

*25th International Symposium on Analytical and Environmental Problems***UV AND UV/VUV PHOTOLYSIS OF SULFAMETHAZINE****Ilaria Minzini¹, Máté Náfrádi², Luca, Farkas², Dalma Fuderer², Tünde Alapi²**¹*University of Padova, Department of Chemical Sciences, Via Marzolo, 1-35131, Padova, Italy*²*Department of Inorganic and Analytical Chemistry, University of Szeged, H-6720 Szeged, Dóm tér 7, Hungary
e-mail: alapi@chem.u-szeged.hu***Abstract**

In this work, UV and UV/VUV photolysis of sulfamethazine was investigated. Sulfamethazine is one of the most often used antibiotic, which can be detected in soils and surface water. The applied light sources were low-pressure mercury vapour lamps having identical geometry and electric parameters. One of the light sources emits only 254 nm UV light, while the other one emits both 254 nm UV and 185 nm VUV light.

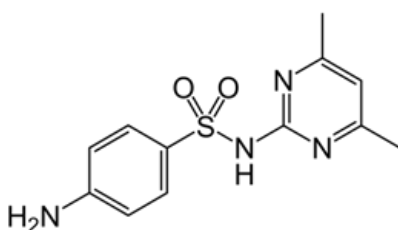
Both UV and UV/VUV photolysis were found to be effective in the transformation of sulfamethazine, but COD decrease was observed only in the presence of VUV light. In parallel with the transformation of sulfamethazine, H₂O₂ formation was detected. Its concentration reached higher value in the case of UV/VUV than in UV radiation.

Spectrophotometric measurements suggested that dissolved oxygen has effect on the formed intermediates in both UV and UV/VUV photolysis.

Transformation rates were determined in purified wastewater and tap water and compared to the values determined in Milli-Q water. Results showed that these mild matrices decreased the transformation rates in both cases. The inhibition effect is more pronounced in the case of UV photolysis.

Introduction

Antibiotics are a main and essential resource for the treatment of multiple types of infectious diseases, both in humans and animals. However, in recent years its widespread use, both to treat diseases and to promote growth the efficiency of food has generated serious concerns, mainly due to the increase in the diversity and dispersion of organisms resistant to these compounds. The amount of antibiotics sold for animals destined to food is approximately four times greater than for human use, whereas the world consumption of antibiotics is estimated an increase of 67% for the year 2030. Among antibiotics, sulfonamides are one of the most widely used in veterinary medicine. In 2014, sulfonamides were the third group of veterinary antibiotics most used in Europe, reaching 11% of the total sale of antibiotics. Its extensive use is due to their broad spectrum against most Gram-positive organisms and many Gram-negative organisms. [1,2]

**Figure 1:** Chemical structure of sulfamethazine

Sulfonamides are poorly absorbed on soils. In the specific case of sulfonamides, they are considered the most mobile antibiotics, and easily transported to water bodies. In fact, these compounds are frequently detected in surface waters, groundwater and in different types of crops. Therefore, the study of the degradation of sulfonamides, both chemical and biological, is crucial to establish the environmental impact of these compounds.

Experimental

Two low-pressure mercury vapour (LP) lamps (GCL307T5/CELL and GCL307T5VH/CELL, 227 mm arc length, both produced by LightTech) were used for UV (254 nm) and UV/VUV185 nm (254 nm/185 nm) irradiations. The parameters (electrical power 15 W and UVC-flux power 4.3 W) of both lamps were the same. The envelope of the UV lamp emitting at 254 nm was made of commercial quartz, while the UV/VUV185 nm lamp's envelope was made of synthetic quartz to be able to transmit the VUV185 nm photons. The flux of 254 nm photons ($5.97 \times 10^{-6} \text{ mol}_{\text{photon}} \text{ s}^{-1}$) of both lamps (UV and UV/VUV185 nm) was determined by ferrioxalate actinometry and found to be the same. The relative radiant power efficiency of the 185 nm VUV light is about 6 - 8% compared to the 254 nm emission.

The reactor geometrical parameters were adapted to the lamp's parameters: 30 mm internal diameter and 320 mm long. Thus the optical path length was 10 mm. The total volume of the treated solution was 500 mL. The aqueous solution was continuously bubbled with oxygen, air or nitrogen to set various dissolved oxygen concentration. The gas was bubbled through the solution using a gas dispersing system. Gas bubbling was started 20 min before the measurement.

Sulfamethazine (Sigma-Aldrich, 99.9%) solutions (500 mL) with initial concentration $1.0 \times 10^{-4} \text{ mol L}^{-1}$ was made in ultrapure MILLI-Q water (MILLIPORE Milli-Q Direct 8/16).

