INHOMOGENITY OF THE 172 nm VUV LIGHT IRRADIATED AQUEOUS SOLUTIONS

Luca Farkas[1], Gábor Peintler[2], Thomas Oppenländer[3], Tünde Alapi[1]

[1]Department of Inorganic and Analytical Chemistry, University of Szeged, H-6720 Szeged, Dóm tér 7, Hungary
[2]Department of Physical Chemistry and Materials Sciences, University of Szeged, H-6720 Szeged, Rerrich Béla tér 1, Hungary
[3]Faculty of Medical and Life Sciences, University of Furtwangen, Villingen-Schwenningen, Jakob-Kienzle-Straße 17. 78054 VS-Schwenningen
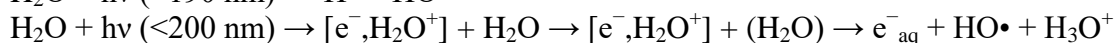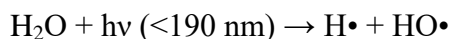*e-mail: alapi@chem.u-szeged.hu*

Abstract

Vacuum ultraviolet (VUV) photolysis is one of the Advanced Oxidation Processes (AOPs) for the elimination of trace pollutants from water and air. The ultraviolet (UV) radiation below 200 nm is named VUV, because it is strongly absorbed by air. Using VUV photolysis reactive species ($\bullet$H and $\bullet$OH) can be generated directly from water without addition of any chemicals. Consequently VUV radiation is used for producing ultrapure water and often investigated as a possible method for elimination of organic pollutants from water. In the case of VUV photolysis low pressure mercury vapor lamp (emits both 254 nm UV and 185 nm VUV photons) or Xe excimer lamp (emits both 172 nm VUV photons) can be applied as light source. In latter case the absorption coefficient of water at 172 nm is 550 cm^{-1}. Consequently, the penetration depth of VUV radiation is very small, only 0.04 mm. In this work we have investigated the effect of inhomogenity caused within this very thin VUV irradiated layer on the concentration of the primary formed reactive species, such as $\bullet$H and $\bullet$OH, using model calculation.

Introduction

Advanced Oxidation Processes (AOPs) are based on hydroxyl radical ($\bullet$OH) initiated transformations. One of the possibilities of the $\bullet$OH generation is the irradiation of water with light having shorther wavelength than 190 nm. Generally low-pressure mercury vapor lamp is used as light source when VUV photolysis is applied to reduce the TOC content of purified water and produce ultrapure, high quality water. Another possible light source is the Xe excimer lamp which emits quasi-monochromatic light with maximum at 172 nm. There are several benefits of this excimer lamp, such as high average specific power radiation, high energy of emitting photons, quasi-monochromatic radiation, high spectral power density, absence of visible and IR radiation, low heating of radiating surface (cold lamps), no fixed geometry, no warm up time etc. The availability of multiple-wavelength UV radiation by simultaneous excitation of several kinds of working excimer molecules is also possible. Finally, excimer lamps based on noble gases are non-hazardous and are much more environmentally friendly than mercury vapor lamps. [1-4]

In VUV irradiated aqueous systems the first step is the excitation of water molecules. Absorption of the VUV radiation results in the homolysis or photochemical ionization of water molecules. The value of quantum yield of ionization (0.05) is much smaller than the quantum yield of homolysis (0.42):

$H_2O + h\nu$ (<190 nm) $\rightarrow H\bullet + HO\bullet$
$H_2O + h\nu$ (<200 nm) $\rightarrow [e^-, H_2O^+] + H_2O \rightarrow [e^-, H_2O^+] + (H_2O) \rightarrow e^-_{aq} + HO\bullet + H_3O^+$

Despite the many advantages of this technology and the promising results obtained through lab scale studies, there are still some factors that stymie the wide scale application of the VUV reactors for water treatment. Lack of proper model and simulation tool for predicting and analyzing the performance of VUV irradiated systems is among the key factors hindering their practical implementation. Model calculations generally do not take care about the effect of inhomogenity caused by the extremely short penetration depth of 172 nm VUV light.

Results and discussion

The first step of the present work was the collection of the kinetic data reported and used in the published papers related to the 172 nm irradiated solutions. The origin of these data were also checked and compared. The rate constants of the recombination of •H (resulting in H_2) and •OH (resulting in H_2O_2) were originated from experimental data obtained of gamma irradiated system. Opposite 172 nm irradiated water, the intensity of gamma photons decreases only with 10% in a few cm thin water layer. Thus gamma irradiated solution can be defined as a „homogen system", while the 172 nm irradiated one is an „inhomogen system".

