



Kinetic and mechanistic investigation of azathioprine degradation in water by UV, UV/H₂O₂ and UV/persulfate

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HIGHLIGHTS

- Degradation of azathioprine (AZA) was studied by UV and UV-AOPs.
- UV/persulfate is the most efficient and economical for azathioprine removal.
- AZA degradation efficiency in both UV-AOPs reduces with increasing pH.
- Presence of NOM and inorganic anions inhibits azathioprine degradation.
- The possible azathioprine degradation pathways are proposed.

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ABSTRACT

This study investigated the removal of azathioprine (AZA), an immunosuppressant xenobiotic found in hospital effluent, using direct UV-254 nm photolysis, UV/H₂O₂ and UV/persulfate (UV/PS). AZA cannot be effectively degraded by direct UV photolysis, while the photodegradation efficiency of AZA significantly increases with addition of H₂O₂ or PS, due to the generation of HO[•] and SO₄^{•-}, respectively. Compared with AZA removal of 10% by direct UV photolysis at UV dose of 510 mJ cm⁻², UV/H₂O₂ and UV/PS can remove 68% and 87% of AZA, respectively, at an oxidant dose of 100 μM. The second-order rate constants of AZA with HO[•] and SO₄^{•-} are 1.86 × 10⁹ M⁻¹ s⁻¹ and 2.16 × 10⁹ M⁻¹ s⁻¹, respectively. There is a proportional increase of AZA degradation efficiency with the increasing oxidant dose in the range of 10–100 μM, beyond which radical scavenging effect can negate the radical generation process. The effects of water quality, including pH, NOM and inorganic anions, were also investigated. The removal efficiency of AZA in the UV/H₂O₂ and UV/PS processes constantly decreases with the increasing pH. NOM significantly reduces the degradation efficiency of AZA through radical scavenging and UV absorption. The inhibition of AZA photodegradation is also affected by the presence of inorganic anions, following the order of HCO₃⁻ > Cl⁻ > NO₃⁻ ≈ SO₄²⁻. Real water samples of treated water from a water treatment plant and secondary effluent from a wastewater treatment plant were used for the assessment of the UV treatment performances. Various AZA transformation by-products were identified to investigate the degradation mechanism of AZA in the UV-AOP systems. The addition of 100 μM oxidant significantly decreases the treatment cost from 0.844 (for UV photolysis) to 0.078 (for UV/H₂O₂) and 0.067 US\$ m⁻³ order⁻¹ (for UV/PS), respectively, indicating that UV/PS is the most cost-effective process for AZA degradation.

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1. Introduction

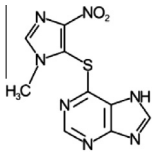
Due to the population growth and aging, the requirement for organ transplantation by patients has been considerably increasing

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[1,2]. Among them, azathioprine (AZA), chemically known as 6-[(1-methyl-4-nitroimidazole-5-yl)thiol]-prine, has been designed to decrease the risk of organ rejection through suppressing the body's immune system [3,4]. AZA was once used as a chemotherapy drug. AZA shows extremely high toxicity by giving rise to severe drug side-effects, such as nausea, fatigue, hair loss and blood disorders [5–7]. With high water solubility at 272 mg L⁻¹ and low log_{ow} of 0.1 (Table 1), AZA can get into aquatic environment and remain soluble, leading to the potential health and environmental risks

Table 1
Physico-chemical characteristics of AZA.

Molecule	MW (g mol ⁻¹)	Structure	pK _a	Water solubility (mg L ⁻¹)	Log ₁₀ k _{ow}	Henry's law constant (atm m ³ mol ⁻¹)
C ₉ H ₇ N ₇ O ₂ S	277		8.2	272	0.1	2.64 × 10 ⁻¹⁵

Data source: ChemIDPlus Advanced <http://chem.sis.nlm.nih.gov/chemidplus/>, PUBChem <http://pubchem.ncbi.nlm.nih.gov/>.