Separation of the aromatic components in the treated solutions was performed by Agilent 1100 type HPLC equipped with diode array detector (DAD) using LiChroCart® (250-4, RP-18, 5 μm) reverse-phase column.

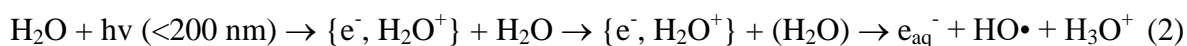
The COD measurements were performed using LCK1414 (Hach) colorimetric cuvette test with a 5.0-60.0 mg dm^{-3} measuring range and a DR2800 spectrophotometer. The concentration of H_2O_2 was measured with a cuvette test by Merck, with a 0.015 - 6.00 mg dm^{-3} measuring range. The NO_3^- concentration was determined by using colorimetric cuvette test provided by Merck, with a 0.4-111 mg dm^{-3} range. For the experiments in various matrices, drinking water from Szeged (Hungary), and industrial wastewater (purified with reverse osmosis) has been chosen. The main analytical parameters available for both matrices are compared in Table 1.

Table 1. Typical parameters of the used matrices that could affects water treatment

Parameters	Drinking water	Purified wastewater
pH	7.3	5.5
Conductivity ($\mu\text{S cm}^{-1}$)	482	21.9
COD (mg dm^{-3})	0.69	< 15
$\text{NH}_4\text{-N}$ (mg dm^{-3})	< 0.4	< 0.4
NO_3^- (mg dm^{-3})	< 0.7	1.5
Cl (mg dm^{-3})	8.75	-
TOC (mg dm^{-3})	8	-

Results and discussion

Comparing the transformation rate of sulfamethazine in UV and UV/VUV radiated solutions, we could observed that the presence of VUV strongly enhanced the transformation rate opposite that it has a quite low intensity comparing to the UV light intensity. In UV radiated solution the direct photolysis of sulfamethazine takes place, its efficiency depends on the molar absorbance of the target substance at 254 nm and quantum yield of its transformation. In VUV radiated aqueous solution, the 185 nm VUV light is absorbed by water and results in the formation of reactive species, namely hydrogen radical ($\text{H}\cdot$), hydroxyl radical ($\text{HO}\cdot$) and with lower yield hydrated electron (e_{aq}^-) [3-6].



$$\Phi(\text{e}_{\text{aq}}^-) = 0.045 - 0.05$$

Thus, the transformation of sulfamethazine in UV/VUV irradiated solution can take place by two different ways: direct UV photolysis and radical based reactions. The relative contribution of the radical based reaction seems to be similar to that of direct UV photolysis, since the transformation rate determined in UV/VUV irradiated solution is about two times higher than that determined in UV radiated one.

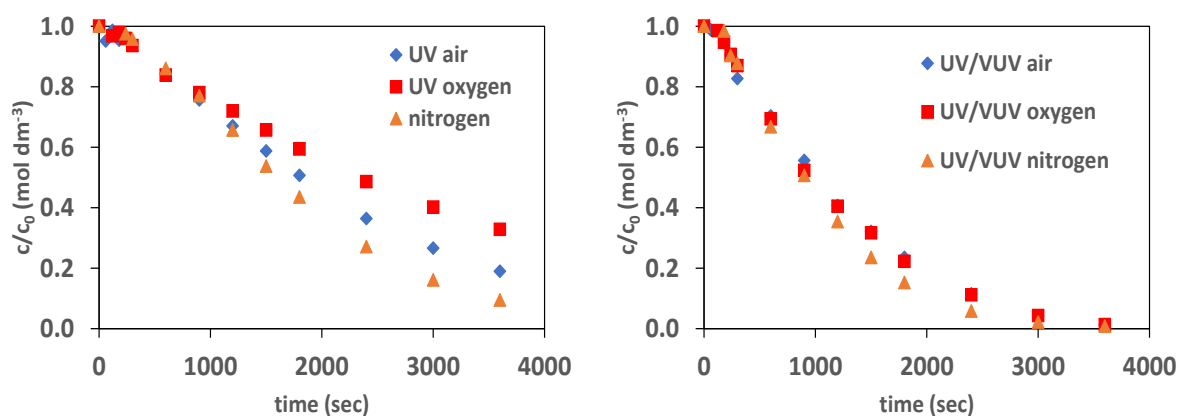


Figure 1. Relative concentration of sulfamethazine versus time of irradiation in the case of UV and UV/VUV photolysis

