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Original Research

Spectrophotometrically and Chemometrically Assisted Studies on the Photostability of Terazosyne in an Aqueous Environment

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Abstract

The behavior of terazosine hydrochloride (TR), representative of the selective α_1-adrenergic blockers in river water under the influence of sunlight, was tested. Details of the photodegradation process were obtained using principal component analysis (PCA) and multivariate curve resolution alternating least squares (MCR-ALS) chemometric methods and confirmed by HPLC analysis. Additionally, the impact of some factors important for efficient waste treatment were studied. For this purpose a stability of terazosine aqueous solutions under the influence of UV, UV+H_2O_2, Fenton, and photo-Fenton processes and sunlight was studied. The presence of H_2O_2 and Fe (II) ions increases the rate of transformation. The process of direct photolysis and H_2O_2-assisted photoreaction showed first order kinetics, while dark and photo-Fenton reactions exhibited second-order kinetics.

Keywords: terazosine, Fenton reaction, photostability, chemometric analysis

Introduction

Today's, consumption of pharmaceuticals in developed countries has been estimated at a high level and it is still growing. Pharmaceuticals are not completely metabolized in human bodies, and then parent compounds as well as their metabolites are excreted. They are able to enter the aqueous environment *via* wastewaters. Residues of pharmaceuticals are frequently found in surface waters [1] and their presence in the environment is recognized as a new kind of pollution [2]. They have been considered as persistent due to their stability, lipophilicity, and continuous delivery from various sources [3-6]. Their existence in waters has caused serious problems like immune resistance of bacterial strains, endocrine changes, and others [7, 8]. Sunlight is the main factor that influences the persistence of pharmaceuticals in an aqueous environment. Solar irradiation initiates a chain of direct and indirect phototransformation of organic compounds. Photoprocesses are complicated, consisting of many steps that lead in the end to the formation of small molecules, e.g. carbon dioxide and water [9, 10]. The produced intermediates usually are not environmentally neutral and sometimes are more harmful than their parent compounds [10, 11]. So the recognition of photoprocesses occurring in natural conditions is important for environmental protection as well as for the protection of human health [12]. From the other side, knowledge of reactions occurring in water under the influence of sunlight and other factors [13-16] could allow improvement of purification processes of drinking water or wastewater in water treatment plants [13, 17-19].

The aim of the presented paper is to study behavior of terazosine hydrochloride (Fig. 1) in an aqueous environment, its photostability in natural waters, and to specify fac-

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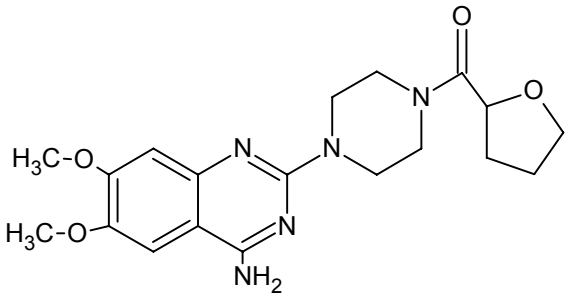

Fig. 1. Molecular structure of terazosine.

tors influencing its stability in this environment. Terazosine (2-[4-(2-tetrahydrofuranyl carbonyl]-1-piperazinyl-6,7-dimetoxy-4-quinazolinamine, TR) belongs to the group of selective α_1-adrenergic blockers [20, 21]. It is used for the treatment of hypertension and benign prostatic hyperplasia [22]. TR is very well adsorbed from the gastro-intestinal tract after oral administration with bioavailability about 90% [23]. It is excreted with urine (1.6±0.3% of the total dose in the case of patients with severe renal insufficiency and 5.1±1.4% in urine of patients with normal renal function) [23]. It undergoes ionization in an aqueous solution [23]. The protonated form is responsible for solubility of the compound in water and its interaction with receptors, while the neutral form enables permeation of terazosine molecules through cells membranes. Terazosine slowly hydrolyzes in aqueous solutions. The rate of hydrolysis increases with increasing pH [24]. Terazosine has been found as a relatively stable compound under thermal and photochemical stress conditions, and in water at room temperature [24]. It degrades rapidly in acidic, neutral, and alkaline solutions at elevated temperatures [24]. Although photostability of every pharmaceutical is extensively tested before its introduction into the market, information of its behaviour under the influence of sunlight in a natural aqueous environment is limited. Terazosine transformation under environmental conditions has not yet been recognized. The stability of terazosine in natural water under the influence of UV and simulated solar light was checked. Additionally, studies on terazosine stability under the influence of factors significant for waste treatments such as UV-A irradiation, mild oxidative agent (H_2O_2), and $OH^{\cdot}$ radical alone and in combination with UV-A radiation. The Fenton system was used for generations of $OH^{\cdot}$ radicals. The tasks mentioned above were realized by studying a decomposition process of terazosine in distilled and in surface water solutions by spectrophotometric, chemometric, and chromatographic methods.

