset for the HY-SC/O_3 method was 164 °C [barely perceptible in Fig. 7(a)]. The nitrogen atoms in atrazine were only negligibly converted to NO_3^- ions at 300 °C by the HY-SC and HY-SC/O_3 methods. No nitrate ions were detected for the HY-SC/UV/O_3 combination under otherwise identical conditions. We deduce that the initial formation of NO_3^- ions originates from the conversion of the nitrogen atoms in the substituent groups of the atrazine structure, and not from the triazine skeleton. The negligible quantity of NO_3^- ions produced decreased on addition of ozone to the HY-SC combination.

The nitrogen atoms in atrazine were nearly completely converted to NH_4^+ ions under supercritical water conditions. Evidently, each of the degradation method was able to induce cleavage of the triazine skeleton in the atrazine structure. The initiation of dechlorination by the HY-SC and HY-SC/O_3 methods occurred at temperatures slightly below 100 °C, with cleavage of the chlorine substituent to yield Cl^- ions being nearly complete under supercritical conditions. Although the initial formation of Cl^- ions for the HY-SC/UV/O_3 method occurred at *ca.* 164 °C, complete dechlorination did not occur; only about 75–80% chloride ions were formed. It is evident that the preferred method to dechlorinate atrazine is the HY-SC/O_3 method [Fig. 7(b)].

The dependence of the concentration of TOC on temperature assayed during the degradation of atrazine is depicted in Fig. 8. Using the HY-SC method, the TOC increased somewhat relative to its initial concentration of *ca.* 9.5 ppm at temperatures less than 100 °C. The near 40% increase in TOC under hydrothermal conditions at 84 °C was likely due to the high pressure (23 MPa) to which the solution was subjected in the reactor. This may have led to concentrating atrazine and any of the intermediates formed as a result of the sudden pressure drop from 23 MPa to ambient pressure in the reservoir (Fig. 1). At temperatures from ambient to *ca.* 280 °C, this was followed by a slow decrease subsequent to which the TOC

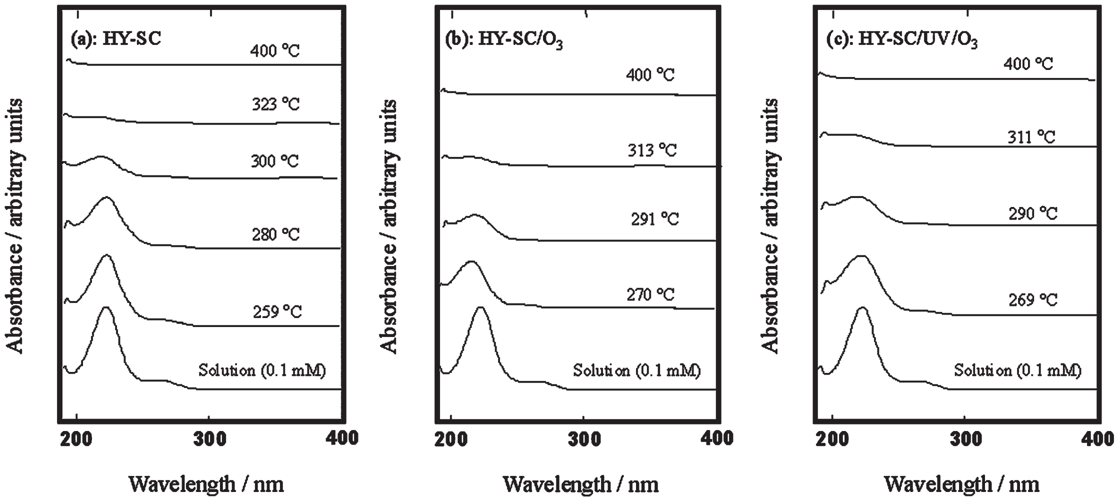


Fig. 5 Temperature dependent changes of the UV spectral patterns at selected temperatures during the degradation of an aqueous solution of atrazine (0.1 mM) under different conditions: (a) HY-SC, (b) HY-SC/O_3 and (c) HY-SC/UV/O_3.

decreased rapidly upon further heating. In contrast, the increase of TOC below 100 °C was not as significant when employing the HY-SC/O_3 and HY-SC/UV/O_3 methods for reasons that remain somewhat elusive.[16] Nonetheless, we cannot preclude variations in the hydrophilic/hydrophobic characteristics of the intermediates formed, and to some extent, any influence of the added ozone gas. The rate of decrease of TOC by the HY-SC/O_3 method was only slightly lower than the rate by either the HY-SC or HY-SC/UV/O_3 methods. The percent loss of TOC at about 400 °C was 89% by the HY-SC method, 95% by the HY-SC/O_3 method and 89% by the HY-SC/UV/O_3 method.