The effect of dissolved oxygen concentration on the transformation rate was investigated at 1.0×10^{-4} M initial concentration. The $\text{H}\cdot$ and e_{aq}^- , reacts with dissolved oxygen and produce by this way a less reactive $\text{HO}_2\cdot$ and $\text{O}_2^{\cdot-}$ radicals. Opposite that, highly reactive species are eliminated by this way, oxygen generally has a positive effect on the transformation of organic substances because of the formation of peroxy type radicals [4-8]. Although, a positive effect of oxygen was expected in both cases, using UV photolysis, the transformation rate was slightly decreased with increase of the dissolved oxygen concentration after the first period. This can be explained by the formation of various intermediates, having different absorption at 254 nm and able to competes for 254 nm photons with sulfamethazine. At the same time, the effect of dissolved oxygen in UV/VUV irradiated solution was found to be negligible. Probably the negative effect (elimination of $\text{H}\cdot$) and the positive effect (formation of peroxy radical) compensates each other's.

The changing of the absorbance of the solutions was followed by taking spectra of the samples. There was no difference between the spectra series taken in air and nitrogen saturated UV irradiated solutions, while both of the shape of spectra and the changing of absorbance at characteristic wavelengths showed significant difference in the case of UV/VUV photolysis, and depended on the dissolved oxygen concentration. The observed effect of dissolved oxygen is most probably can be explained by the possibility of peroxy radical formation.

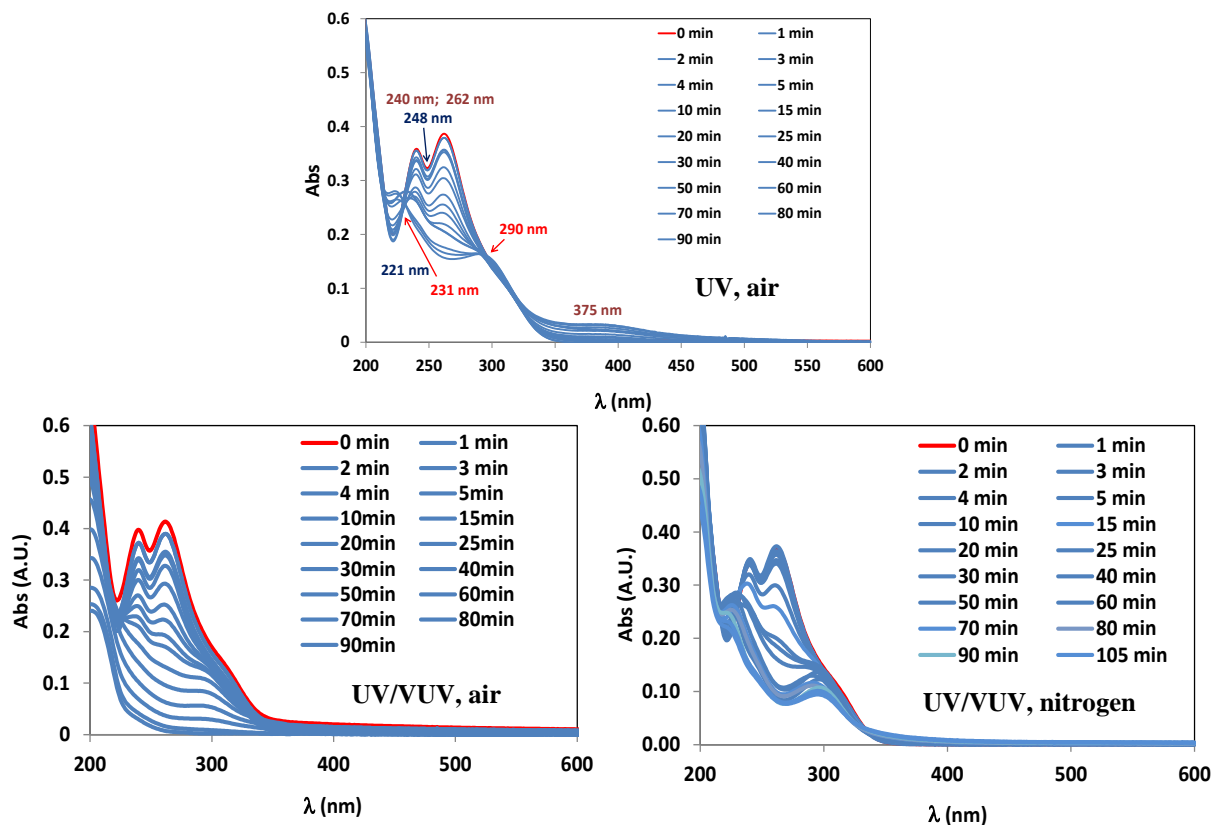


Figure 2. Spectra of sulfamethazine solutions radiated with UV and UV/VUV light

The pH decreased during both treatments, probably because of the formation of organic acids due to the fragmentation and oxidation processes. Although oxygen has no effect on the initial transformation rates, it has significant effect on the COD decrease and H_2O_2 formation. Using UV photolysis the decrease of the COD value is negligible, which suggests that hardly oxidizable intermediates form in this case. Using UV/VUV photolysis the COD decrease is no more than 25% during the time required for the transformation of sulfamethazine. After this period the COD decrease became faster and reached almost 70% by the end of treatment (120 min). Without dissolved oxygen there is no COD decrease proving the essential role of oxygen in the mineralization.