Materials and Methods

Materials

All solutions were prepared using MilliQ water. Terazosine hydrochloride was purchased from Sigma-Aldrich (Germany). Other chemicals used in experiments were H_2O_2 30% (w/w) from CHEMPUR (Poland), $FeSO_4 \cdot 7H_2O$, NaOH, acetic acid, and H_2SO_4 from POCh (Poland).

Sample Preparation

Terazosine stock solution 10^{-2} mol·L^{-1} was prepared from the pure product by dissolving an appropriate weight in 50 mL of MilliQ water with the addition of 0.5 mL of 4 mol·L^{-1} solution of acetic acid. Stock solution was protected from light and stored in a refrigerator. Such prepared solution was stable for at least one month. Working solution $2.52 \cdot 10^{-5}$ mol·L^{-1} was prepared fresh daily by an appropriate dilution of the stock solution in MilliQ water in a 25 ml calibrated flask. Its pH was equal to 3.85 without the addition of any portion of acid.

Fe(II) standard solution 10^{-2} mol·L^{-1} was prepared every two days by dissolving an appropriate weight of $FeSO_4 \cdot 7H_2O$ in MilliQ water with the addition of 2 mL of concentrated H_2SO_4 in a 100 mL calibrated flask. Working solutions were prepared by an appropriate dilution of the stock solution.

Stock solution of hydrogen peroxide (10^{-1} mol·L^{-1}) was prepared fresh daily by an appropriate dilution of 30% solution in MilliQ water.

Irradiation Systems

All irradiation experiments were done using a UV lamp – standard 16AV, (Cobrabid, Poland) equipped with two light sources emitting radiation at 254 and 365 nm. All samples were irradiated at 365 nm as representative of natural solar radiation UV-A.

Solar Light simulator SUNTEST CPS$^+$, ATLAS USA emitting radiation in the range 300-800 nm was used for experiments simulating natural conditions.

Quantitative Evaluation of Radiation Sources

Light intensity was determined using the potassium Reinecke's salt ($K[Cr(NH_3)_2(SCN)] \cdot H_2O$). Potassium Reinecke's salt stock solution $5 \cdot 10^{-2}$ mol·L^{-1} was prepared from the pure product by dissolving an appropriate weight in 50 ml of MilliQ water with the addition of 1 mL 7.8 mol·L^{-1} solution of nitric acid. A 0.5 ml stock solution of potassium Reinecke's salt was diluted with 1 mL of 0.74 mol·L^{-1} $Fe(NO_3)_3 \cdot 9H_2O$ and 1 mL of 7.8 mol·L^{-1} HNO_3 in 50 mL calibrated flask. Next, the solution was placed in a 50 mL crystallization dish with surface of 28.26 cm^2 area open to atmosphere and irradiated by a UV-lamp emitting radiation at 365 nm for about 10 minutes. The reference solution was prepared with 0.5 mL of unexposed potassium Reinecke's salt actinometer solution ($5 \cdot 10^{-2}$ mol·L^{-1}), 1 mL of 0.74 mol·L^{-1} $Fe(NO_3)_3 \cdot 9H_2O$ and 1 mL of 7.8 mol·L^{-1} HNO_3 in 50 mL calibrated flask. The photo-released thiocyanate was monitored by measurement of absorbance at 456 nm in various periods of time. The quantum yield of potassium Reinecke's salt in aqueous solution is 0.3 at 365 nm.

The number of quanta (q) absorbed by the actinometer (I_a) was $5.418 \cdot 10^{19}$q.

UV-Lamp

The basic parameters important for photochemical processes were determined. The energy of the quantum of emitted radiation (E_q) at λ = 365 nm was $5.444 \cdot 10^{-19}$ (J).

The radiant power (P) absorbed during the time interval of irradiation (t) was $4.914 \cdot 10^{-2}$ (W).

Given the exposed surface area of the actinometer equal to 28.26 cm^2, the fraction of the absorbed light power per unit surface area, generally called intensity of irradiance (E_s), was calculated as:

$$E_s = 17.39 \ (W \cdot m^{-2})$$

The same parameters were calculated for the xenon lamp applied in the Suntest apparatus. As the Sunlight apparatus emits radiation in the range 300-800 nm, intensity of the irradiance was estimated as:

$$E_s = \int_{\lambda=350}^{\lambda=750} E_s(\lambda) = 19.53(W \cdot m^{-2})$$

Photostability Studies

All experiments were carried out in a 50 mL crystallization dish with surface of 28.26 cm^2 area open to the atmosphere. 25 mL of working solution of terazosine at concentration $2.52 \cdot 10^{-5}$ $mol \cdot L^{-1}$ was subjected to irradiation by a UV-lamp emitting radiation at 365 nm. The spectra of the solution were recorded every 10 minutes. A mixture of reagents without terazosine irradiated at the same period of time was applied as a blank. pH of aqueous solution was adjusted with 0.1 $mol \cdot L^{-1}$ H_2SO_4 or 0.1 $mol \cdot L^{-1}$ NaOH and then measured with an Elmetron CP-501 pH-meter (produced by ELMETRON, Poland) equipped with a pH-electrode EPS-1 (ELMETRON, Poland). Hydrogen peroxide-assisted photodegradation was studied by adding an appropriate volume of 10^{-1} $mol \cdot L^{-1}$ solution of H_2O_2 to the aqueous solution of terazosine.

