Гетерогенний фотокаталіз для селекційних нетипових антипсихотичних речовин з річкових вод

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Гетерогенний каталіз має величезний потенціал, оскільки його можна використовувати для знищення різноманітних небезпечних речовин у стічних водах. [1]. В сотанні роки з'явився новий тип забрудників у вигляді фармацевтичних відходів. Зростаюче занепокоїння у суспільній та науковій сфері стосовно цих речовин пов'язане з їхнім потенційним впливом на здоров'я людини та довкілля. [2]. Було підраховано, що у світі половина стічних вод фармацевтичних виробництв викидаться без жодної обробки. Це і пояснює важливість знаходження нових ефективних методів зменшення фармацевтичних відходів.

TiO_2 – найбільш поширений фотокаталізатор, тому що він нетоксичний, рентабельний, а також біологічно- та хімічно-інертний. Окрім цього, вивчення Сонця підтвердили, що вищезгаданий оксид металу ефективний у зниженні фармацевтичних відходів, оскільки зменшує витрати на використання ультрафіолетового випромінювання [3]. Дослідження шляхів усунення фармацевтичних відходів з використанням TiO_2, включає, але не обмежується дослідженням антибіотиків, регуляторів жирів, рентгеноконтрастних засобів, антиепілептиків та протизапальних засобів. [4].

Основною метою цього дослідження було оцінити рівень знищення оланзапіну під впливом змодельованого сонячного світла та ультрафіолетової радіації. Ми дослідили фотокаталітичне знищення оланзапіну у деіонізованій воді, а також у розчині зразків справжньої води. Зразки води для досліджень дули взяті з двох річок Польщі, а саме з річок Нарев та Мариха. Обидві вони знаходяться на сході Польщі , біля міста Білосток. Ефективність фотодеструкції та наявність можливих проміжних продуктів були вивчені з допомогою високоефективної хроматографії води з використанням ультрафіолетового опромінення.

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Heterogeneous photocatalysis for selected atypical antipsychotic removal from river waters

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Heterogeneous photocatalysis of selected atypical antipsychotic, namely olanzapine, was examined. Photocatalytic degradation of above mentioned pharmaceutic was investigated in deionized and river water solution in the presence of titanium dioxide as a photocatalyst. River water samples were collected from Narew and Marycha, which run in the east of Poland. Studied irradiation sources included ultraviolet radiation and simulated solar light. Photodegradation efficiency and the presence of possible arising intermediates were examined by high-performance liquid chromatography with ultraviolet detection. Photocatalytic degradation efficiencies were significantly enhanced in the river water solutions compared to the synthetic deionized water. They also reached higher levels in case of utilizing solar light instead of ultraviolet radiation. Degradation extent was assessed by the HPLC peak area for olanzapine after exact time of irradiation.

Keywords – atypical antipsychotic, heterogeneous photocatalysis, olanzapine, titanium dioxide

I. Introduction

Heterogeneous photocatalysis represents an example of advanced oxidation processes able to achieve a complete oxidation of organic and inorganic species. It takes advantage of some semiconductor solids, which can be used as photocatalysts suspended in the water effluent to be treated, or immobilised on various types of supports. By far the most researched photocatalytic material is TiO_2, because it has provided the most efficient photocatalytic activity, highest stability, lowest cost and toxicity as well as biological and chemical inertness.

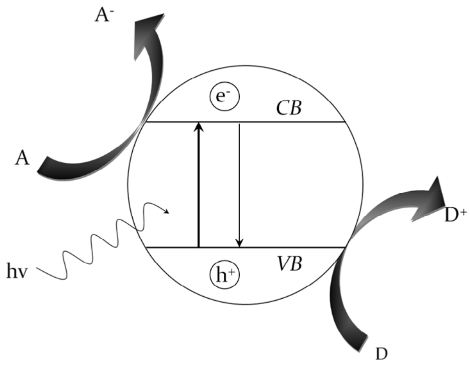

Fig. 1. Schematic presentation of the processes occurring during heterogeneous photocatalysis

During photocatalysis electron-hole pairs (e^--h^+) are generated. This phenomenon takes place upon light illumination of energy greater than 3.2 eV which corresponds with ultraviolet radiation. Above mentioned energy results from the distance between conduction (CB) and valence bands (VB). These photo-generated electrons and holes migrate to the surface, where they react with the molecules, objects of degradation and give rise to the generation of hydroxyl radicals, responsible for the complete decomposition of the chemical substances [2,5]. Electron acceptors (A) are reduced, while its donors (D) – oxidized (Fig. 1).

