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EFFECT OF INORGANIC IONS ON THE VACUUM-UV PHOTOLYSIS OF WATER

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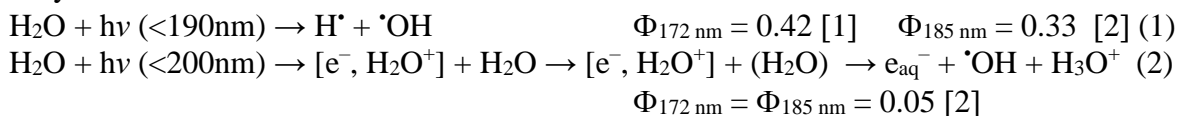
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Abstract

Vacuum-ultraviolet (VUV) photolysis is based on high-energy radiation ($\lambda < 200$ nm) where photons are absorbed by water and produce highly reactive species; primarily HO \cdot and H \cdot , and in smaller quantities e_{aq}⁻. VUV photolysis, due to the radicals formed, can efficiently transform and mineralize organic contaminants without any other additives. In this work, the effect of different inorganic ions (Cl⁻, NO₃⁻, HCO₃⁻), present in large amounts in wastewater, was investigated in the case of two different types of VUV light sources. The conventionally used low-pressure mercury-vapor lamp emits both 254 nm UV and 185 nm VUV photons and is widely used in water treatment for disinfection (254 nm) and producing high purity water (254/185 nm). The other applied light source was the Xe* excimer lamp, used mainly in the laboratory scale, emits quasi-monochromatic 172 nm VUV light. The effect of inorganic ions during VUV photolysis depends on the radical scavenging capacity, molar absorbance of ions, and the properties of the radicals and radical ions formed from them by VUV or UV photolysis (for UV/VUV_{185nm}), which is well reflected by the results presented.

Introduction

VUV photolysis is based solely on high-energy ($\lambda < 200$ nm) radiation. In the case of VUV photolysis the decomposition and mineralization of organic contaminants are initiated by the reactions with reactive hydroxyl (\cdot OH) and hydrogen radicals (\cdot H) formed during the VUV photolysis of water:



The quantum yield of the \cdot OH formation from water is slightly different at 172 nm (0.42) and 185 nm (0.33). A much more significant difference was reported between the absorption coefficients at these wavelengths. The absorption coefficient of water at 185 nm is 1.62 cm⁻¹ [3,4], while, at 172 nm, this value is 550 cm⁻¹. Consequently, the penetration depth of VUV radiation is about 11 millimeters for 185 nm, but no more than 0.04 mm for 172 nm [5,6].

It is generally accepted that water absorbed VUV photons exclusively due to its much higher concentration than dissolved substances. Most studies about the application of VUV photolysis to eliminate organic substances from aqueous solutions focus on reactions with primary radicals, mainly \cdot OH, and do not address the effect of matrix components; experiments are performed mainly in pure aqueous solutions. However, from the practical application point of view, the effect of matrix components must be considered. Moreover, according to recent literature [7], some inorganic ions have significant absorption in the VUV wavelength range, and their molar absorbance highly exceeds that of water. Thus, competition can occur between the inorganic ions and water for the high-energy photons. By acting as a radical scavenger, inorganic ions may also reduce the efficiency of VUV photolysis. Some data about the molar absorbance of inorganic ions at 185 nm were reported, but no data about the molar absorbance of inorganic ions at 172 nm.

This study aims to investigate the effect of various inorganic ions (NO_3^- , Cl^- , HCO_3^-) present in relatively high concentrations in biologically treated wastewater. This work used two types of VUV light sources: the conventionally used low-pressure mercury-vapor (LPM) lamp emitting both 254 nm UV and 185 nm VUV photons, and a Xe^* excimer lamp, emitting quasi-monochromatic 172 nm VUV light. For LPM lamp, the molar absorbance of inorganic ions not only at 185 nm but also at 254 nm must be considered.

Experimental

The Xe^* excimer lamp (130 mm long, 46 mm diameter, 20 W, from Radium XeradexTM) light source for VUV_{172nm} photolysis and LPM (GCL307T5WH, 227 mm arc length, 15 W, from LightTech) for UV/VUV_{185nm} photolysis were used. The VUV photon flux of the lamps was measured by methanol actinometry; the photon flux of 172 nm VUV light was $1.04 \times 10^{-5} \text{ mol}_{\text{photon}} \text{ s}^{-1}$, while the photon flux of 185 nm VUV light was $3.23 \times 10^{-7} \text{ mol}_{\text{photon}} \text{ s}^{-1}$. For the LPM lamp, the photon flux of 254 nm UV light was $\text{mol}_{\text{photon}} \text{ s}^{-1}$, determined by ferrioxalate actinometry. The H_2O_2 concentration was measured with a Spectroquant H_2O_2 cuvette test from Merck, using a Spectroquant Multy spectrophotometer (Merck, SN072188). All high purity salts, used for the investigation were purchased from Sigma-Aldrich, and their purity was $\geq 99.9\%$.