UV-Fenton process was examined using 25 mL of $2.52 \cdot 10^{-5}$ $mol \cdot L^{-1}$ solution of terazosine acidified to pH 3 by 0.1 $mol \cdot L^{-1}$ H_2SO_4 with the addition of appropriate volumes of 10^{-2} $mol \cdot L^{-1}$ solutions of Fe^{2+} and H_2O_2.

Absorbance Measurements

The current concentration of terazosine was monitored by measurement of absorbance at 244 nm. All spectrophotometric determinations were done using a U-2800A Hitachi spectrophotometer (Japan). The following working conditions of the apparatus were applied: scan speed 1200 nm/min and spectral bandwidth (1.5 nm).

Chromatographic Analysis

The chromatographic system (Thermo Separation) consisted of a 3D Spectra System UV 3000, a low-gradient pump P2000, a vacuum membrane degasser SCM Thermo Separation, and a Rheodyne loop injector (20 μL). ChromQuest Chromatography Data system software for Windows NT was applied for acquisition and storage of data. A Waters Spherisorb ODS-2 150 mm × 4.6 mm (5 μm) column was employed with the mobile phase of acetonitrile: water: methanol: concentrated acetic acid: concentrated ammonia (35:25:40:1:0.017) [24]. The flow rate was kept constant at 1 mL/min. The wavelength of the UV detector was set at 245 nm. Under these chromatographic conditions retention time of TR was 5.66 min.

Chemometric Procedure

A PC-computer equipped with an Excel 2003 calculation sheet for Windows XP was used for mathematical treatment of data.

The photodecomposition of terazosine in surface water was monitored with the application of principal component analysis (PCA) and multivariate curve resolution alternating least squares (MCR-ALS) methods. For this purpose terazosine solution in surface water at concentration $2.52 \cdot 10^{-5}$ $mol \cdot L^{-1}$ was prepared. 25 mL of this solution was subjected to irradiation in the Sunlight simulator chamber. The spectra of irradiated solution were recorded in 10 min intervals in the range 400-230 nm. The obtained set of spectra registered in numerical form were recalculated to molar extinction values and presented in the form of data matrix **W** [25, 26]. The constructed matrix of spectral data consists of r=86 rows and c=13 columns, where each row represents the different individual spectra collected at various reaction times, and columns include values of absorbance measured at each spectral wavelength [27]. The obtained matrix **W** was next subjected to analysis by PCA and by MCR-ALS numerical decomposition of spectra [27-30].

Results and Discussion

Spectral Studies

The aim of the presented study is to determine the photochemical behaviour of terazosine and its fate in surface waters. All kinetic studies were done with the use of a $2.52 \cdot 10^{-5}$ $mol \cdot L^{-1}$ solution of terazosine. At the beginning of the investigation, the spectral characteristic of terazosine was defined. The spectrum of aqueous solution of terazosine exhibits two main bands at 244 nm and 330 nm (Fig. 2 a). As the band at 244 nm showed the highest intensity, it was applied for monitoring the changes in TR concentration. The dependence of absorbance spectrum shape on pH of solution was observed during the studies. The following changes in spectrum occur with increasing pH: the intensity of the band at 244 slightly decreases with the bathochromic shift to 250 nm. The more distinct bathochromic shift with reduction of intensity is observed in the band at 330 nm, which is shifted to 340 nm. Simultaneously, a weak maximum at 275 nm appears at pH 8. Appropriate calibration graphs were recorded using standard solutions in which pH

was adjusted to desired values. Quantification of terazosine concentration was done spectrophotometrically using an adequate calibration graph. All calibration curves obeyed Beer's law in the concentration range $3.36 \cdot 10^{-6}$ mol·L^{-1}-$3.36 \cdot 10^{-5}$ mol·L^{-1}. Full validation and statistical evaluation were done and proved the high precision and accuracy of applied UV-spectrophotometric methods. Relative errors of determination do not exceed ±4% and RSD was less than 1%.

Studies of Terazosine Photostability in River Water under the Influence of Solar Light