The UV absorption features of atrazine and the quantity of TOC did not totally disappear, even under SC conditions. However, to the extent that some nitrogen-free and chlorine-free intermediates were generated by the three techniques, effluents emanating from treated wastewaters containing atrazine are expected to be relatively non-toxic and more biodegradable.

LC-MSD mass spectra in the positive and negative ion modes were recorded at all temperatures used in order to detect and substantiate the nature of the intermediates produced in the degradation of atrazine. These spectra are depicted in Fig. 9 (spectra i-positive and i-negative) for the initial atrazine solution, followed by selected mass spectra of possible intermediates obtained at 196, 259 and 343 °C (positive ion mode, left column) and at 83.5, 133, and 364 °C (negative ion mode, right column). Molecular peaks of atrazine appear at m/z 216 and 238 (positive ion mode, M + H and M + Na peaks, respectively) and at m/z 214 (negative ion mode, M − H peak) in accord with a mono-chlorinated species (note the Cl-35 and Cl-37 isotopes). The positive peak of atrazine at m/z 216 is in accord with the database of standards from the LC-MSD manufacturer Agilent Technologies. The formation of cyanuric acid during the degradation of atrazine by the HY-SC combination was not observed at m/z 128 (negative mode) by mass spectral methods at all temperatures without the use of the liquid chromatographic technique. The peak at m/z 196 (M − H; 83.5 °C; ii-negative spectrum) is attributed to a dechlorinated species, which displayed a major peak last seen at 364 °C (v-positive spectrum). This intermediate was also seen in the mass spectra at $m/z = 222$ (positive

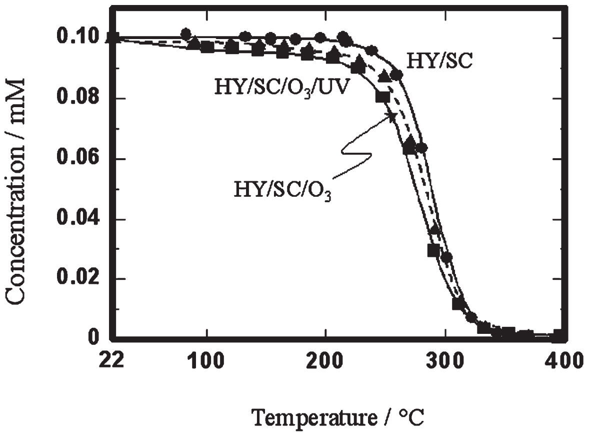


Fig. 6 Loss of atrazine as evidenced by UV absorption spectroscopy in the degradation of atrazine by the HY-SC, HY-SC/O_3 and HY-SC/UV/O_3 methods (O_3 concentration maintained at 0.2 ppm).

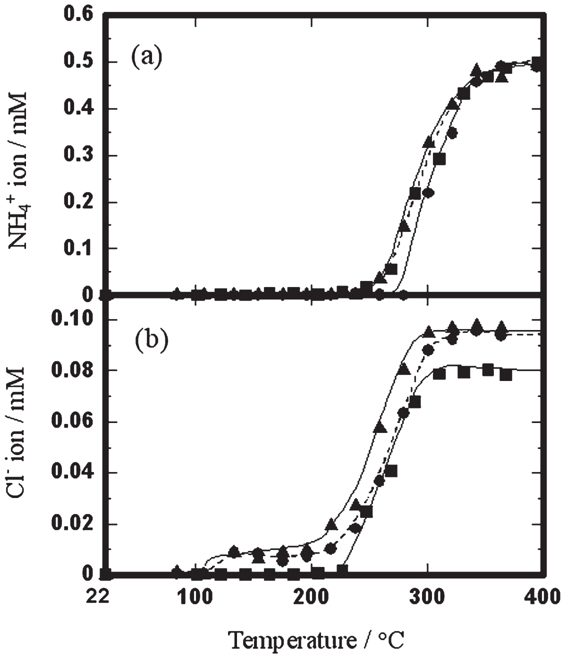


Fig. 7 Temperature dependence of the formation of (a) NH_4^+ and (b) Cl^- ions during the degradation of 0.1 mM atrazine (circles: HY-SC; triangles: HY-SC/O_3; squares: HY-SC/UV/O_3).