Results and discussion

During VUV photolysis of water, reactive $\cdot\text{OH}$ and $\cdot\text{H}$ are formed (1,2). In the absence of organic matter and dissolved O_2 ; H_2O_2 can form exclusively by the recombination of $\cdot\text{OH}$ radicals (3)[8]:



The dissolved O_2 changes the radical set, due to the addition to $\cdot\text{H}$, and reaction with e_{aq}^- :

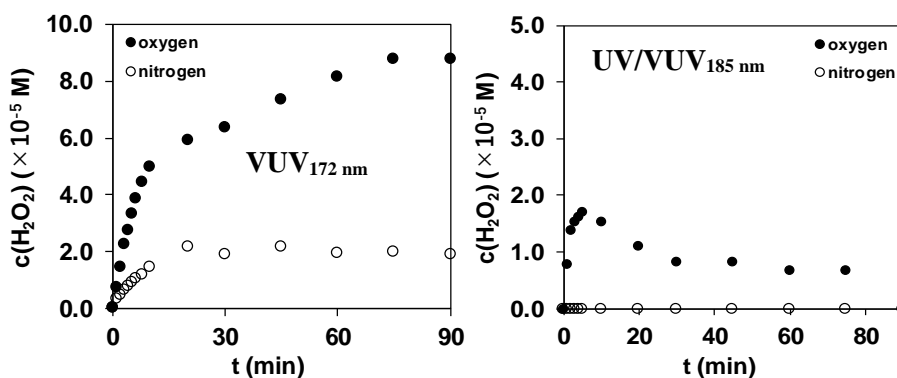
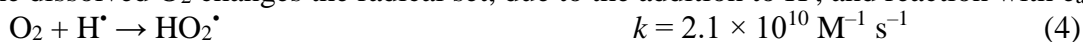
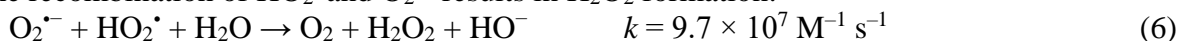


Fig. 1. The concentration of H_2O_2 as a function of time during UV/VUV_{185nm} and VUV_{172nm} photolysis of pure water

The recombination of $\text{HO}_2\cdot$ and $\text{O}_2^{\cdot-}$ results in H_2O_2 formation:

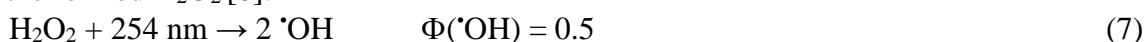


Consequently, dissolved O_2 significantly increases the rate of H_2O_2 formation, partly by inhibiting the recombination of $\cdot\text{H}$ and $\cdot\text{OH}$ radicals and mainly by the formation of $\text{HO}_2\cdot$ and $\text{O}_2^{\cdot-}$. The pH is also a key factor because it determines the concentration ratio of $\text{O}_2^{\cdot-}$ and $\text{HO}_2\cdot$ ($\text{pK}_a = 4.8$ [9]).

Table 1: Molar absorbance, concentration, relative absorbed photons, the equilibrium concentration of H₂O₂, and its initial (r₀) and relative formation rate (r₀/r₀^{ref}, where r₀^{ref} is the formation rate of H₂O₂ determined in pure water)

	c ₀ (M)	ε _{185nm} (M ⁻¹ cm ⁻¹)	185 nm photons absorbed (%)	UV/VUV _{185nm}			VUV _{172nm}		
				r ₀ (×10 ⁻⁸ mol/s)	r ₀ /r ₀ ^{ref}	c _{eq} ^{UV/VUV} (×10 ⁻⁵ M)	r ₀ (×10 ⁻⁸ mol/s)	r ₀ /r ₀ ^{re} _f	c _{eq} ^{VUV} (×10 ⁻⁵ M)
pure water	55.50	1.62	100	5.2	–	0.68	24.7	–	8.54
Cl ⁻	2.82×10 ⁻⁴	2791	0.9	4.4	0.85	0.63	23.5	0.95	7.44
Cl ⁻	3.40×10 ⁻³		9.5	2.0	0.39	0.49	9.3	0.38	3.73
NO ₃ ⁻	2.42×10 ⁻⁴	5000	1.3	0.93	0.18	0.34	5.9	0.24	5.48
NO ₃ ⁻	1.60×10 ⁻³		8.2	0.38	0.07	0.83	3.3	0.13	2.39
HCO ₃ ⁻	3.69×10 ⁻³	269	1.1	3.3	0.64	0.16	8.4	0.34	8.81
HCO ₃ ⁻	8.60×10 ⁻³		2.5	2.6	0.51	0.18	7.7	0.31	8.88