[8,9]. The presence of AZA in the hospital wastewater has been reported, due to its irresponsible disposal [10]. Moreover, AZA cannot be effectively removed via conventional wastewater treatment processes, owing to its biorefractory and recalcitrance [11]. As a result, it is of great significance to develop effective treatment methods to degrade AZA in water.

UV-based advanced oxidation processes (AOPs) have been considered as promising alternatives to conventional water treatment and reclamation processes, due to the generation of highly reactive free radicals, e.g., HO[•] and SO₄^{•-} [12,13]. UV/H₂O₂ has been extensively investigated in microorganism disinfection and micropollutant degradation [14,15]. Non-selective HO[•] can be promptly generated from H₂O₂ by absorbing UV irradiation at wavelengths of 200–280 nm (Eq. (R1), Table 2). It attacks various organic compounds through electron transfer, hydrogen abstraction or electrophilic addition reactions [16]. However, the degradation efficiency by HO[•] oxidation is significantly affected by the presence of natural organic matters (NOMs) or inorganic anions [17,18]. More recently, UV/persulfate (PS, S₂O₈²⁻), which is based on the production of SO₄^{•-} (Eq. (R2), Table 2) [19], has also attracted broad interest in pharmaceutical degradation due to the easy storage and moderate stability of PS [20–22]. SO₄^{•-} has a higher oxidizing power (2.5–3.1 V) than that of HO[•] (1.8–2.8 V) especially at higher pH values, and is more selective for electron transfer reactions [23]. Therefore, it has been reported to be more effective than HO[•] in the organic pollutants destruction, such as cyanotoxin cylindros-

permopsin [18], antipyrine [24], and atrazine [25]. However, the degradation of AZA by UV-based AOPs has been seldom reported.

In this study, the degradation efficiencies of AZA by direct UV photolysis, UV/H₂O₂ and UV/PS were evaluated and compared. The effects of oxidant dose, solution pH, NOM and inorganic anions were systematically investigated. Real water samples of treated water from a water treatment plant and secondary effluent from a wastewater treatment plant were used for the assessment of the UV treatment performances. The intermediates of AZA were identified to investigate the possible degradation pathways. Total treatment cost per order was analyzed to provide an indicator of the cost-effectiveness of the three treatment processes, and to determine the optimal [oxidant]/[AZA] ratios for the AOPs.

2. Materials and methods

2.1. Materials

All the chemicals and reagents, including AZA, H₂O₂, Na₂S₂O₈, NaHCO₃, NaNO₃, Na₂SO₄, NaCl, Na₂HPO₄, NaH₂PO₄, NaOH, H₂SO₄, *para*-chlorobenzoic acid (*p*CBA), *meta*-toluic acid (*m*TA), *tert*-butanol (*t*-BuOH) and atrazine were purchased from Sigma-Aldrich (USA) and used as received without further purification. High purity deionized (DI) water was obtained from Milli-Q Water System.

2.2. Experimental procedures

Experiments were carried out using a 14 cm high cylindrical glass photoreactor with an inner diameter of 11 cm, which was filled with 1 L AZA solution and magnetically agitated using a stirrer at 500 rpm to maintain the homogeneity of solution throughout the reaction. A low-pressure Hg lamp (5W, Philips, Netherlands) emitting UV irradiation at 254 nm and a quartz sleeve were placed coaxially in the photoreactor. The direct UV photolysis, UV/H₂O₂ and UV/PS processes were carried out at AZA concentration of 3.3 μM, which is at least 10-fold larger than the quantitative AZA detection limit (0.33 μM) by the LC/MS/MS used in this study. An appropriate dose of H₂O₂ or PS was added to the water sample before UV irradiation. Molar ratios [Oxidant]/[Pollutant] of 3–600, namely oxidant concentrations of 10–2000 μM, were used in this study. The solution pH was adjusted using 0.1 M H₂SO₄ or NaOH. Aliquots were collected at time intervals of 30 s for up to 3 min, and stored in amber vials pre-filled with 10 μL methanol to quench any residual oxidants.