Surface waters constitute a very complicated chemical system. Organic substances in aqueous environment undergo transformations under solar light (direct photolysis) or by reactions with other reactive species naturally occurring in surface waters like $OH^{\cdot}$, $CO_3^{\cdot-}$, $^1O_2$, and ^{3}CDOM (Colored Dissolved Organic Matter). Direct and indirect processes of photolysis of nitrate and nitrite [31], dissolved organic matter (DOM) [32] and ^{3}CDOM (Colored Dissolved Organic Matter), and the presence of metal ions (the photo-Fenton-like reaction [33, 34]) forms a very efficient oxidative system. The value of $t_{1/2}$ (half-life time) of an organic pollutant is affected by many factors, e.g. its lipophility/hydrophility, intensity of solar radiation, concentration of reactive species, and presence of DOM, which can compete with studied compounds for radiation absorption. The photodegradation of organic compounds could proceed in a different way compared to model systems examined under laboratory conditions. So, the photochemical behavior of terazosine in natural water under the influence of solar light was examined. For this purpose, samples of surface water taken from the local Biała River were used. Samples of water were taken according to analytical sampling requirements on about 1/3 river depth about 50 cm from the river bank into polyethylene flasks. The flasks were completely filled to the cap with the sample. The waters were not preserved, so they were carried to the laboratory and immediately subjected to chemical analysis. Samples of water were taken from the same place every two days. Bottles with water were protected from light and stored in a refrigerator before experiments. At the beginning of experiments, samples of water were filtered through filter paper. The basic chemical parameters of the studied water samples important for photochemical processes were assayed. The examined sample of surface water exhibited pH 7.48 with conductivity 52.9 mS. The determined concentration of inorganic ions was: 16 mg·L^{-1} of SO_4^{2-}, 39.05 mg·L^{-1} NO_3^-, 70.01 mg·L^{-1} Cl^-, 110.73 mg·L^{-1} Ca^{2+}, 4.85 mg·L^{-1} Mg^{2+}, and 0.16 mg·L^{-1} Fe^{2+}. The values of TOC and O_2 were found to be 99.79 mg·L^{-1} and 2.12 mg·L^{-1}, respectively. All assayed parameters did not exceed reference range, except TOC value, which was almost twice higher than accepted reference value (<40 mg·L^{-1}) [35, 36]. Examined river water was used as the solvent for the preparation of working solutions of terazosine at concentration $2.52 \cdot 10^{-5}$ mol·L^{-1}. Prepared solution was subjected to simulated sunlight. Terazosine behavior under solar light was checked using the following procedure. A 25 mL portion of compound solution in river water was placed into a simulator sample chamber. The examined sample was subjected to xenon lamp radiation for 120 minutes. Every 10 minutes an appropriate portion of solution was taken and absorbance spectrum was recorded versus blank sample. As a blank, we used a sample of surface water subjected to irradiation under the same conditions as the sample with terazosine.

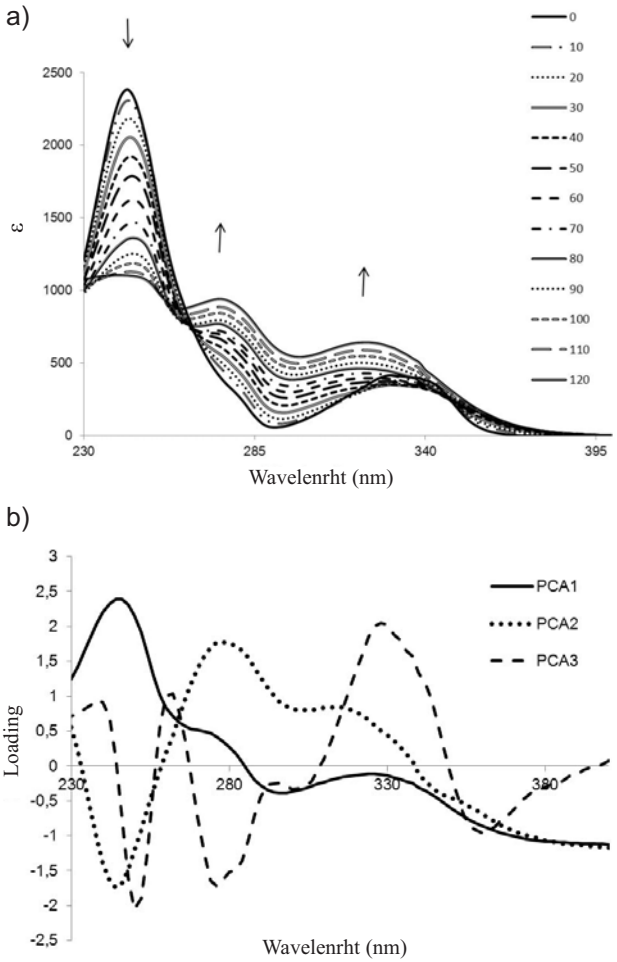

Fig. 2. a) Changes in spectral characteristics (in extinction scale) of TR solution ($2.5 \cdot 10^{-5}$ mol·L^{-1}) during irradiation by simulated sunlight (time of exposition 120 min.), b) Plots of normalized loadings for PCA 1-3.

We observed significant changes in spectral characteristics of the irradiated solutions (Fig. 2a). The main absorption band of terazosine at 244 nm slowly declined. A new shoulder with the maximum at 274 nm was observed after 60 minutes. It underwent transformation into a regular absorbance peak with continuation of radiation. A hypsochromic shift of peak was observed at 330 nm with an increase in intensity. Spectral characteristic of the irradiated solution after 120 minutes exhibited less intense peak at 246 nm and new peaks at 274 and 320 nm. The observed changes allowed us to assume that under the influence of solar light new spectral forms were generated. As a direct recording of spectra does not give qualitative and quantitative information about the intermediates derived from tera-

