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Degradation of sertraline in water by suspended and supported TiO_2

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Pharmaceutical pollutants have been detected in many countries in surface and ground water after treatment in wastewater treatment plants. The presented studies concern the photocatalytic removal of one of SSRI antidepressants - sertraline from water using TiO_2 photocatalyst. The process was conducted using two laboratory installations with periodic and flow reactors. Two forms of TiO_2 was used in the photocatalytic reactions: suspended and supported onto a glass fabric. The studies shown that with increasing initial concentration of pharmaceutical, photoactivity decreases. For the initial concentration of 0.025 g/dm^3, the best results – 94% removal – was achieved for the process conducted in the periodic reactor with TiO_2 supported onto a glass fabric.

Keywords: photocatalysis, titanium dioxide, pharmaceuticals, sertraline, water treatment.

INTRODUCTION

The quality of water is one of the major factors effecting directly the state of natural environment, condition of inhabit organisms and health of people consuming the water. A new type of organic contaminants, being pharmaceutical residue, emerges in waters and become a growing problem during last years[1–14]. Medicaments, after consumption, get to the environment as metabolites or in original form[7, 14, 15]. The other source of bioactive compounds are pharmaceutical production plants, hospitals, households and farms introducing a lot of pharmaceuticals to the environment without their adequate utilization[16, 17].

Stability of pharmaceuticals plays the key role in disadvantageous effect to the environment. Medicaments are designed in a way to be resistant to the outer conditions like humidity, air or light. Most of them do not undergo the complete biodegradation during sewage treatment and can enter the surface and ground waters. Stability of pharmaceuticals in the water environment depends on various factors like presence of suspended organic matter, inorganic ions concentration or sunlight intensity. A lot of medicines is potentially photosensitive since they include units like aromatic rings, heteroatoms or coupled unsaturated configurations that can absorb sunlight. Therefore, except such a processes of organics removal like biodegradation or sorption, photodegradation can play a primary role in decomposition of pharmaceuticals in surface waters.

In 1998 Thomas Ternes[18] analyzed the amount of medicines present in the environment for the first time. He showed the presence of analgesics, antiepileptics, psychotropics, cardiacs, hormonals and other drugs in surface waters and treated sewage in Germany[18, 19]. These shocking findings initiated the monitoring of waters condition around the world[16]. The presence of pharmaceuticals was detected not only in treated sewage but also in drinking water (France: diclofenac, Germany: clofibric acid, Great Britain: diazepam, antibiotics, Canada: naproxen, ibuprofen)[13, 14, 18, 20–22].

Also in Poland the problem with drug contamination of water environment was revealed. The data concerning contamination of environment by pharmaceuticals in Poland was not published. In 2000 Medicines Institute gave access to the information about medicines consumption in Poland and on these basis theoretical concentrations of individual pharmaceuticals in municipal wastes were calculated[23]. In the same year, an actual examination of water was conducted at wastewater treatment plant in Zabrze. The obtained results showed that actual concentrations of pharmaceuticals are lower than theoretically calculated but still problematic[24].

Unfortunately, only a small number of papers concerning the presence of medicines in water environment refer directly to antidepressive drugs so the exact concentrations of these pharmaceuticals is not well-known[4, 8, 12, 25, 26].

Reports published in 2011 show considerable growth of people suffer from the psychical diseases in the European Union[27]. It is estimated that more than 160 million EU's residents suffers from problems connected to the mental health. Unfortunately, a great majority of cases requires pharmacological treatment. The mostly described thymoleptics are selective serotonin reuptake inhibitors (SSRI). One of the mostly used medicine in psychiatric therapy is sertraline: (1S-cis)-4-(3,4-dichlorophenyl)-1,2,3,4-tetrahydro-N-methyl-1-naphthalenamine. Sertraline is a very bioactive and resistant to degradation medicine.

Study on fathead minnows demonstrated that antidepressant drugs such as sertraline and venlaflexine caused mortality, and fluoxetine results in anatomical alternations[25]. Research on brook trout exposed to selected serotonin reuptake inhibitors shows that these pharmaceuticals caused decrease brain activity, and the dominant substances in fish tissues are sertraline and desmethylsertraline – its metabolite[26].

