Spectrophotometry and spectrofluorimetry to analyze the destruction of pharmaceuticals during wastewater treatment by enhanced oxidation

Liudmila Molodkina¹, and Diana Tryastsina² and Alexey Cheremisin³

¹Peter the Great St. Petersburg Polytechnic University, St. Petersburg, Russian Federation
²“GRADISS” Ltd., St. Petersburg, Russian Federation
³All Russian Research Institute of Phytopathology, 143050, Moscow Region, Russia

Abstract. The work is devoted to the treatment of wastewater from pharmaceuticals by enhanced oxidation. Some studies have shown the high degree and speed of pharmaceutical degradation under the action of a hydroxyl radical formed by the combined action of UV and H₂O₂ (enhanced oxidation, which was fully confirmed by a decrease in absorption in the UV spectrum. This paper shows that, unlike spectrophotometry, the spectrofluorimetry method can be used in the analyzing the process of destruction of hard-to-degrade pharmaceuticals. The object of the study was synthetic alkaloid vinpocetine, which has an indole core. Vinpocetine solutions were irradiated in a laboratory setup which included a TUV 30w / GTV low-pressure argon-mercury lamp (Philips) for 5–15 min, and also irradiated for 1-10 minutes after adding hydrogen peroxide at a concentration of 100 mg / L. The spectrophotometry method showed an increase (instead of a decrease) in the absorption spectra with an increase in the duration of UV irradiation. Under the same conditions, the spectrofluorimetry method recorded a decrease in the signal intensity in the registration and excitation spectra, and under enhanced oxidation, the appearance of new bands characteristic of the phenolic group.

1 Introduction

In recent decades, the pharmaceutical industry has been developing and people are consuming pharmaceuticals [1,2], which leads to an increase in their content in domestic wastewater [3-8]. So, the authors of paper [3] sought the identification of 22 pharmaceuticals in two secondary effluent wastewaters. Concentration of 11 pharmaceuticals was 0.15 ng/L – 413.03 ng/L that is higher then quantitation limit of liquid chromatography mass spectrometry method. The occurrence of antidepressants in sewage effluents has been demonstrated in [4-6].

* Corresponding author: molodkina.lm@mail.ru
Most of pharmaceutical preparations have a complex structure with aromatic rings, condensed aromatic fragments or heterocyclic, most of such preparations are hard-to-degrade. And many of them are persistent in conventional wastewater treatment plants [9,10]. In recent years, research on the treatment of containing pharmaceuticals wastewater has been actively conducted. A number of studies are devoted to enhanced oxidation processes, which are considered a highly competitive water treatment technology for the removal of high chemical stability organic pollutants [11-16]. For example, in [12] the kinetics of the pharmaceuticals oxidation by ozonation and enhanced oxidation was compared, and it was shown that the studied drugs reacted 2–3 times faster with hydroxyl radicals. In [14] it was shown for six preparations that the effectiveness of the process depends on the concentration of the preparations in wastewater and on the properties of the medium and correlates with a decrease in ultraviolet absorption at 254 nm. In [15], the three preparations showed a high degree and rate of their destruction under the action of a hydroxyl radical formed under the combined action of UV and H₂O₂. The destruction is fully confirmed by a decrease in absorption in the UV spectrum.

In spite of the fact that UV-visible spectrophotometric analysis of pharmaceuticals is currently widely used [17-19], it may be uninformative in the analysis of the processes of their enhanced oxidation. It should also take into account the potential of the method in registering by-products, since the removal of pharmaceuticals from wastewater using enhanced oxidation can lead to their formation [20].

The objective of the present paper was to compare the capabilities of the spectrophotometry and spectrofluorimetry methods in analyzing the process of destruction of hard-to-degrade pharmaceutical preparation vinpocetine by UV-radiation and enhanced oxidation (combined action of H₂O₂ and UV radiation).

2 Methods

The object of the study was synthetic alkaloid vinpocetine. Vinpocetine has an indole core, which determines its basic physicochemical properties (Fig. 1).

![Fig. 1. The structural formula of vinpocetine](image)

Water samples of vinpocetine were prepared from a solution for injection. A bicarbonate buffer solution, pH ~ 8, was used as a solvent. The final concentration of vinpocetine was 10–40 mg/L. Absorption spectra obtained on spectrophotometer SF-56 (OKB Spectr, Russia) were consistent with the results obtained in [21]. The luminescence excitation and registration spectra were obtained on a Fluorat-02-Panorama spectrofluorimeter (Lumex, Russia). Vinpocetine solutions were irradiated in a laboratory setup (used earlier [22]), which included a TUV 30w / GTV low-pressure argon-mercury lamp (Philips), a metal case, a control unit, a flowing quartz cuvette formed by coaxial cylinders, and the small table for standard 10 mm quartz cuvettes. At the cylindrical surface passing through the cuvettes centers the radiation power was 6 mW/cm².