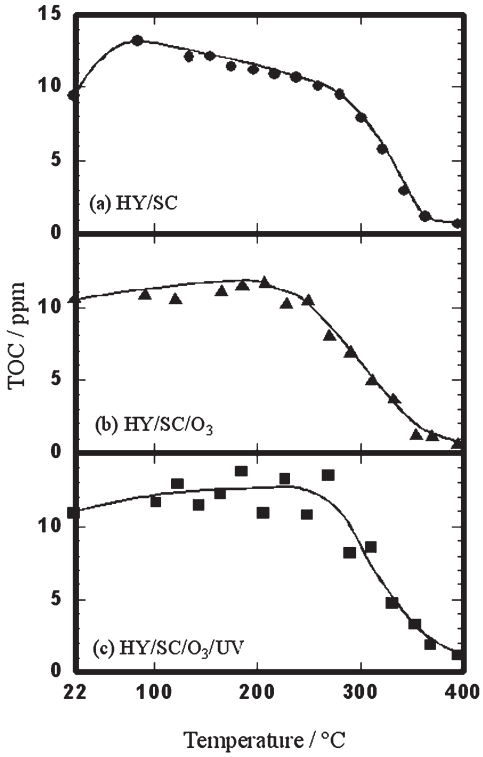


Fig. 8 Disappearance of TOC during the degradation of atrazine by the (a) HY-SC, (b) HY-SC/O_3 and (c) HY-SC/UV/O_3 methods.

mode, M + Na) recorded at 238 and 259 °C. We assign this peak to the 2,4-diamino-6-hydroxy-*N*-ethyl-*N*′-(1-methylethyl)-1,3,5-triazine species (**I**, see Scheme 1below). The second intermediate with m/z 126 (M + H) was first observed at 133 °C (see iii-negative mode spectrum), which we attribute to the unsaturated 2,4-diamino-6-hydroxy-1,3,5-triazine species (**II**). An intermediate with m/z 102 (M + H) first appeared at 238 °C and was still observable at 343 °C (see *e.g.* the iii-positive spectrum). It is likely due to the unsaturated hydroxylamine species CH_3–N=CH–N=CH–NHOH. At higher temperatures, another species was first detected at 322 °C (m/z = 129; M + H) and was prominent at 395 °C. It is attributed to the intermediate species 2-amino-4,6-dihydroxy-1,3,5-triazine (**III**; see also *e.g.* the v-positive spectrum). The chlorine-containing intermediate with m/z = 169 (positive ion mode; M + Na) was detected in mass spectra taken at 322, 343, 364 and 400 °C (*e.g.*, iv- and v-positive mode spectra). The peak is assigned to the intermediate 6-chloro-2-amino-4-dihydroxy-1,3,5-triazine (**IV**). The signal at m/z 170 (positive ion mode; M + Na; iv-positive spectrum) observed at 343 °C is due to the 6-chloro-2,4-dihydroxy-1,3,5- triazine species (**V**).

For the HY-SC/O_3 and HY-SC/UV/O_3 combinations, the initial formation of cyanuric acid occurred around 100 °C. Undoubtedly this difference in temperature must be due to differences in the degradation processes. Nonetheless, the quantity of cyanuric acid formed was rather small with these two methods.

In principle, a molecule such as atrazine can be degraded through either of two mechanistic sequences: (1) dechlorination followed by dealkylation and then deamination; or (2) dealkylation as the initial step followed by deamination and/or dechlorination as the subsequent steps (see Scheme 1). The mechanistic details of the heterogeneous photocatalyzed degradation of atrazine in irradiated aqueous TiO_2 dispersions have been reported.[11,12] In these earlier studies, the degradative oxidation process occurred *via* $^{\bullet}$OH radical attack on the surface of titania particles. The major pathway (*ca.* 90%) involved deethylation followed by further dealkylation, deamination and ultimately dechlorination to yield the final product cyanuric acid, which under the photocatalytic conditions used degraded no further. The minor pathway (~10%) involved dechlorination first, followed by dealkylation and ultimately deamination to cyanuric acid.