zosine, chemometric analysis of spectra was applied. The principal components analysis was used to obtain information on how many new spectral forms were generated upon irradiation. Fig. 2a shows transformations into extinction scale spectra of irradiated terazosine solutions. As can be seen, there are no distinct isosbestic points. This fact suggests that recorded spectra are the sum of more than two spectral forms. The PCA method and analysis of residual spectra were applied for estimation of the number of spectral forms co-existing in solution. The determined eigenvalues 12.2879, 0.7000, 0.0119, 0.0002, and 0.0000, respectively, indicated that the three first principal components contained 97% of total variance. The fourth and fifth principal components (PC) described only 0.02% of variance. These results suggest that in solution three spectral forms were generated. The plots in Fig. 2b show the normalized loadings of the first five principal components. The relationship between loadings and wavelength for the fourth and the fifth PC has a noisy, randomized character. The presence of three spectral forms in the system was confirmed by analysis of the residual spectra (Fig. 3). It was found that the second order residual spectra were intense

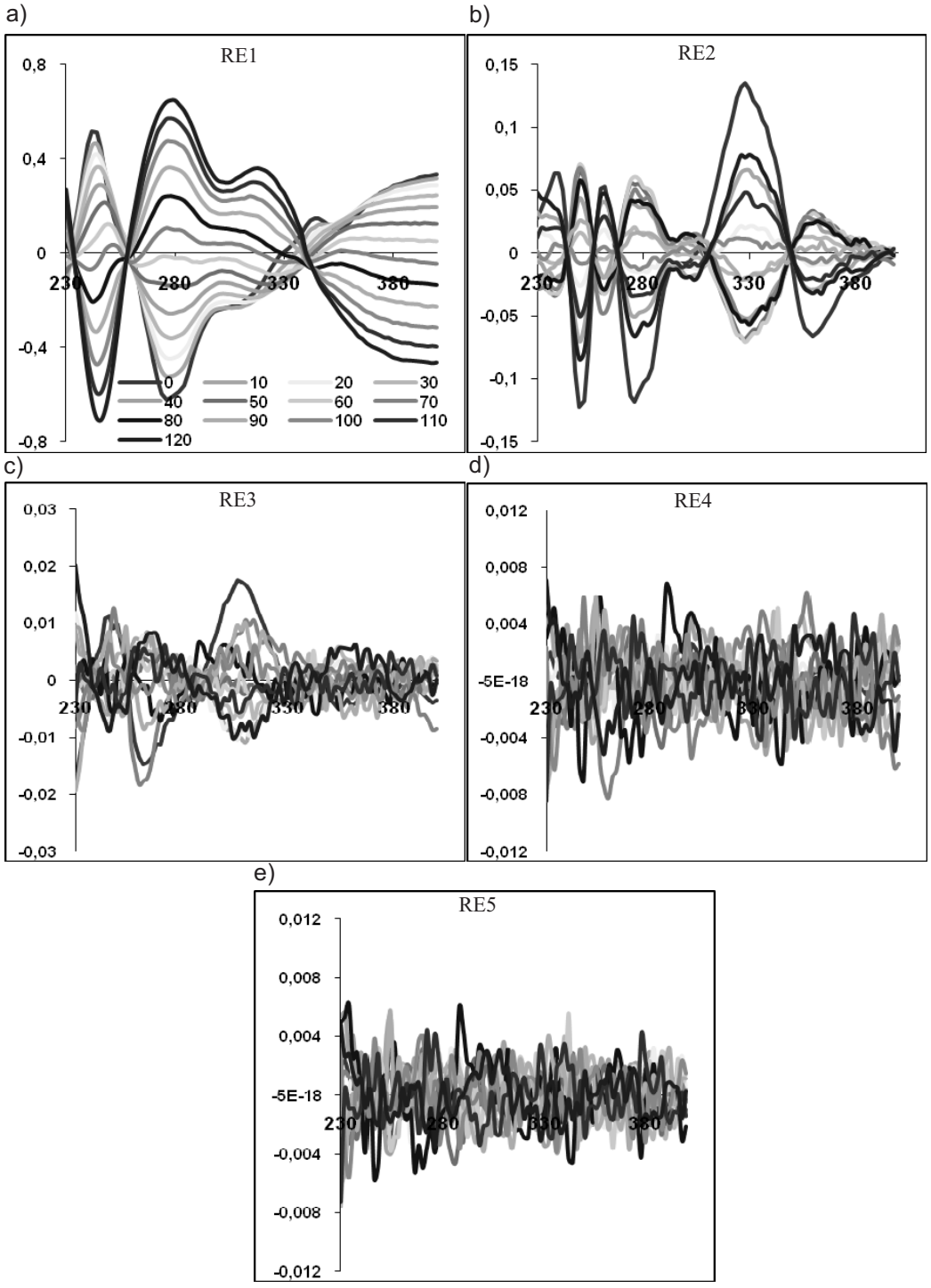

Fig. 3. Residual spectra of terazosine solution in river water irradiated by simulated sunlight; a-e) consecutive residual spectra from the first up to the fifth orders.