However heterogeneous photocatalysis can be used for removal of pharmaceutics from different classes, presented work focuses on the investigation of a selected atypical antipsychotic, namely olanzapine, degradation process upon solar and ultraviolet radiation.

Atypical antipsychotics include clozapine, olanzapine, quetiapine, resperidone, sertindole etc [6]. Recently, olanzapine (2-methyl-4-(4-methyl-1-piperazinyl)-10H-thieno[2,3b][1,5]benzodiazepine) is the most commercially available atypical antipsychotic drug [7]. Its chemical structure was presented in Fig. 2.

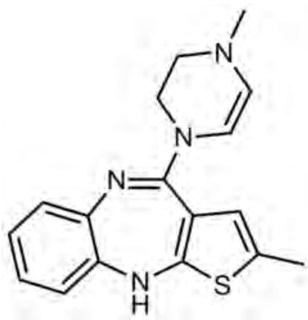

Fig. 2. Chemical structure of olanzapine

Olanzapine is an effective and commonly prescribed drug in the treatment of schizophrenia and bipolar disorder [8]. It causes less extrapyramidal side effects than most typical antipsychotics and has a positive effect on cognitive deficits [9]. Due to given above reasons the consumption of described drug is continuously rising. On the assumption of that, higher amounts of olanzapine are presumably getting in the wastewater and river waters. If the wastewater were not purified, olanzapine, as well as other pharmaceutics, could get in the drinking water, which could lead to disastrous consequences. Therefore, there is a need to seek for new effective methods of water detoxification. The huge potential lies in heterogeneous photocatalysis.

The main objectives of this research were to assess the degradation of the olanzapine by simulated solar and ultraviolet radiation in the presence of titanium dioxide as a photocatalyst. Photodegradation efficiency and the presence of possible arising intermediates were examined by high-performance liquid chromatography with ultraviolet detection.

II. Materials and reagents

TiO_2 (100% anatase) was purchased from Sigma-Aldrich. Olanzapine was obtained from 5 mg Zalasta tablets, which were purchased as available on the market and prescribed for human patients. HPLC-grade acetonitrile was purchased from Merck. All solutions were prepared using deionized water, which was obtained by Polwater apparatus.

III. Photolysis and photocatalysis conditions and equipment

Photolytic as well as photocatalytic degradation experiments were carried out using SUNTEST CPS+ (ATLAS, USA) and UV-Standard lamp (220-240 V, 50-60 Hz, 16VA, Cobrabid) emitting monochromatic radiation of 366 nm.

The experiments were performed in 50 mL glass cell. The reaction mixture consists of 20 mL of OLA sample ($5x10^{-5}$ mol/L) and TiO_2 (1.6 g/L) as a photocatalyst. Prior the irradiation the pharmaceutic catalyst suspension with stirring was kept in the dark for 1 hour to ensure an adsorption-desorption equilibrium. To further chromatographic analyses the samples were collected after 1 and 2 hours of irradiation and centrifuged to remove photocatalyst.

IV. Chromatographic conditions and equipment

The chromatographic experiments with HPLC-UV system were carried out on a Varian 920 liquid chromatograph using a binary solvent pump and a manual injector. The chromatographic column used Lichrospher®100 RP-18 125 mm x 4.6 mm packed with 5μm particle size. Separation was achieved using a linear gradient method. Mobile phase was a linear gradient prepared from 10 mM disodium hydrogen phosphate, pH adjusted to 7.4 with orthophosphoric acid (A) and acetonitrile (B). The gradient was as follows: 0 min, 70% A; 15 min, 70% A; 25 min, 20% A; 30 min, 20% A; 35 min, 70% A. The flow rate of the mobile phase was 1 mL/min and the injection volume was 100 ul. The column was maintained at room temperature. The eluent was monitored at 256 nm.

V. Results and discussion

As it was proved, heterogeneous photocatalysis is one of the advanced oxidation processes which has been shown to be very effective in oxidizing a large variety of toxic organic compounds in water and wastewater. In presented studies this process was used as potential metod of olanzapine removal from selected river waters, namely Marycha and Narew.