For VUV_{172nm} photolysis, the H₂O₂ concentration changes according to a saturation curve as expected. Both equilibrium concentration and the formation rate determined in O₂-saturated solution exceeded that in O₂-free solution (Fig. 1.). For UV/VUV_{185nm} photolysis, the equilibrium concentration was reached after a maximum value (Fig. 1.), and no H₂O₂ formation was in the O₂-free solution. This kind of time dependence of H₂O₂ concentration is probably due to the additive effect of 254 nm UV light, which causes the photochemical decomposition of the formed H₂O₂ [8]:



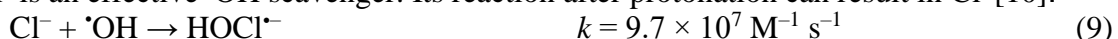
The reaction between H₂O₂ and ·OH consumes ·OH and produce HO₂· [8]:



The equilibrium concentration of H₂O₂ is more than ten times higher in the case of excimer lamp due to the much higher photon flux and slightly higher quantum yield of the ·OH formation. However, probably the combination of primary radicals (H· and ·OH) is more pronounced in this case due to the extremely high radical concentration within the thin (0.04 mm) photoreaction zone.

The concentration of Cl⁻, NO₃⁻, and HCO₃⁻ in biologically treated domestic wastewater is around 3.4×10⁻³ M, 2.4×10⁻⁴ M, and 8.6×10⁻³ M, respectively. In this study, the effect of these anions on H₂O₂ formation was investigated. Two concentration levels were used; one of them was set close to the concentrations of the given ions in the biologically treated water. The other concentration was set to the value where the inorganic ion absorbs between 1% and 10% of the VUV photon.

The Cl⁻ is an effective ·OH scavenger. Its reaction after protonation can result in Cl· [10]:



The direct VUV photolysis of Cl⁻ most probably also result in Cl· and e_{aq}⁻ (7) [1]:



In the presence of O₂ the reaction with e_{aq}⁻ can enhance the H₂O₂ formation via O₂^{·-}. Moreover, in the case of LPM lamp, the direct UV photolysis can cause the dissociation of the HOCl, which is the recombination product of Cl· and ·OH. Thus, the effect of Cl⁻ is quite complex and not easily interpreted.

The negative effect of Cl⁻ was observed on the equilibrium concentration of H₂O₂ at its higher concentration only in the case of VUV_{172nm} photolysis (Fig. 1.). However, in the case of

UV/VUV_{185nm}, the negative effect is mainly observed at the beginning of the kinetic curve; the equilibrium concentration changes only slightly.

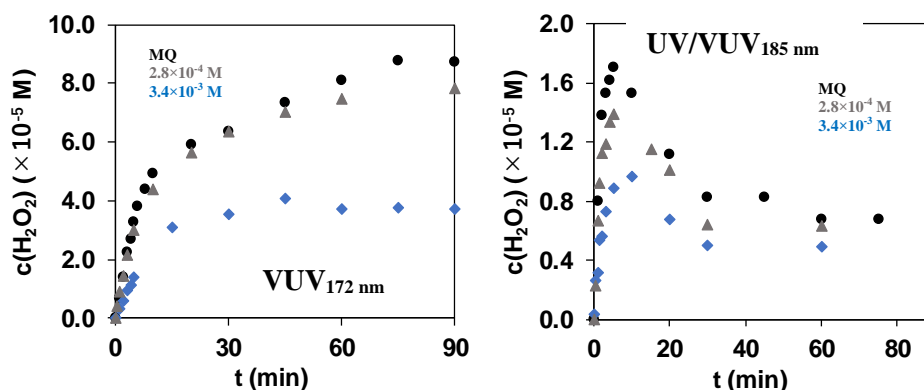


Fig. 2. Effect of Cl^- on the H_2O_2 formation during UV/VUV_{185nm} and VUV_{172nm} photolysis