Photocatalysis is one of the Advanced Oxidation Processes finding applications in decomposition of various organic pollutants in water[28–33]. In this work, we demonstrated that photocatalysis is an effective method to remove sertraline from water. This approach for sertraline decomposition in water was not yet described in the literature.

In purpose of efficiency verification of this process, photolysis was also executed. To define the best operating conditions many tests with different parameters were made: change in the concentration of sertraline, the amount of photocatalysts, the type of titanium dioxide, the kind of reactor and different process configurations.

Experimental section

The source of sertraline was a commercial product named Asentra (KRKA, Slovenia). An active component of Asentra tablets is sertraline hydrochloride.

Two types of titanium dioxide (TiO_2): intermediate product taken from the production line in Grupa Azoty Zakłady Chemiczne Police SA Poland (TA) and Aeroxide P25 form Evonik Industries AG Germany (P25) were used as a photocatalysts. The support for titania photoactive coating was a glass fabric (Polonit, Poland). Ethanol was purchased from Chempur (Poland).

The process of photocatalytic decomposition of sertraline in water was conducted using two types of laboratory installations.

The glass reactor produced by Heraeus (Germany) with a medium pressure mercury lamp was a main component of the periodic mode installation (Figure 1). The solution of sertraline with specified concentration was placed in the reactor in the quantity of 650 cm^3. The photocatalyst was introduced to the reactor either as a powder forming a suspension in the solution (suspended system) or immobilized onto a glass fabric (immobilized system). The reaction mixture was stirred continuously using the magnetic stirrer. After 15 minutes of stirring (achieving of adsorption equilibrium) the medium pressure mercury lamp emitting radiation in the range of 250–800 nm with high maximum at 254, 436 and 536 nm was turned on. The samples of reaction solution was taken from the reactor, at set time intervals, for analysis of sertraline concentration.

Trojan UVMax photoreactor (Trojan Technologies, Canada) with a medium pressure mercury lamp was a main component of the flow mode installation (Figure 2). The photocatalyst was either suspended in the reaction solution in the form of powder (suspended system) or immobilized onto a glass fabric (immobilized system). The solution of sertraline was poured in to the container and placed on the magnetic stirrer. In case of suspended system, the photocatalyst was introduced to the container. In case of immobilized system, the glass fabric covered with titania layer was placed inside the reactor so that it stick to the inner walls of the reactor. The reaction solution (2.5 dm^3) was pumped from the container to the reactor by a peristaltic pump with the flow rate of 36 dm^3/h. The solution circulated in the system for 15 minutes without illumination (adsorption stage) and then the medium pressure mercury lamp emitting radiation in the range of 250–800 nm with high maximum at 254, 436 and 536 nm was turned on. The samples of reaction solution was taken from the reactor, at set time intervals, for analysis of sertraline concentration.

P25 titania photocatalyst was immobilized onto glass fabric according to the following procedure. Ethanol with TiO_2 was sonicated for 1h to obtain a fine suspension of titania particles in the solvent matrix. A piece of glass fabric with dimensions of 19 cm × 24 cm was immersed in the ethanolic suspension of TiO_2 (5% by weight) for 30 seconds followed by drying for 1 hour at the temperature of 105°C. This step was repeated two more times and finally the fabric was subjected to thermal treatment at the temperature of 150°C for 24 hours. Next, the fabric with immobilized titania was placed in reactor with distilled water and irradiated, with continuous stirring, for about 240 minutes to remove the excess of photocatalyst particles and stabilize the coating. The amount of P25 titania immobilized onto the glass fabric was about 5 g/m^2, which gives 0.25 g per the piece of fabric used in the individual processes.

The analysis of sertraline concentrations in the reaction solution were made using UV-vis spectroscopy (Jasco V-630, Japan). The absorbance of the samples at the maximum absorption wavelength of 507 nm was recorded and recalculated for the sertraline concentration according to the equation of the analytical curve.