1. Table. Rate constants of the recombination reactions of •H and •OH radicals

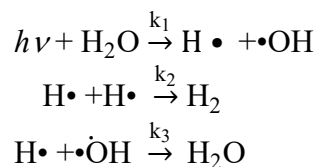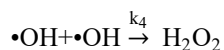| Ref.	k_{H+OH} $(M^{-1}s^{-1})$	k_{H+H} $(M^{-1}s^{-1})$	k_{OH+OH} $(M^{-1}s^{-1})$	reaction partner	method for radical generation
[10]	$1,00 \cdot 10^{10}$			Fe(II)/Ce(III), H_2O_2, H_2SO_4	
[11]		$5,00 \cdot 10^9$		H_2O_2, Fe(II), kénsav	Van Slyke
[12]			$8,20 \cdot 10^9$		
[4]	$1,2 \cdot 10^{10}$ *	$6,00 \cdot 10^9$	$6,00 \cdot 10^9$ *	H_2O_2, H_2O, H_2SO_4, Fe(III)	Van De Graaff
[13]		$1,50 \cdot 10^{10}$ *		Fe(II)	Van De Graaff
[5]	$7,00 \cdot 10^9$ **		$5,25 \cdot 10^9$**		
[14]			$6,30 \cdot 10^9$	Ferro-cianide	Osram Xe-excimer lamp
[15]		$1,25 \cdot 10^{10}$			Osram Xe-excimer lamp
[9]	$1,04 \cdot 10^9$**	$7,75 \cdot 10^9$**	$8,70 \cdot 10^9$**		

* experimental data (relative method)
** experimental data (absolute method)

The basic of the model calculation using Octave [17] program were the followings:

1. Generally about 40 various reactions take place in a VUV irradiated water. In this work we used a simplified reaction system containing only the following four main steps:

$$h\nu + H_2O \xrightarrow{k_1} H \bullet + \bullet OH$$
$$H\bullet + H\bullet \xrightarrow{k_2} H_2$$
$$H\bullet + \bullet\dot{O}H \xrightarrow{k_3} H_2O$$

$$\cdot OH + \cdot OH \overset{k_4}{\rightarrow} H_2O_2$$

2. The reaction rate constants were the average of the rate constants reported in **Table 1** ($k(h\nu) = 9\times10^{13}$ M^{-1}s^{-1}, $k(\cdot H + \cdot H) = 1\times10^{10}$ M^{-1}s^{-1}, $k(\cdot H + \cdot OH) = 1.5\times10^{10}$ M^{-1}s^{-1}, $k(\cdot OH + \cdot OH) = 6\times10^{9}$ M^{-1}s^{-1}).

3. The actual concentration of photon was calculated via Lambert-Beer law, using the value of the absorption coefficient of water at 172 nm 550 cm^{-1} [16].

4. The diffusion constants of various species ($D(\cdot H)=8\cdot10^{-5}$ cm^{2}s^{-1}, $D(\cdot OH)=2\cdot10^{-5}$ m^{2}s^{-1}, $D(H_2)= 8\cdot10^{-5}$ m^{2}s^{-1}, $D(H_2O_2)=1{,}5\cdot10^{-5}$ m^{2}s^{-1}) were also incorporated of the model.

5. The total thin of the treated water layer was 0.2 cm, which was divided into 950 cells. In each cells, the intensity of the VUV light and concentration of primary radicals were supposed to be constant and homogenous. Near the lamp, the cells size were very small (40 nm). Farther from the wall of the light source cells size were bigger and the the biggest one were 200 nm.
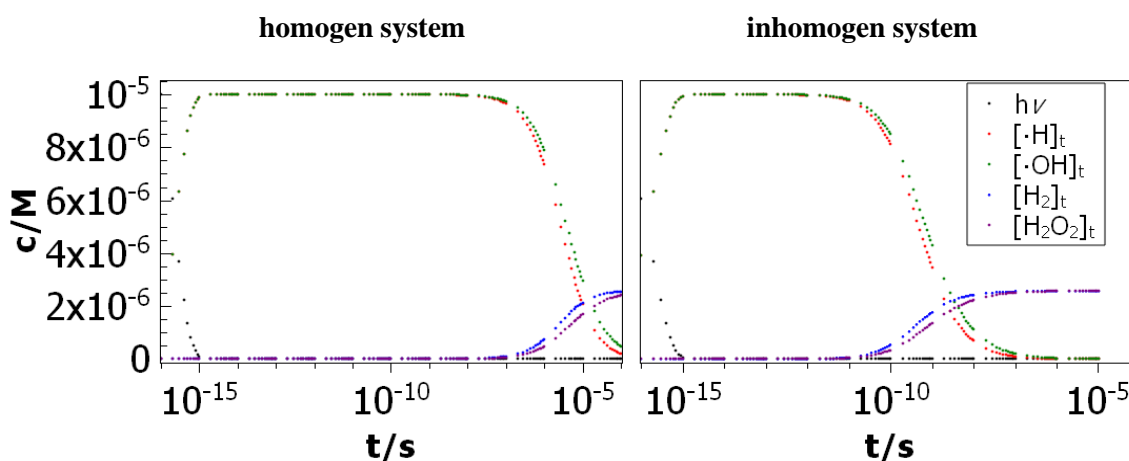