with small contribution of noise, while the intensity of the third-order residual spectra was comparable to ±0.02 with noisy character. The application of the MCR-ALS procedure allows reconstructing pure spectra of terazosine photodegradation products (Fig. 4). As can be seen in Fig. 4, the reconstructed spectra correspond with real spectra recorded during the irradiation experiment. Based on kinetic data, the zero-approximation of molar ratios of each spectral form was calculated (Fig. 5). The analysis of changes of molar contribution of each product (Fig. 5) suggest that the photodecomposition process of terazosine is a chain of subsequent reactions. In the first step of reaction two new spectral forms appeared: one unstable form $\mathbf{x}_2$, which was gradually transformed into form $\mathbf{x}_3$. The molar contribution of x_2 form reached the maximum after 50 minutes of irradiation. Transformation of terazosine (spectral form x_1) was almost completed after 80 minutes of irradiation. The observation time was extended up to 120 min. It was noticed that after this time the transformation of form

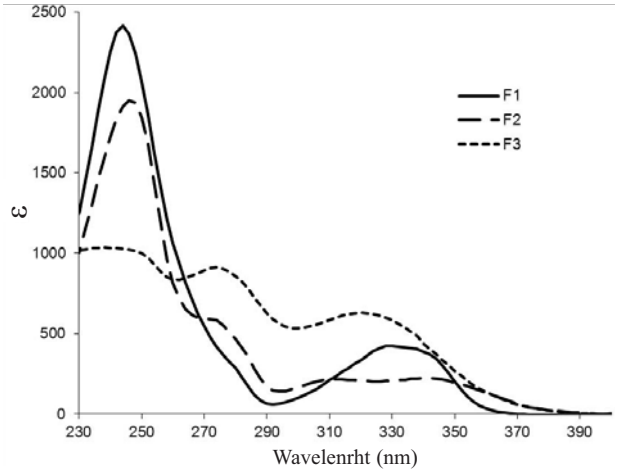

Fig. 4. Resolved pure spectra of TR photodegradation products obtained by the MCR-ALS procedure.

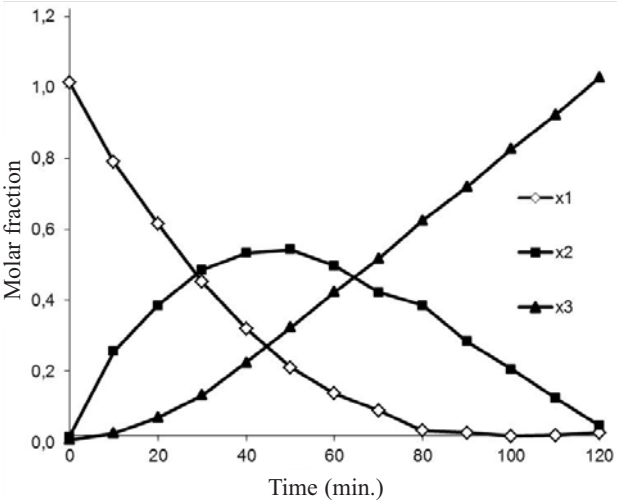

Fig. 5. Optimum molar fraction profiles of TR and its degradation products obtained from numerical analysis.

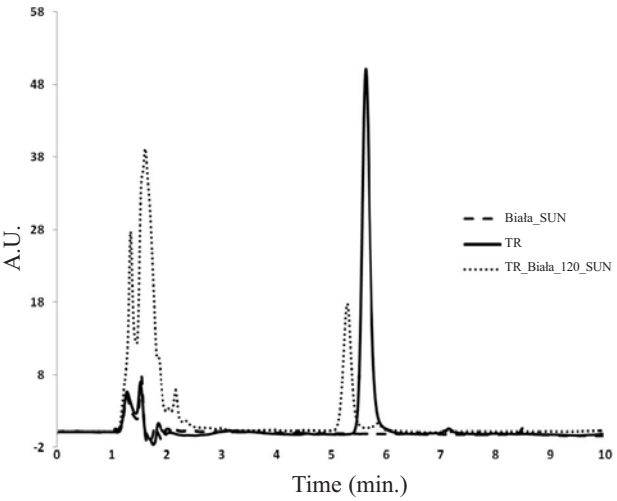

Fig. 6. Chromatograms of irradiated terazosine solution ($2.5 \cdot 10^{-5}$ mol·L^{-1}) in river water at 0 and 120 min. of irradiation.

x_2 as well as its parent compound is completed. The dominant product existing in the solution is the second spectral form x_3. The observed processes can be represented by the following scheme:

$$x_1 \xrightarrow{k_1 = 2.6\ 10^{-2}\ s^{-1}} x_2 \xrightarrow{k_{2(disap.)} = 2.5\ 10^{-2} s^{-1}} x_3$$

As spectrophotometric technique does not allow us to detect an individual compound in mixture, the results obtained by the MCR-ALS method gives only spectral information about a generated group of species. The results obtained by chemometric analysis were confirmed by HPLC analysis (Fig. 6). For this purpose terazosine solution at $2.5 \cdot 10^{-5}$ mol·L^{-1} with the use a sample of river water was prepared and subjected to irradiation in a solar simulator chamber. Next, a small portion of the examined solution was taken every 10 minutes and analyzed by HPLC technique. At the same time the chromatograms of irradiated "pure" river water were recorded. No significant changes in chromatograms of blank were noticed. The recorded chromatograms of solution of terazosine showed that during irradiation the intensity of the terazosine peak gradually decreased. After 120 min of irradiation a group of not separated peaks appeared at the beginning of the chromatogram. This observation suggests that some small unidentified products of photoreaction are created during irradiation. A new intense peak at retention time 5.34 min is noticed. Its UV spectrum posses absorption bands at 214, 222, and 246 nm, confirming observations done by chemometric analysis.