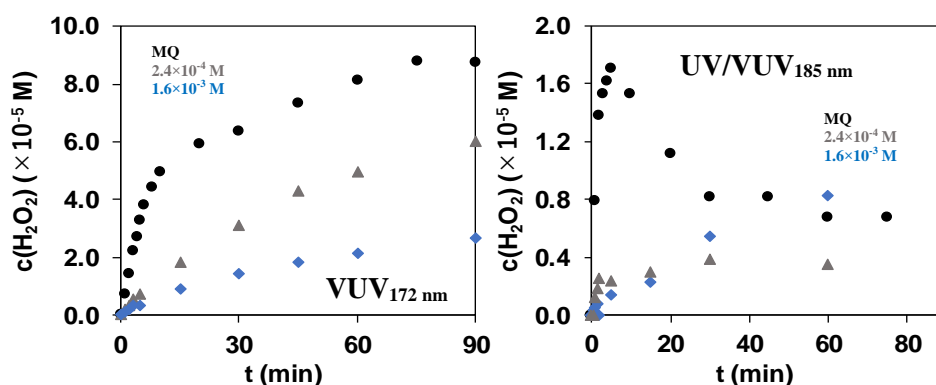
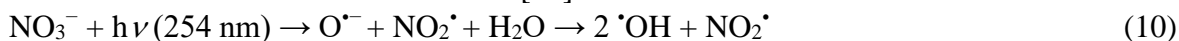


Fig. 3. Effect of NO_3^- on the H_2O_2 formation during UV/VUV_{185nm} and VUV_{172nm} photolysis

Gonzalez and Braun [11] investigated the VUV photolysis of NO_3^- and NO_2^- . The primary species induced a series of reactions partially depleting NO_2^- and NO_3^- . Transformation rates depended on the presence of O_2 , and NO_3^- , NO_2^- , peroxyxynitrite, and N_2O were identified as reaction products after irradiation of NO_2^- or NO_3^- in aqueous solutions. A reaction mechanism was proposed, where NO_2^\cdot and NO^\cdot are key intermediates and include many redox reactions and reaction equilibria. The formed NO_2^- react fast with $\cdot OH$ [11]:



In the case of LPM lamp the UV light must have a significant role besides VUV. The NO_3^- absorb 254 nm UV photons ($3.51 \text{ M}^{-1} \text{ cm}^{-1}$), and its UV photolysis (10) increase the amount of $\cdot OH$ and thus the concentration of H_2O_2 [11].



In the case of VUV_{172nm} photolysis, the formation rate and the equilibrium concentration of H_2O_2 significantly decreased with NO_3^- concentration. This can be explained by the NO_2^- formation and its reaction with $\cdot OH$ (8,9). The absorption of VUV photons also has a significant contribution to the inhibition of H_2O_2 formation. In the case of UV/VUV_{185nm} photolysis, the lower NO_3^- concentration has a negative, while the higher NO_3^- concentration has a positive effect on the equilibrium concentration of H_2O_2 , which can be interpreted by the enhanced $\cdot OH$ formation due to direct UV photolysis of NO_3^- (10).

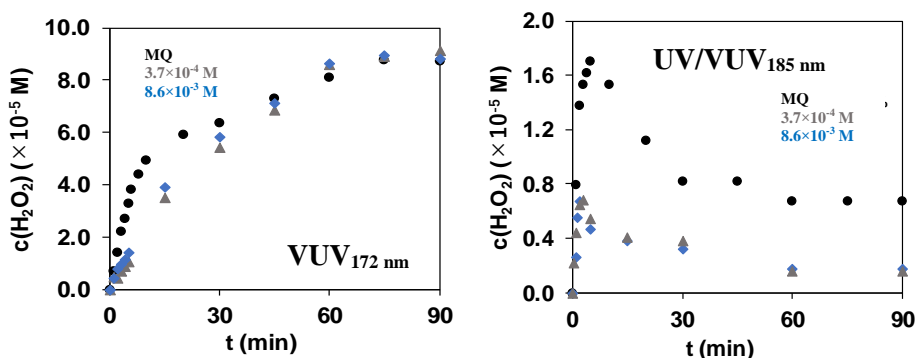


Fig. 4. Effect of HCO_3^- on the H_2O_2 formation during $\text{UV/VUV}_{185\text{nm}}$ and $\text{VUV}_{172\text{nm}}$ photolysis

HCO_3^- significantly reduced the initial formation rate of H_2O_2 . HCO_3^- did not affect the equilibrium concentration during $\text{VUV}_{172\text{nm}}$ photolysis but strongly decreased that in the case of $\text{UV/VUV}_{185\text{nm}}$ photolysis. The initial concentration of HCO_3^- has no significant effect in both cases. The different behavior can be explained by the significantly different $\cdot\text{OH}$ concentrations and the presence of UV light.

Conclusion

The effect of inorganic ions depends on their radical scavenging capacity, molar absorbance in VUV range, and the properties of the radicals and radical ions formed from them by VUV photolysis and/or UV photolysis (for $\text{UV/VUV}_{185\text{nm}}$). This work represents the significant difference between Cl^- , NO_3^- and HCO_3^- on the H_2O_2 formation, in the application of high intensity 172 nm VUV and low intensity 185nm VUV radiation. Proper interpretation of the experimental results requires further investigation.

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