The concentration of hydrogen peroxide in samples of vinpocetine was 100 mg/L.
The obtained excitation and registration luminescence spectra were corrected for the spectrum of the lamp, as well as for the absorption of the lamp input (into the cuvette) and the fluorescent output signal.

3 Results and Discussion

The results of UV irradiation of vinpocetine solutions in 10 mm cuvettes for 5-15 minutes were analyzed by spectrophotometry and spectofluorimetry. Fig. 2 shows that UV absorbance increases with increasing of exposure time in contrast to the decline recorded for a number of drugs [14,15].

Fig. 2. Absorption spectra of vinpocetine solutions (20 mg/l) at different duration of UV radiation, min: 1 – 0; 2 – 5; 3 – 10; 4 – 15

At the same time, spectrofluorimetric analysis reveals structural changes in the vinpocetine molecule, which manifest themselves in a sharp decrease in the fluorescence intensity in the registration spectrum at a wavelength of 345 nm, and the appearance of a band with a maximum of 300 nm (Fig. 3).

Fig. 3. Changes in the fluorescence registration spectrum with increasing of UV irradiation duration, min: 1 – 0; 2 – 1; 3 – 2; 4 – 5; 5 – 7; 6 – 10. λ_excl = 230 nm

The fluorescence intensity in the band with a maximum of 285 nm decreases slightly. The obtained changes are confirmed by the excitation spectra (Fig. 4).
Fig. 4. Dependences of the fluorescence intensity in the excitation spectra on the time of UV radiation, min: 1: Reg.285 nm, max length 216 nm (1), 286 nm (2); Reg.345 nm, max length 226 nm (3), 275 nm (4).

Much more significant changes are recorded by spectrofluorimetry with enhanced oxidation (combined action of H₂O₂ and UV radiation) (Fig. 5).

Fig. 5. Changes in the fluorescence registration spectrum due to enhanced oxidation. H₂O₂ concentration: 2–6 – 100 mg/l; Duration of UV radiation, min: 1,2 – 0; 3 – 1; 4 – 2; 5 – 5; 6 – 10. λ_exc. = 230 nm.

When H₂O₂ is added without UV radiation, the fluorescence registration spectrum of vinpocetine (curve 2) coincides with the initial registration spectrum (curve 1). With simultaneous action of H₂O₂ and UV irradiation, OH radicals are formed, that leads to the destruction of the vinpocetine molecule, which is accompanied by the appearance of a luminescence band with a maximum at 300 nm and a sharp increase (with an increase in the oxidation time) of the signal intensity (curves 3-6).

The changes in the signal at the maxima of the bands of the excitation spectra obtained during the registration of luminescence at wavelengths of 300 and 345 nm are shown in Fig. 6.
Fig. 6. Dependences of the fluorescence intensity in the excitation spectra on the time of UV radiation, min: Reg.300 nm, max length 220-226 nm (1), 273 nm (2); Reg.345 nm, max length 226 nm (3), 275-278 nm (4)

The appearance of a luminescence registration band with a maximum at a wavelength of 300 nm (Fig. 5), as well as luminescence excitation bands characteristic of the phenol group [23] (Fig. 6), can be caused by the conversion of the indole group to phenolic.

New oxidation products and free radicals derived from tryptophan (Trp) (indole group) oxidation using hydrogen peroxide and iron (II) system (Fenton reaction) were identified using mass spectrometry [24]. Dimer formation by cross-linking between two Trp radicals (Trp-Trp) was also noted. It is possible that an increase in the signal with increasing UV exposure time (in the presence of hydrogen peroxide) in the luminescence registration spectra at the wavelength of 345 nm (Fig. 5), as well as in the excitation bands (Fig. 6), indicates the formation of dimers.

Thus, the obtained luminescence registration and excitation spectra can demonstrate the complex process of the conversion of vinpocetine as a result of enhanced oxidation [25-2].

4 Conclusions

The results demonstrate significant changes in the structure of vinpocetine, both during prolonged UV irradiation (starting from 5 minutes) and during enhanced oxidation at a concentration of hydrogen peroxide of 100 mg/l and the duration of ultraviolet radiation, starting from 1 minute. It is shown the informativeness of the spectrofluorimetry method (in contrast to spectrophotometry) in registration of destruction of vinpocetine functional groups.