The kinetic parameters of terazosine photodecomposition in natural water under solar light were assayed. The pseudo first-order kinetics was assumed for this process. The assayed kinetic parameters of solar transformation of TR are presented in Table 1. It is evident from Table 1 that the chemical system created by natural water and solar light is very efficient for the degradation of terazosine. The reac-

Table 1. Kinetic characteristics of studied processes of degradation of terazosine in model and river water solutions.

	pH of solution	Concentration/ mol·L^{-1}			Observed rate constant k_{0-75}	$t_{1/2}$/min	Removal (after 80 min)/%
		H_2O_2	Fe^{2+}	TR			
TR+H_2O_2	3.85	10^{-4}	-	$2.52\cdot10^{-5}$	Not observed	-	-
TR+UV	3.85	-	-		Not observed	-	-
	8	-	-		$1.3\cdot10^{-3}\pm8.00\cdot10^{-6}$ min^{-1}	533.19±21.52	1.4
TR+H_2O_2+ UV	3.85	10^{-2}	-		$1.7\cdot10^{-3}\pm1.30\cdot10^{-4}$ min^{-1}	408.36±31.29	9.5
	8	10^{-4}	-		$2.06\cdot10^{-3}\pm6.8\cdot10^{-5}$ min^{-1}	336.60±11.22	0.5
		$5\cdot10^{-4}$	-		$2.22\cdot10^{-3}\pm1.04\cdot10^{-4}$ min^{-1}	312.52±14.82	5.1
		10^{-3}	-		$3.36\cdot10^{-3}\pm6.80\cdot10^{-5}$ min^{-1}	206.29±4.20	10.1
		$5\cdot10^{-3}$	-		$5.01\cdot10^{-3}\pm1.04\cdot10^{-4}$ min^{-1}	136.45±2.78	30.6
		10^{-2}	-		$7.68\cdot10^{-3}\pm1.03\cdot10^{-4}$ min^{-1}	90.24±1.22	53.2
TR+H_2O_2+Fe^{2+}	3	$2.5\cdot10^{-4}$	10^{-4}		42.25±1.04 min^{-1}·mol^{-1}·L	1122.34±8.03	20.5
		$5\cdot10^{-4}$			67.73±1.66 min^{-1}·mol^{-1}·L	712.34±5.33	24.1
		10^{-3}			140.19±3.40 min^{-1}·mol^{-1}·L	355.16±2.98	32.6
TR+H_2O_2+Fe^{2+}+UV	3	$2.5\cdot10^{-4}$	10^{-4}		153.38±3.77 min^{-1}·mol^{-1}·L	306.03±2.47	30.6
		$5\cdot10^{-4}$			359.43±8.44 min^{-1}·mol^{-1}·L	164.90±2.01	52.4
		10^{-3}			1014.48±12.85 min^{-1}·mol^{-1}·L	79.90±1.64	73.1
River water + Sunlight	7.84	-	$2.86\cdot10^{-6}$		$3.3\cdot10^{-3}\pm5.2\cdot10^{-5}$ min^{-1}	210.05±10.10	15.7

tion of terazosine decomposition under environmental conditions can proceed in two ways: as direct photolysis under action of light alone or as the results of the action of natural reactive species naturally occurring in surface waters. Additional experiments were conducted in order to explain this problem. Terazosine solutions at $2.52\cdot10^{-5}$ mol·dm^{-3} in ultrapure water with pH adjusted by HCO_3^-/CO_3^{2-} buffer to 7.48 were subjected to irradiation by a Sunlight simulator. As the observed reaction rate is comparable with that in river water (Fig. 7), it could be assumed that direct photolysis is the main process responsible for terazosine decomposition in river water.

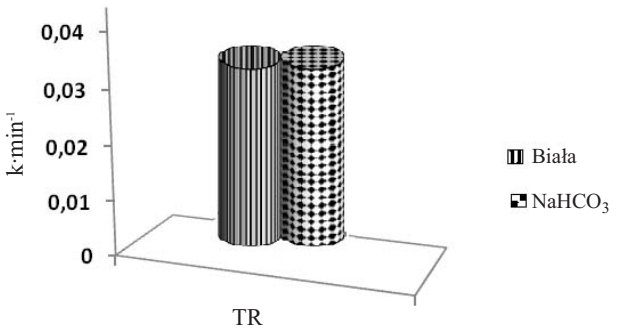

Fig. 7. Kinetic rates of terazosine($2.5\cdot10^{-5}$ mol·L^{-1}) photodegradation in river water (pH 7.48) and in MilliQ water, (pH 7.48 by carbonate buffer).