The sertraline solution was prepared from powdered tablets of Asentra drugs. The specified amount of powder (recalculated for the adequate amount of sertraline itself) was added to distilled water and sonicated for 30 minutes followed by filtration to separate the insoluble components of the tablets.

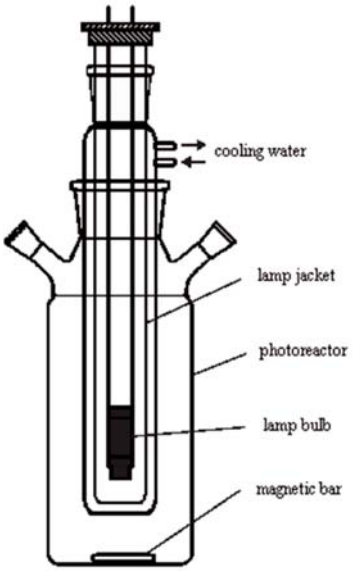

Figure 1. Scheme of the batch photoreactor with a medium pressure mercury lamp

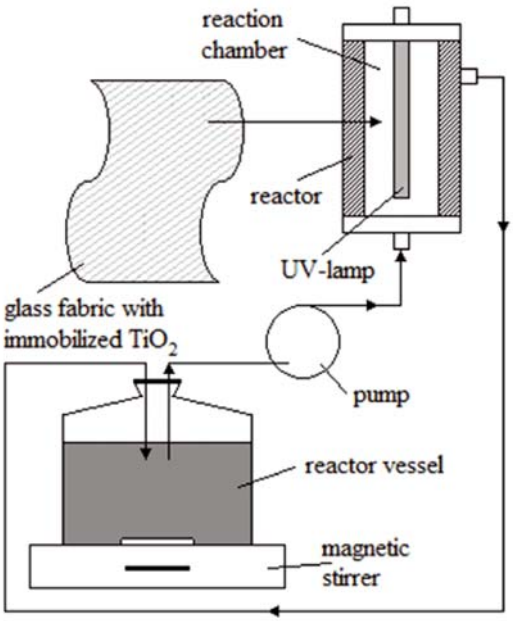

Figure 2. Scheme of the flow photoreactor

RESULTS AND DISCUSSION

The blank test conducted in the dark, in the presence of the photocatalyst only, showed no decomposition of sertraline in water. Illumination of sertraline solution without photocatalyst (photolysis) revealed decrease in sertraline concentration in the reaction mixture (Figure 3). However, the efficiency of this process was much lower than during the photocatalytic process where the photocatalyst together with illumination was applied.

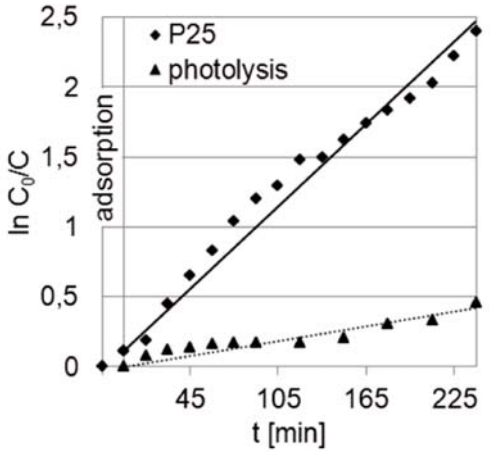

Figure 3. Kinetics of the degradation of sertraline in the periodic reactor by photolysis and photocatalysis using suspended TiO_2. Initial concentration of sertraline – 0.1 g/dm^3, amount of photocatalyst – 1.15 g/dm^3

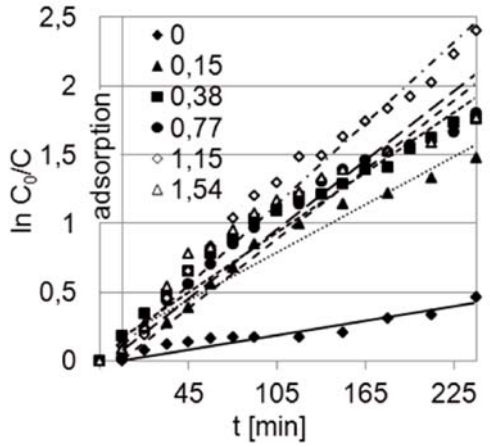

Figure 4. Kinetics of the photocatalytic degradation of sertraline in the periodic reactor for different amount [g/dm^3] of suspended TiO_2. Initial concentration of sertraline – 0.1 g/dm^3