Figure 1. The time dependence of the various radicals and their recombination products in homogen and inhomogen system. Data used for modeling: $k(h\nu)=9\cdot10^{13}$ M^{-1}s^{-1}, $k(\dot{H}+\dot{H})=1\cdot10^{10}$ M^{-1}s^{-1}, $k(\dot{H}+\dot{O}H)=1{,}5\cdot10^{10}$ M^{-1}s^{-1}, $k(\dot{O}H+\dot{O}H)=6\cdot10^{9}$ M^{-1}s^{-1}, $D(\dot{H})=8\cdot10^{-5}$ cm^{2}s^{-1}, $D(\dot{O}H)=2\cdot10^{-5}$ m^{2}s^{-1}, $D(H_2)= 8\cdot10^{-5}$ m^{2}s^{-1}, $D(H_2O_2)=1{,}5\cdot10^{-5}$ m^{2}s^{-1}, $c_0(h\nu)= 1\cdot10^{-5}$ M, $c_0(H_2O)= 55{,}5$ M.

The results obtained in the case of homogen and inhomogen system are presented on Figure 1. The time dependence of the various radicals and their recombination products in the two system show, that inhomogenity has significant effect on the time scale. In homogen system the recombination of primary formed radicals take place within 10^{-5} sec. In the case of simulation obtained this time is decreased with 4 orders because of the reactions take place only in a very small part of the total volume of the reaction system. Within this photorection zone the radical concentration is much higher than in the homogen system.
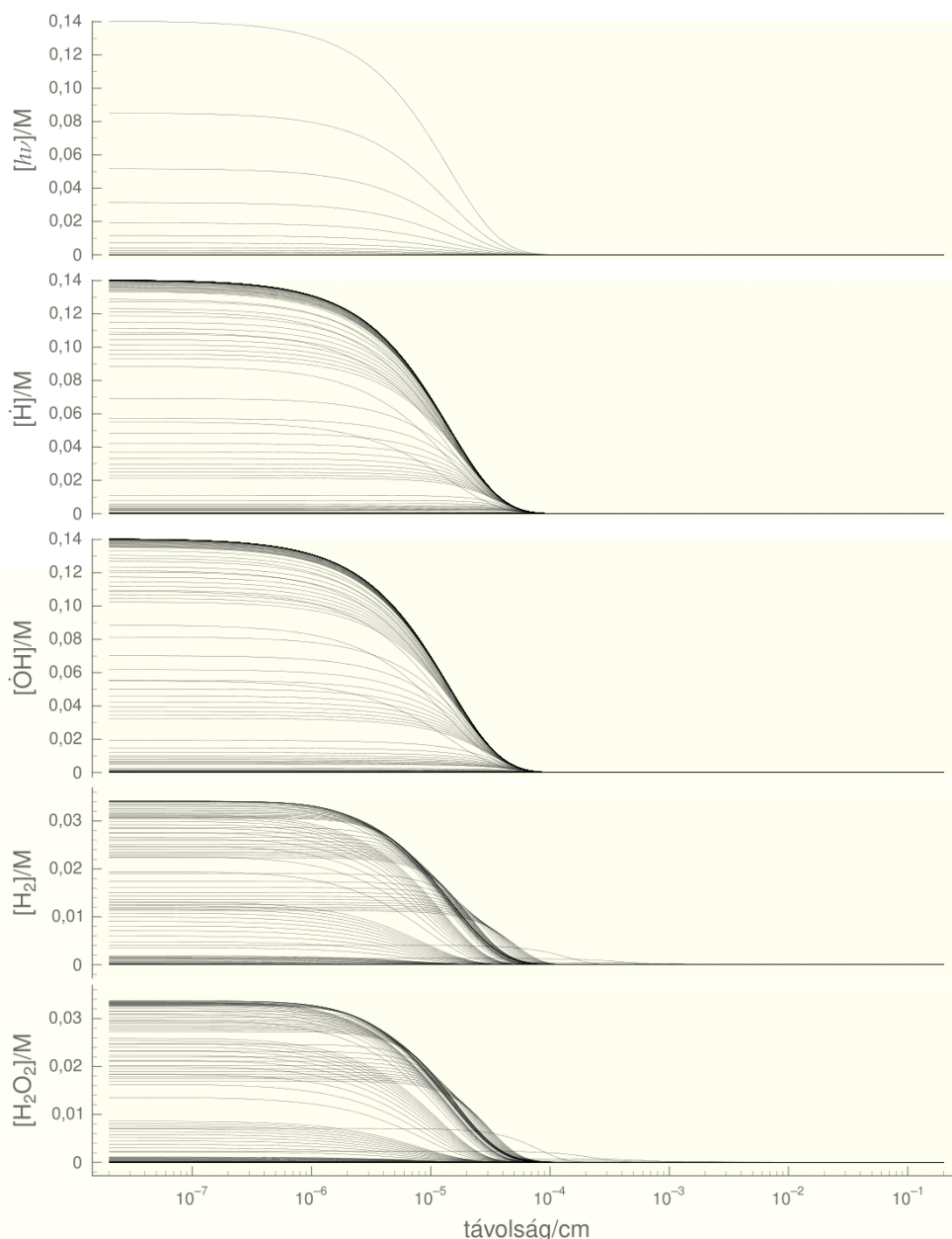
2. Figure Concentration of primery radicals and their recombination products versus the
distance from the light source, taking into consideration the inhomogenity.