Studies on Photodegradation Process of Terazosine in Model Systems

In order to obtain information significant for efficient water treatment, additional experiments in model systems were performed. The stability of terazosine under the influence of UV_{365} nm, UV_{365} nm/H_2O, dark Fenton and photo-Fenton systems were investigated.

The behavior of terazosine under UV radiation in model solution was examined at the beginning of the study. As the main goal of the studies was to determine the influence of environmental conditions, UV- radiation at 365 nm, representative of the UV-A part of the solar spectrum, was used for this purpose. Quantification of terazosine concentration was done by measurements of absorbance at 244 nm. It was observed that TR exhibits high stability at acidic pH. There were not noticeable changes in spectral characteristics. So the influence of pH of reaction medium on TR photostability was examined. It was found that the rate of photodegradation increases with increasing pH of irradiated solution. Perceptible reduction of terazosine concentration was observed at pH above 7. Below this value the rate of the studied reaction was negligible. The studied process was very fast at pH 9. At pH 8 the course of photoreaction was convenient for observation, so the rate constant and half time of reaction were assayed (Table 1). It was found that photodegradation of terazosine under the influence of UV radiation exhibits first-order reaction kinetics.

It was observed that addition of hydrogen peroxide to the aqueous solution of TR enhanced its photodegradation in comparison to direct photolysis. The rate of the observed reaction depends on the concentration of H_2O_2 and pH of TR solution. It was substantially higher in the presence of 10^{-2} mol·L^{-1} solution of hydrogen peroxide even at low pH in comparison to the rate of direct process of photolysis of terazosine. The increase in medium pH promotes photodegradation reaction of TR assisted by H_2O_2. The observed enhancement was by a factor of 4.5 at pH 8 in comparison to the rate of reaction at pH 3.85. The degradation mechanism of terazosine in the presence of H_2O_2 exhibited pseudo-first-order reaction kinetics. The kinetic characteristics of the reaction are gathered in Table 1. The influence of hydrogen peroxide alone was studied next. For this purpose terazosine solutions at concentration $2.52 \cdot 10^{-5}$ mol·L^{-1} were mixed with hydrogen peroxide solutions. The final concentrations of oxidant varied in the range $1 \cdot 10^{-5}$-$1 \cdot 10^{-4}$ mol·L^{-1}. All solutions were protected from the light. No changes were observed in the intensity of absorbance at the analytical wavelength, even after 24 hours. Analysis of obtained results showed that light and pH of reaction medium play a key role in the observed process.

The behavior of terazosine under the influence of dark- and photo-Fenton systems was studied next. The classical Fenton reaction system consists of inorganic salt of divalent iron and hydrogen peroxide in acidic solution. The efficiency of Fenton and photo-Fenton systems depends on concentrations of constituents, their molar ratio, acidity of reaction medium, and type of organic compound. After a series of experiments optimal conditions of the studied processes were found. It was stated that the runs of studied reactions are convenient for observation if final concentration of Fe^{2+} ions and H_2O_2 is equal to 10^{-4} mol·L^{-1}. At higher concentrations very fast degradation of terazosine occurred. pH 3 was selected as optimal for both processes. The experiments carried out with the various molar ratios of constituents of Fenton systems showed that degradation rate and efficiency of terazosine removal was promoted with increasing H_2O_2 concentration in ratio to iron ions. The comparison of rates of studied processes (Table 1) showed that classical and photo-Fenton reagents efficiently enhanced the degradation process of terazosine. The increase in degradation rate of Fenton reaction can be explained by the action of strong oxidation agent such as $OH^{\cdot}$ radical, which is generated according to the reaction:

$$Fe\ (II) + H_2O_2 \rightarrow Fe\ (III) + OH^{\cdot} + OH^{-}$$

The presence of UV radiation forced the regeneration of Fe (II) ions and new portions of $OH^{\cdot}$ radicals were produced. So, under the influence of such combination of the reagents the highest rate of terazosine disappearance was observed. Kinetic parameters of Fenton and photo-Fenton processes are assembled in Table 1. The obtained results give information of factors influencing persistence of studied compound and can be useful for improving water purification processes.

Conclusions

The photostability of terazosine under environmental conditions was examined. It was shown that direct photolysis is the main process responsible for its removal from surface waters. The observed rate of terazosine transformation in natural water solution under the influence of solar light is comparable to that exhibited by laboratory TR solutions in the presence of carbonate buffer. The realized experiments proved that natural water acts as an efficient reagent system. The additional experiments showed that terazosine at acidic pH is a stable compound, resisted to a mild oxidation agent such as hydrogen peroxide. The value of pH is a key factor that determines its stability. It is observed that UV light works as an additional factor, intensifying the rate of terazosine transformation. The disappearance of studied compound has occurred with the highest rate under the influence of Fenton and photo-Fenton processes. Application of PCA and MCR-ALS methods gave enough information in order to describe the kinetic pathway involved in the photodegradation process of TR. By the use the resolution power of MCR-ALS modelling it was possible to estimate the spectra of the degradation products and to determine the rate constants of the degradation transformations.

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