H_2O_2 forms only in the presence of dissolved oxygen. After a slight increase, the H_2O_2 concentration became constant in UV radiated solution. In the presence of VUV light the H_2O_2 concentration is higher and its formation is faster. H_2O_2 concentration reaches highest value, when sulfamethazine decomposed completely. After that decrease slowly and getting closer to the value detected in pure Milli-Q water.

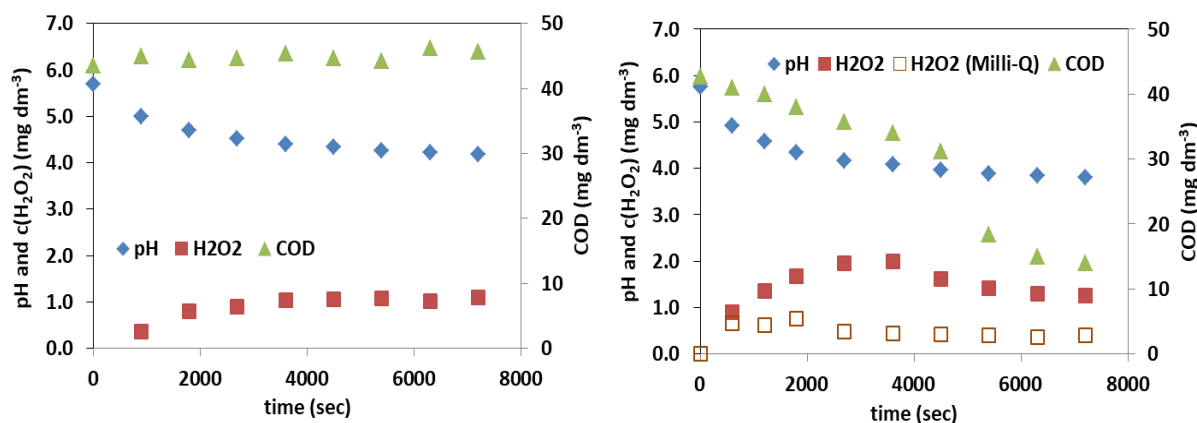


Figure 3. pH, COD and H₂O₂ concentration versus time of irradiation in aerated UV (A) and UV/VUV (B) radiated solutions

Transformation rates were determined in purified wastewater and tap water and compared to the values determined in Milli-Q water. Results showed that these mild matrices decreased the transformation rates in both cases. The inhibition effect is more pronounced in the case of UV photolysis.

Conclusion

- Both UV and UV/VUV photolysis effective for the elimination of sulfamethazine from aqueous solutions
- Dissolved oxygen has no significant effect on the transformation rate
- VUV light having low intensity highly increase the transformation rate
- COD decrease can be observed only in the case of combination UV and VUV photolysis

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References

- [1] I.T. Carvalho, L. Santos, *Environ. Int.* 2016. 94, 736–757.
- [2] M. Biošić, M. Mitrevski, S. Babić, *Environ. Sci. Pollut. Res.* 2017. 24, 9802–9812.
- [3] M.C. Gonzalez, E. Oliveros, M. Worner and A. Braun *J Photochem and Photobiol C: 5* (3), 225–246. (2004)
- [4] T. Oppenländer: *Vacuum-UV Oxidation, The H₂O-VUV AOP*, in book *Photochemical Purification of water and air*, Wiley-VCH, 2003
- [5] T. Alapi, K. Schrantz, E. Arany, Zs. Kozmér; Ed.: Mihaela I. Stefan, *Advanced oxidation processes for water treatment : fundamentals and applications*. IWA, 2018
- [6] G. Heit, A. Neuner, P.-Y. Saugy, A. M. Braun; *J. Phys. Chem. A* 1998, 102, 5551-5561
- [7] E. J. Hart, M. Anbar; *Journal of Molecular Structure*, 1970, 9, p. 486-486
- [8] S. Al-Gharabli, P. Engeßer, D. Gera, S. Klein, T. Oppenlander, *Chemosphere*, 2016, 144, 811-5