Using the model taking into consideration the inhomogenity of the VUV irradiated
aqueous solution, the concentration of the primary radicals and their recombination products
were calculated (Figure 2.). Radicals disappear from the system within the distance, which
can be reached by photons. The concentration of recombination products (H_2 and H_2O_2)
decrease and increase with the time and finally reach a constant value. The effect of diffusion
can be observed on the curves related to H_2 and H_2O_2 concentration versus the distance from
the wall of the lamp and their concentration is much lower than the radical concentration.

Conclusion
- Inhomogenity must be incorporated into the model calculation in the case of 172 nm
  irradiated aqueous solutions

Acknowledgements

References

[1] T. Oppenländer: Vacum-UV Oxidation, The H_2O-VUV AOP, in book Photochemical Purification of water and air, Viley-VCH, 2003

[2] Gonzalez M. C., Oliveros E., Worner M. and Braun A. *J Photochem and Photobiol C:* **5** (3), 225–246. (2004)

[3] T. Alapi, K. Schrantz, E. Arany, Zs. Kozmér: Vacuum-UV radiation driven processes (Chapter 5), Advanced Oxidation Processes for Water treatment: Fundamentals and applications Ed.: Mihaela I. Stefan, IWA, 2017.

[4] J.K. Thomas, The Journal of Physical Chemistry, 1963. 67(12) 2593-2595.

[5] J.K. Thomas, Transactions of the Faraday Society, 1965. 6 702.

[9] P. Pagsberg, P. The Journal of Physical Chemistry, 1969. 73(4) 1029-1038.

[10] J. Rotblat and H.C. Sutton Proc. of the Royal Soc A: Math. Phys. and Eng. Sci., 1960. 255(1283) 490-508.

[11] J.K. Thomas and E.J. Hart Radiation Research, 1962. 17(3): p. 408.

[12] H.A. Schwarz The J. of Physical Chemistry, 1962. 66(2) 255-262.

[13] H.A.Schwarz, H.A., The J. of Physical Chemistry, 1963. 67(12): p. 2827-2830.

[14] J. Rabani and M.S. Matheson The J. of Physical Chemistry, 1966. 70(3) 761-769.

[15] P.Y. Feng The J. of Physical Chemistry, 1970. 74(6) 1221-1227.

[16] J.L. Weeks, G.M.A.C. Meaburn, S. Gordon Radiation Research, 1963. 19(3): p. 559.

[17] J.W. Eaton, D. Bateman, S. Hauberg, R. Wehbring (2016). GNU Octave version 4.2.0 manual: a high-level interactive language for numerical computations. URL http://www.gnu.org/software/octave/doc/interpreter/