On the basis of the results obtained under our conditions, we deduce that dechlorination was the major step at low temperatures in the overall process, followed by dealkylation and deamination (see Scheme 1). Cleavage of the atrazine heteroring competes with these events. Accordingly, it was relevant that we also examine the degradation of the refractory cyanuric acid under conditions otherwise identical to those used for atrazine.

Degradation of cyanuric acid

The UV absorption spectral patterns recorded during the degradation of cyanuric acid at selected temperatures from ambient to *ca.* 400 °C by the HY-SC, HY-SC/O_3 and HY-SC/UV/O_3 methods are illustrated in Fig. 10. For the HY-SC method, the initial UV absorption band of a solution of cyanuric acid (0.1 mM; enol form) at ambient temperature occurs at 193 nm. Upon heating the solution to 103 °C this band remained but an additional band at 214 nm evolved, which we ascribe to a keto-enol tautomeric equilibrium[17–19] between the keto form mostly present below pH 6 and the enol form present at pH above 6 (see Scheme 2). Interestingly, the presence of ozone appears to affect this keto-enol equilibrium [compare Fig. 10(b) and Fig. 10(c) with Fig. 10(a)]. At higher temperatures, the intensity ratio of the two bands varied because of changes in pH with increase in temperature. The enol form was produced as a result of an increase in pH from initial pH = 5.1 at ambient temperatures to pH = 7.0 at 400 °C. To test this notion we also recorded absorption spectra, under otherwise identical conditions, of an aqueous solution of cyanuric acid upon varying the pH from 5.1 to 7.5. In the slightly acidic media (pH = 5.1), the spectrum displayed only the band at ~193 nm, whereas in the pH range 6.0–7.5 the band at 214 nm also appeared, in exact accord with the recent study of Cantu and coworkers[17] (see their Fig. 3, left panel) and identical to our observations illustrated in Fig. 10. Cyanuric acid has two ionization constants (25 °C), $K_{a_1} = 6.31 \times 10^{-8}$ ($pK_{a_1} = 7.2$) and $K_{a_2} = 7.94 \times 10^{-12}$ ($pK_{a_2} = 11.1$).[20] Only in strongly alkaline solutions are these two ionized forms of any relevance to the absorption spectra.[19]

Perusal of the spectral features in Fig. 10 show that the 214 nm band disappeared almost completely at temperatures greater than *ca.* 300 °C for all three methods. Concomitantly, the 193 nm band also decreased considerably, but did not completely disappear under these conditions.

The relative loss of cyanuric acid at 400 °C by the HY-SC, HY-SC/O_3 and HY-SC/UV/O_3 methods evidenced spectroscopically was 87%, 78% and 76%, respectively. Clearly, the presence of O_3 and UV/O_3 had little effect on the decrease of the UV absorption features. No shift of the initial peak at 193 nm was observed for the degraded solution. Also, since no additional UV absorption features were observed in the decomposition of cyanuric acid (except for the 214 nm band), we deduce that no intermediates formed that had the atrazine skeleton. Alternatively, intermediate(s) that did form must have degraded fairly rapidly, and in all cases the triazine ring in cyanuric acid was cleaved.

The decrease of TOC and the increase of NH_4^+ ions produced during the degradation of cyanuric acid are illustrated in Fig. 11. The initial concentration (3.60 ppm) of the acid's TOC increased to 7.12 ppm (HY-SC) at 100 °C as already observed above for atrazine.[15] Concomitantly, the maximal concentration of cyanuric acid for the HY-SC/UV/O_3 method increased to 4.74 ppm at 206 °C. In contrast, there was no increase in all the temperature ranges examined when the