Figure 4 shows the results of photolytic and photocatalytic decomposition of sertraline in water conducted in the periodic reactor. The initial concentration of sertraline was the same in each case and it was 0.1 g/dm^3. The amount of photocatalyst was different for each individual test: no photocatalyst in the case of photolysis and 0.15, 0.38, 0.77, 1.15, 1.54 g/dm^3 in the case of photocatalytic processes (0.1, 0.25, 0.5, 0.75 and 1 g of photocatalyst per volume of reaction solution – 650 cm^3). After 240 minutes of photolytic process, the loss of substrate concentration was about 37%. In the case of photocatalysis, in every process, this value was over twice as high. It means that even a small amount of titanium dioxide significantly impacts the rate of decomposition of sertraline in water. The removal efficiency of this drug largely depends on the amount of TiO_2 applied. It can be seen that the rate of sertraline decomposition increases together with the increasing amount of titania in the reaction system up to 1.15 g/dm^3, where the concentration loss of sertraline was about 91%. The application of higher amount of photocatalyst resulted in decrease of sertraline decomposition (with 1.54 g/dm^3 of titania, decomposition degree was 83%). It is related to the shielding effect of the photocatalyst.

The effect of the initial concentration of sertraline on the rate of the photocatalytic process conducted with the application of different reaction configurations (periodic or flow reactor and with application of suspended or supported TiO_2) is presented on Figures 5–8.

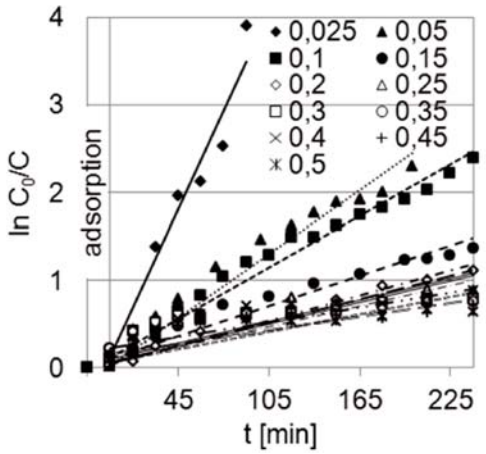

Figure 5. Kinetics of the photocatalytic degradation of sertraline in the periodic reactor for different initial concentrations [g/dm^3] of sertraline with suspended TiO_2. Amount of photocatalyst – 1.15 g/dm^3

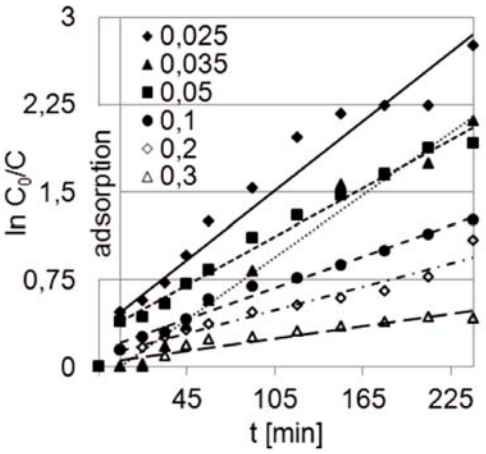

Figure 6. Kinetics of the photocatalytic degradation of sertraline in the periodic reactor for different initial concentrations [g/dm^3] of sertraline in the supported system

The obtained results revealed that titanium dioxide shows a high effectiveness in the degradation of sertraline in water. During a relatively short time, decomposition the majority of substrate can be achieved. The photoactivity decreases with increasing initial concentration of sertraline.