Firstly, photolytical studies were performed using solar simulated light (E=250 W/m^2) and monochromatic ultraviolet radiation (λ=366 nm). Registered chromatograms after photolysis experiments performed using solar light and ultraviolet radiation were shown in Figs. 3 and 4, respectively. Olanzapine was found to be resistant to photolytic degradation.

Many pharmaceuticals are readily susceptible to photolytic transformation. Those which do not absorb light above 290 nm are more resistant to direct photolysis with natural light [10]. As olanzapine possesses a maximum absorption band at 256 nm it is clear that its resistance for direct photolysis was not a surprise.

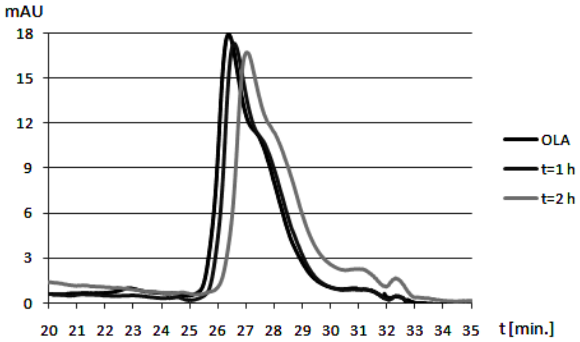

Fig. 3. Chromatograms of deionized aquatic olanzapine solutions after 1 and 2 hours of photolysis under solar simulated light in compare with undegradated solution of olanzapine (OLA)

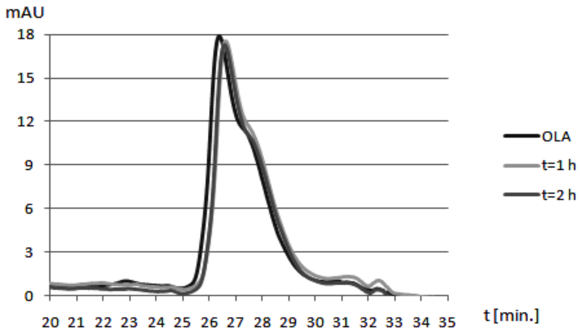

Fig. 4. Chromatograms of deionized aquatic olanzapine solutions after 1 and 2 hours of photolysis under ultraviolet radiation in compare with undegradated solution of olanzapine (OLA)

Degradation of olanzapine in aquatic solution was investigated upon photocatalytic conditions using solar light (E=250 W/m^2) and monochromatic ultraviolet radiation (λ=366 nm). Chromatograms registered after 2 hours of irradiation were compared with the chromatogram of olanzapine without any treatment and shown in 5.

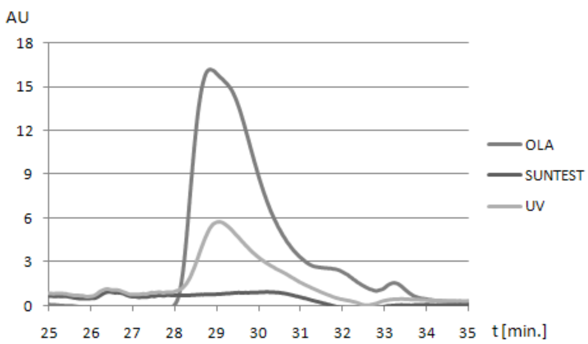

Fig. 5. Chromatograms of deionized aquatic olanzapine solutions after 2 hours of solar simulated light (SUNTEST) and ultraviolet (UV) irradiation in a presence of TiO_2 in compare with undegradated solution of olanzapine (OLA)

In contrast to photolytical conditions, photocatalytical ones lead to the significant degradation of examined pharmaceutic. It is also easily to noticed that simulated light contributes to major photodegradation efficiency than ultraviolet radiation. It can be assumed on a higher energy that accompanied solar light.

Photolysis (Figs. 6 and 7) and photocatalysis (Figs. 8 and 9) of olanzapine solutions in river waters (Marycha and Narew) were investigated similarly to those presented previously in aquatic (deionized water) environment. Experiments were performed by means of solar light and ultraviolet radiation.