2.3. Analytical methods

TOC of the water sample was determined by a Shimadzu TOC-VCSH analyzer with an ASI-V auto sampler. The concentrations of AZA were analyzed using a triple quadrupole liquid chromatograph mass spectrometer (LC/MS/MS), which consists of a high performance liquid chromatograph mass spectrometer module (LCMS-

Table 2
Rate constants of principal reactions in this study.

Number	Reaction	k (M ⁻¹ s ⁻¹)	References
R1	H–O–O–H + hν → 2HO [•] (Φ = 1.0 mol E ⁻¹)		[16]
R2	⁻ SO ₃ –O–O–SO ₃ ⁻ + hν → 2SO ₄ ^{•-} (Φ = 1.8 or 1.4 mol E ⁻¹)		[19]
R3	SO ₄ ^{•-} + H ₂ O → HO [•] + SO ₄ ²⁻ + H ⁺ (pH = 7)	<60	
R4	SO ₄ ^{•-} + OH ⁻ → HO [•] + SO ₄ ²⁻ (pH = 11)	6.5 × 10 ⁷	[29]
R5	HO [•] + H ₂ O ₂ → HO ₂	2.7 × 10 ⁷	[23]
R6	SO ₄ ^{•-} + S ₂ O ₈ ²⁻ → SO ₄ ²⁻ + S ₂ O ₈ ^{•-}	6.6 × 10 ⁵	[29]
R7	HO [•] ↔ H ⁺ + O ⁻ (pK _a = 11.9)		[23]
R8	HO [•] + HO [•] → H ₂ O ₂	5.5 × 10 ⁹	[23]
R9	SO ₄ ^{•-} + SO ₄ ^{•-} → S ₂ O ₈ ²⁻	3.1 × 10 ⁸	[29]
R10	HO [•] + OH ⁻ → H ₂ O + O ⁻	1.2 × 10 ¹⁰	[23]
R11	H ₂ O ₂ ↔ HO ₂ + H ⁺ (pK _a = 11.6)		[38]
R12	HO [•] + HO ₂ → HO [•] + HO ₂	7.5 × 10 ⁹	[39]
R13	NOM + HO [•] → Products	2.23 × 10 ⁸	[40]
R14	NOM + SO ₄ ^{•-} → Products	6 × 10 ⁶	[41]
R15	HCO ₃ ⁻ + HO [•] → CO ₃ ^{•-} + H ₂ O	8.5 × 10 ⁶	[23]
R16	HCO ₃ ⁻ + SO ₄ ^{•-} → HCO ₃ + SO ₄ ²⁻	2.8 × 10 ⁶	[42]
R17	Cl ⁻ + HO [•] → ClOH ^{•-}	4.3 × 10 ⁹	[23]
R18	ClOH ^{•-} + H ⁺ → Cl [•] + H ₂ O	3.0 × 10 ¹⁰	[43]
R19	ClOH ^{•-} + Cl ⁻ → Cl ₂ ^{•-} + OH ⁻	1.0 × 10 ⁵	[23]
R20	Cl ⁻ + SO ₄ ^{•-} → Cl [•] + SO ₄ ²⁻	3.1 × 10 ⁸	[44]
R21	Cl [•] + H ₂ O → H ⁺ + HO [•] + Cl ⁻	2.5 × 10 ⁵	[23]
R22	NO ₃ ⁻ + SO ₄ ^{•-} → NO ₃ + SO ₄ ²⁻	5 × 10 ⁴	[45]
R23	SO ₄ ^{•-} + HO [•] → SO ₄ ²⁻ + OH ⁻	3.5 × 10 ⁵	[43]
R24	SO ₄ ^{•-} + SO ₄ ^{•-} → S ₂ O ₈ ²⁻ + e _{aq} ⁻		[23]

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