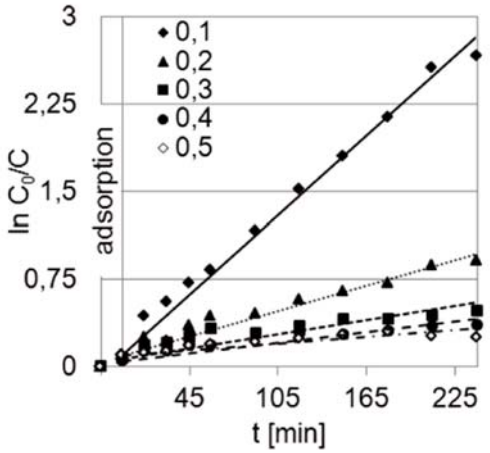

Figure 7. Kinetics of the photocatalytic degradation of sertraline in the flow reactor for different initial concentrations [g/dm^3] of sertraline with suspended TiO_2. Amount of photocatalyst – 0.5 g/dm^3

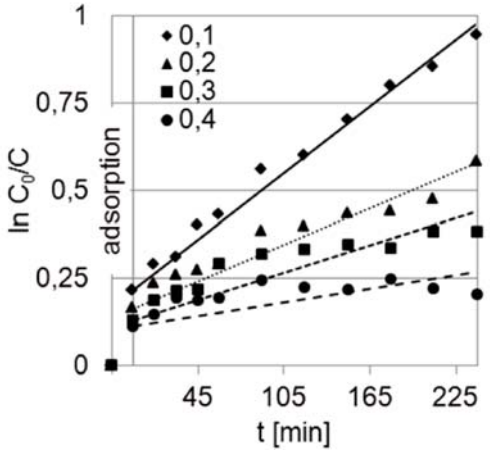

Figure 8. Kinetics of the degradation of sertraline in the flow reactor for different initial concentrations [g/dm^3] of sertraline in the supported system

The results of tests conducted for sertraline solutions with different, established concentrations in the periodic photoreactor using suspended system are shown on Figure 5. At the low concentrations (0.025 and 0.05 g/dm^3) of pharmaceutical, it was decomposed completely after 90 and 200 minutes of the photocatalytic process. At the concentration of sertraline 0.1 g/dm^3, after 240 minutes, the degree of removal was 91% and gradually decreases with the increasing concentration reaching 47% for 0.5 g/dm^3.

The results presented on Figure 6 show that application of the photocatalytic process using titania immobilized on the glass fabric is also an efficient method to decompose sertraline in water. For 0.025 g/dm^3 of the initial concentration of sertraline, 94% of the substrate was degraded after 240 minutes, but the degree of decomposition gradually decreases with the increasing concentration of sertraline giving 34% for 0.3 g/dm^3.

It can be observed from Figure 7 that suspended titanium dioxide applied in the flow reactor proves a high activity toward degradation of sertraline and after 240 minutes of the photocatalytic process 93% of sertraline was removed in the case of initial concentration of sertraline 0.1 g/dm^3. With an increase in initial concentration, the degree of degradation decreases and it was 23% in the case of sertraline concentration 0.5 g/dm^3.

Figure 8 shows the photoactivity of TiO_2 deposited onto the glass fabric in the flow reactor. As can be seen, the degree of degradation of sertraline in water was 61% in the case of 0.1 g/dm^3 of the initial concentration of sertraline and just 18% for 0.4 g/dm^3.

The studies applying titania supported onto the glass fabric also revealed that the photoactive refill (titania immobilized on the glass fabric) loses its activity in the repeated tests conducted with the same refill. However it can be successfully regenerated to a certain degree and reused (see Figure 9).