Degradation extent was assessed by the HPLC peak area for olanzapine after exact time of irradiation. Photocatalytic degradation efficiencies were significantly enhanced in the river water solutions compared to the synthetic deionized water. They also reached higher levels in case of utilizing solar light instead of ultraviolet radiation.

Comparing Figs. 6 and 7 shows that photolytical degradation of olanzapine occurs more efficiently in the environment of water from Narew river. The most differences takes place after 1 hour of degradation under solar simulated light. There is also huge difference between efficiencies under solar light and ultraviolet radiation. This is due to the fact the energy of solar light is higher than that of ultraviolet light, as previously mentioned.

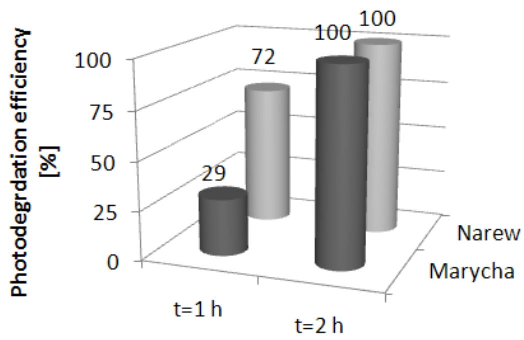

Fig. 6. Photolysis of olanzapine in Narew and Marycha waters under solar simulated light

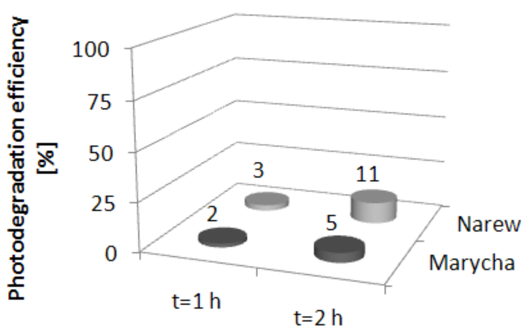

Fig. 7. Photolysis of olanzapine in Narew and Marycha waters under ultraviolet radiation

Degradation of the olanzapine under photocatalytical conditions led to the significant enhancement of the pharmaceutic removal efficiencies in compare with those which were reached after photolysis. Similarly to the photolytical experiments, photodegradation efficiencies reached higher levels in case of olanzapine solutions in the water from Narew river.

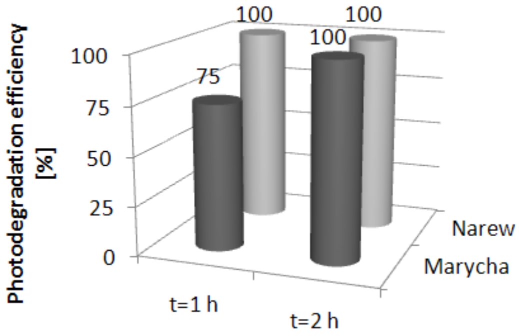

Fig. 8. Photocatalysis of olanzapine in Narew and Marycha waters under solar simulated light

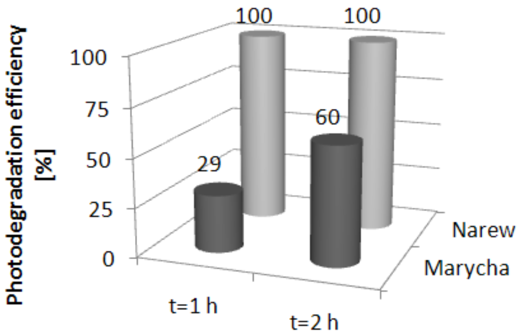

Fig. 9. Photocatalysis of olanzapine in Narew and Marycha waters under ultraviolet radiation

Conclusion

Olanzapine is resistant to photolysis in aquatic environment in the presence of both solar light and ultraviolet radiation as well as in the environment of river waters after illumination of ultraviolet radiation. However, under conditions of heterogeneous photocatalysis olanzapine is efficiently removed from the solution no matter of water character (deionized or river) nor irradiation source (solar simulated light or ultraviolet radiation). Nevertheless, solar simulated light seems to be more effective in pharmaceutic removal from the investigated solution. It was assumed that the reason of that results from a higher energy of solar light emited by SUNTEST CPS+ apparatus in compare with the ultraviolet radiation emited by UV-Standard lamp.

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