References

1. Van Der Aa, G.J. Kommer, J.E. Van Montfoort, J.F.M. Versteegh, Water Sci. Technol. 63 (4) 825 (2011)
2. A. de Wilt, K. van Gijn, T. Verhoek, A. Vergnes, M. Hoek, H. Rijnaarts, A. Langenhoff, Water Research 138, 97 (2018)
3. K. Manoli, L.M. Morrison, M.W. Sumarah, G. Nakhla, A.K. Ray, V.K. Sharma, Water Research 148, 272 (2019)
4. T. Vasskog, T. Anderssen, S. Pedersen-Bjergaard, R Kallenborn, E. Jensen, J. Chromatogr. A. 1185 194 (2008)
5. A. Lajeunesse, C. Gagnon, S. Sauvé, Anal Chem. 80 5325 (2008)
6. C.D. Metcalfe, S. Chu, C. Judt, H. Li, K.D. Oakes, M.R. Servos, D.M. Andrews, Environ Toxicol Chem. 29 79 (2010)
7. Mompelat, B. Le Bot, O. Thomas, Environ. Int., 35 (5) 803 (2009)
8. M. Sacher, S. Ehmann, C. Gabriel, H.-J. Graf, J. Brauch Environ. Monit., 10 (5) 664 (2008)
9. Rivera-Utrilla, M. Sánchez-Polo, M.Á. Ferro-García, G. Prados-Joya, R. Ocampo-Pérez, Chemosphere, 93 (7) 1268 (2013)
10. P. Verlicchi, M. Al Aukidy, E. Zambello, Sci. Total Environ., 429 123 (2012)
11. I. Oller, S. Malato, J.A. Sánchez-Pérez, Sci Total Environ, 409 4141 (2011)
12. M.M. Huber, S. Canonica, G.-Y. Park, U. von Gunten, Environ. Sci. Technol., 37(5) 1016 (2003)
13. M.N. Nemchenko, O.E. Lebedev, Water: Chemistry and Ecology, 6 30 (2011)
14. F. L Rosario-Ortiz, E.C. Wert, S. A. Snyder, Water Research, 44 1440 (2010)
15. N.A. Ivantsova, V.V. Emzhina, N.E. Kruchinina, A.I. Akhtiamova, Water: Chemistry and Ecology, 7 81 (2017)
16. Klavarioti, Environment international, 35(2) 402 (2008)
17. S. Gorog, Ultraviolet-Visible Spectrophotometry in Pharmaceutical Analysis. 1st Edition (CRC Press, 2017)
18. K. Parameswara, M.C. Rao, Int. J. Chem. Sci., 14(4) 2389 (2016)
19. J. Patel, G. Kevin, A. Patel, M. Raval., N. Sheth, Pharm Methods, 2(1) 36 (2011)
20. A. Lajeunesse, M. Blais, B. Barbeau, S. Sauvé, C. Gagnon, Chem Cent J., 7 15 (2013)
21. S.A. Boeva., V.P. Dzuba, A.I. Slivkin, J.A. Polkovnikova. Proceeding of Voronezh State University, Series: Chemistry. Biology. Pharmacy, 2 157 (2009)
22. E. Simonenko, A. Gomonov, N. Rolle, L. Molodkina, Procedia Engineering, 117 342 (2015)
23. E.A. Pernyakov The method of intrinsic protein luminescence. (Moskow, NAUKA, 2003)
24. M. R. M. Domingues, P. Domingues, A. Reis, C. Fonseca, F. M. L. Amado, A. J. V. Ferrer-Correia, J Am Soc Mass Spectrom, 14 406–416 (2003)
25. R. Davydyov, V. Antonov, D. Molodtsov, A. Cheremisin, V. Korablev, MATEC Web of Conference, 245 15002 (2018)
26. V.A. Lyapishev, V.Yu. Rud, M.S. Sokolov, A.V. Cheremisin, Proceedings of the 2018 IEEE International Conference on Electrical Engineering and Photonics, EExPolytech 2018. 8564387 292-294 (2018)
27. M.I. Natorkhin, A.V. Bobyl, A.V. Cheremisin, M.S. Sokolov, Journal of Physics: Conference Series, 1236(1) 012011 (2019)
28. V. Maslikov, E. Negulyaeva, A. Cheremisin, D. Molodsov, A. Stroganov, Solid State Phenomena, 871 199-207 (2016)