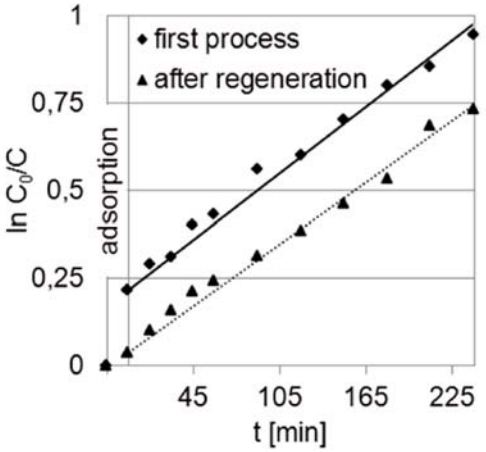

Figure 9. Comparison of the photocatalytic degradation of sertraline with application of fresh and regenerated glass fabric. Initial concentration of sertraline – 0.1 g/dm^3

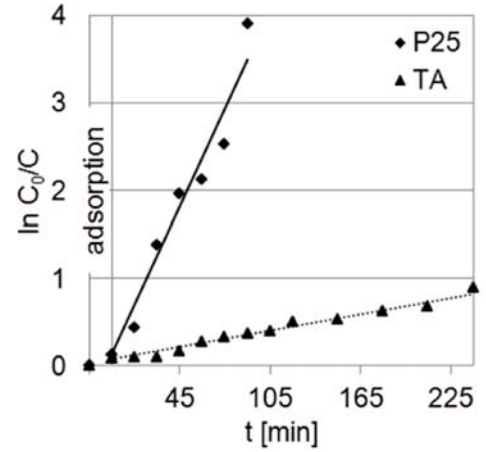

Figure 10. Comparison of the photocatalytic activity of TA and P25 materials. Initial concentration of sertraline – 0.025 g/dm^3, amount of photocatalyst – 1.15 g/dm^3

Figure 10 presents comparison of the photocatalytic activity of TA and P25 materials. The initial concentration of sertraline was 0.025 g/dm^3 and the amount of photocatalytic material was 1.15 g/dm^3. Sertraline was completely removed after 105 minutes over P25 material. At the second case, using TA photocatalyst, after 240 minutes of the process, substrate was decomposed in 59%. It shows that the rate of degradation strongly depends on the type of applied photocatalysts.

The amount of photocatalyst immobilized onto the glass fabric was 0.25 g per individual piece of fabric. It was decided to conduct the photocatalytic process with application of the same amount of powdered titania in the suspended system as the amount of it in the supported system. The results of these experiments, conducted in the periodic reactor, are presented on Figure 11. It can be clearly seen that the process of sertraline removal proceeded similarly.

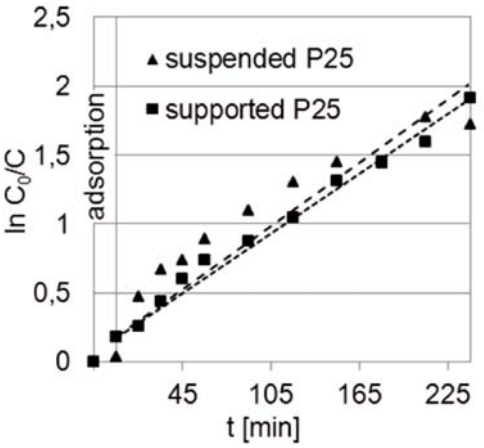

Figure 11. Comparison of the photocatalytic activity of suspended and supported P25. Initial concentration of sertraline – 0.1 g/dm^3, amount of photocatalyst – 0.25 g per reaction volume

Figure 11. Comparison of the photocatalytic activity of suspended and supported P25. Initial concentration of sertraline – 0.1 g/dm^3, amount of photocatalyst – 0.25 g per reaction volume.

CONCLUSIONS

The obtained results show that the photocatalytic process conducted using the various configurations (periodic or flow reactors and also suspended or supported systems) can be successfully applied for removal of sertraline from water. The rate of decomposition of this antidepressant in water depends on the type of reactor configuration, type of the photocatalytic material, the amount of the photocatalyst in the reaction system and the initial concentration of sertraline in water. The process is more efficient for the lower substrate concentrations which is beneficial because of usual low concentration of pharmaceuticals in the environment. It can be stated that each of applied process configurations show advantages and drawbacks, but the immobilized configuration can be better because it gives elimination of the troublesome step of separation of the photocatalyst after the process is completed.

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