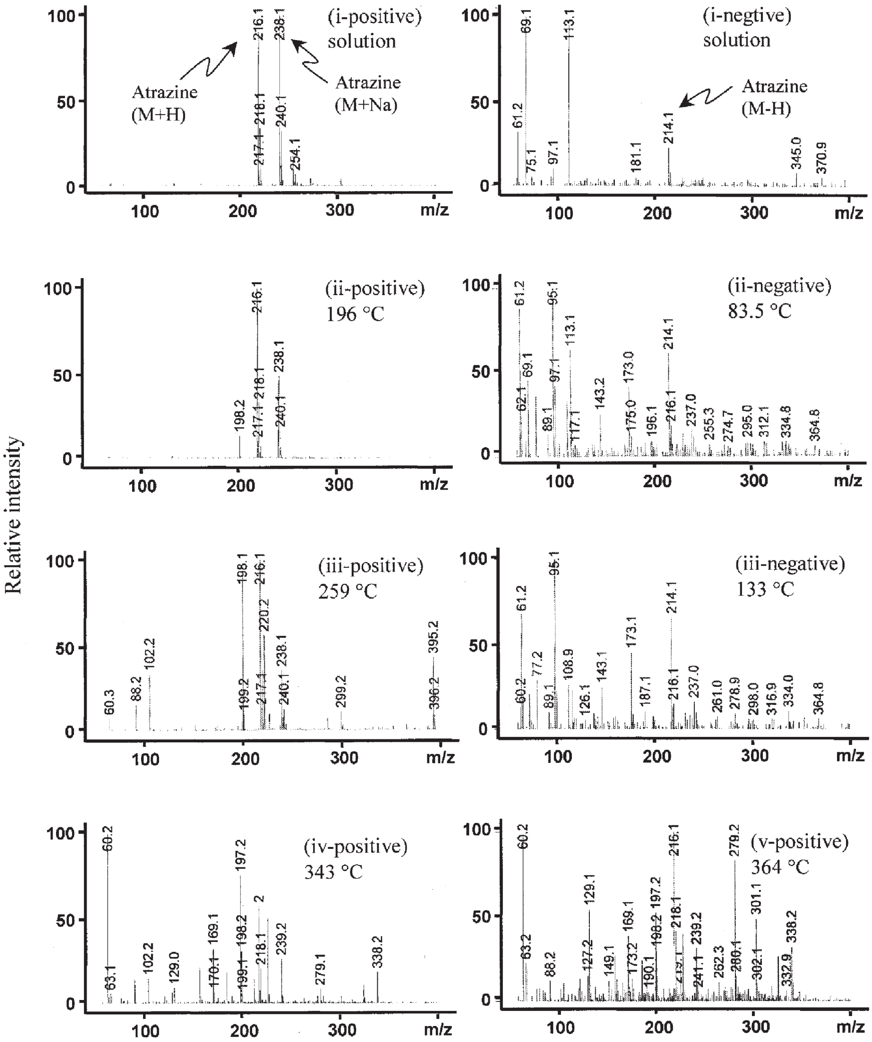
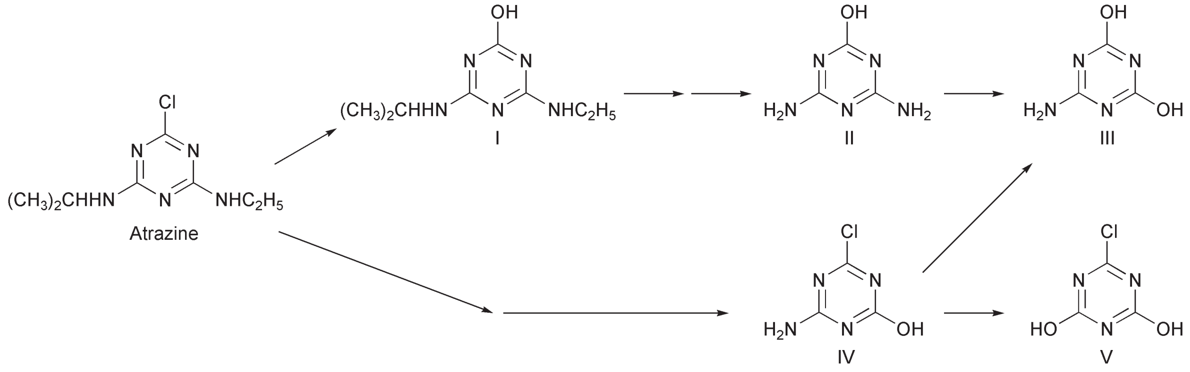


Fig. 9 Electrospray mass spectra of atrazine solutions recorded in the positive ion mode (M + H and M + Na; left column) and in the negative ion mode (M – H; right column) at several selected temperatures during the degradation of atrazine.

HY-SC/O_3 method was employed. Once again, the TOC level decreased rapidly around 260 °C. Under supercritical conditions, the quantity of cyanuric acid remaining in the reservoir solution was 1.21 ppm for the HY-SC method, 0.29 ppm for the HY-SC/O_3 method and 0.37 ppm for the HY-SC/UV/O_3 method.

Formation of NH_4^+ ions was fairly rapid around 200 °C, reaching the expected maximal quantity of NH_4^+ ions at *ca.* 300 °C for all three methods employed (initial concentration of cyanuric acid, 0.1 mM). Formation of NO_3^- ions was rather insignificant up to *ca.* 300 °C by the HY-SC and HY-SC/O_3 methods. Addition of UV radiation in the presence of ozone produced no nitrate ions at all the temperatures examined. Evidently, the nitrogen atoms in cyanuric acid are transformed almost entirely into NH_4^+ ions, with the mineralization yield of all nitrogens for all three sets of conditions being nearly quantitative. In all cases, no cyanuric acid was detected at temperatures greater than 300 °C by LC-MSD analyses.



Scheme 1 Intermediates produced in the degradation of atrazine.

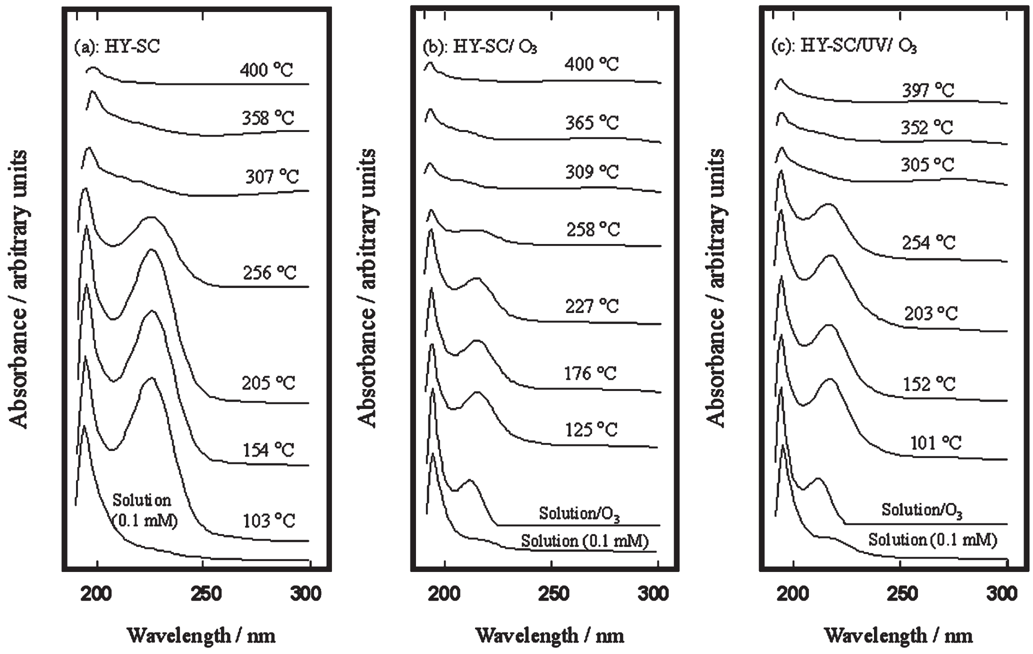
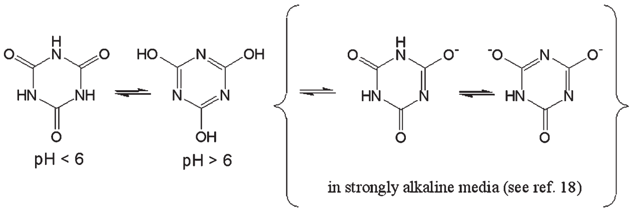


Fig. 10 UV spectral patterns recorded at several selected temperatures during the degradation of cyanuric acid by the (a) HY-SC, (b) HY-SC/O_3 and (c) HY-SC/UV/O_3 methods.



Scheme 2 Relevant structures showing the keto-enol tautomeric equilibrium between the different species of cyanuric acid.

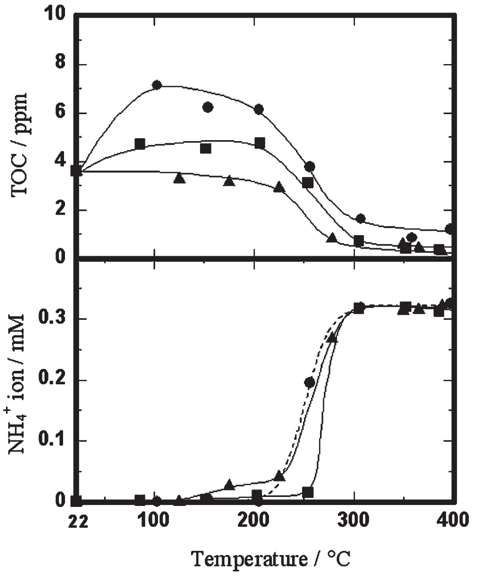


Fig. 11 Temperature dependence of the evolution of NH_4^+ ions and the decrease of TOC in the degradation of cyanuric acid by the HY-SC (circles), HY-SC/O_3 (triangles) and HY-SC/UV/O_3 (squares) methods.

Concluding remarks

The present study has shown that two refractory products, namely atrazine and cyanuric acid, can be degraded to some extent under hydrothermal conditions at a pressure of 23 MPa and almost completely in supercritical water media. Addition of ozone enhanced somewhat the dechlorination of atrazine. The decomposition of intermediates formed in the degradative process was also effective as observed from the decreases of TOC. On the basis of the TOC data, addition of ozone and irradiation with UV light had some positive but small effects on the efficiency of degradation. UV absorption results show that adding O_3 or UV/O_3 to the HY-SC method had little effect on the cleavage of the triazine structure. Nonetheless, the present study demonstrates that cleavage of the triazine ring, dechlorination, deamination and mineralization are significantly different mechanistically in supercritical aqueous media from what transpires in the photocatalytic AOT methodologies[11,12] and by the flash photolytic and radiolytic methods.[10] Unlike the hydrothermal/supercritical water methologies examined herein, however, these last two methods are not very practical to degrade large quantities of these two refractory substrates. In contrast, atrazine and cyanuric acid can be mineralized almost quantitatively by the HY-SC methology, a feat that the photocatalytic method alone does not achieve for atrazine and which hardly affects cyanuric acid for reasons that are still not well understood. The nearly quantitative conversion of the nitrogens into NH_4^+ ions and the negligible (if any) quantities of NO_3^- ions in the degradation of both atrazine and cyanuric acid are noteworthy.

Acknowledgements

We are grateful to the Frontier Research Promotion Foundation sponsored by the Japan Ministry of Education, Sports, Culture, Science and Technology (to H.H.) and to the Natural Sciences and Engineering Research Council of Canada (to N.S.) for financial support of this work and for the fruitful collaboration between our two respective laboratories. One of us (N.S.) thanks Prof. A. Albini of the University of Pavia for his hospitality during the winter semester 2003.

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16 The rise in TOC levels as seen in Fig. 8 for atrazine and in Fig. 11 for cyanuric acid was rather unexpected and enigmatic. Accordingly, we examined the degradation of atrazine at different pressures in the reactor (ambient pressure, 10 MPa and 23 MPa) under hydrothermal conditions in the temperature range from ambient to 200 °C. At the highest pressure used we again observed an approximate 40% increase in TOC at temperatures below 100 °C. In contrast, the TOC level increased only by *ca.* 10% at a pressure of 10 MPa, whereas the data appear normal under ambient pressure. We also considered the possibility that the extra TOC carbon might originate from corrosion of the Hastelloy C276 reactor used. Control experiments carried out at various temperatures in aqueous media alone and in aqueous media containing atrazine and cyanuric acid, however, demonstrated that no corrosion of the reactor occurred and thus no TOC carbon was released. Consequently, we conclude that the unusual behavior seen in Figs. 8 and 11 is due to a pressure effect. In the case of the conditions HY-SC/O_3 and HY-SC/UV/O_3, the presence of O_3 appears to attenuate this effect somewhat.

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