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Total Phenolic Content after Paracetamol Transformation under UV and e-beam Radiation

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Abstract

This study was conducted to determine the total phenolic content after UV and e-beam treatment of paracetamol. Four methods were used to induce the conversion of paracetamol (paracetamol concentrations of 1×10^{-4} mol L^{-1} and 4.6×10^{-7} mol L^{-1}) when the drug is dissolved in water or deposited to TLC plates in a soled state: UV 222 nm photolysis, vacuum ultraviolet (VUV 172 nm) photolysis, UV180-275 nm photolysis and e-beam radiolysis. A spectral-luminescent of paracetamol transformation under UV and e-beam radiation had to be studied. The Folin-Ciocalteu method was used to determine the total phenol content (TPC) in the irradiated samples. New experimental data on TPC in a mixture of paracetamol transformation products in water under the exposure to UV radiation sources (KrCl, Xe_2, UVb-04) and e-beam were obtained. Moreover, this study revealed that the lowest TPC value of 9.76 ± 0.82 mg GAE/g was observed in an aqueous solution of paracetamol irradiated with a Xe_2 excilamp for 128 min. It was found that the conversion reached 92% and 93% after irradiation with e-beams and a Xe_2 excilamp, respectively. Using thin layer chromatography, paracetamol transformation products were found to have formed. A solid-phase paracetamol transformation product preserved after 128 minutes of UV irradiation was detected. The available results suggest that, apparently, after Xe_2 and e-beam treatment, paracetamol that may be present in the treated wastewater will be in the form of residual phenolic compounds. The evidence-based knowledge presented in this paper is useful to support risk analysis processes in the treated wastewater chain to protect human health from exposure to undisposed waste.

Keywords: paracetamol; photolysis; total phenolic content; e-beam; cathodoluminescence; transformation; thin layer chromatography

Introduction

The freshwater shortage has become a reason for saving water resources all over the planet [1, 2]. To solve this problem, various countries are increasingly forced to implement recycling and secondary use of water [3, 4]. However, it turned out that treatment facilities that use outdated technologies for removing pollutants do not cope with wastewater treatment properly [4-6]. The widespread production and use of pharmaceuticals results in their release into the environment [7, 8]. The main sources of pharmaceutical pollution are waste from livestock farms, industrial waste from pharmaceutical production, hospital waste from medical institutions and wastewater from domestic treatment plants [9, 10]. Residual amounts of pharmaceuticals have been found in environmental water samples [11, 12]. Ultraviolet-visible (UV-Vis) spectroscopy is becoming a popular method for water quality monitoring because it provides continuous measurements and is very sensitive to the properties of the object being studied [12, 13]. Phenol and its derivatives are widely used in the production of drugs including antimicrobials, anti-inflammatory medicines, antispasmodics, antipyretics, laxative sand adrenomimetics, as well as vitamins [14]. The greatest contribution to phenolic pollution of water is made by anthropogenic activity [15, 16]. Increased concentrations of phenol and its derivatives become hazardous to living organisms, since phenols tend to persist in the environment and accumulate in bottom sediments [17]. Excess phenols in a living organism promote the development of cancer cells, disrupt the endocrine system, cause genetic defects, and damage the immune system, central nervous system tissues, and internal organs [18]. Therefore, it is necessary to control the residual amount of these substances in wastewater after purification in treatment facilities in order to reduce the environmental impact. Traditional technologies are used to purify wastewater from pollutants: settling, filtration, adsorption, coagulation-flocculation, advanced oxidation processes, and biological processes [19, 20]. The use of electron beam installations has great potential for reducing the concentration of unwanted pollutants [21]. Comparing the energy requirements of the degradation processes, radiolysis was found to be the most economically feasible method, requiring 1–2 orders of magnitude less energy than UV/VUV, VUV, and UV photolysis [22, 23].

The choice of UV sources for the study of paracetamol photolysis was as follows and is determined by their unique properties in terms of energy, penetrating ability and therapeutic potential. KrCl excilamp was taken as an effective tool for simultaneous purification and disinfection of aquatic environments due to its generally recognized ability to destroy organic molecules in water. But at the same time, its supposed lower penetrating ability into living tissues compared to traditional UV-C (254 nm) reduces the risk of undesirable side effects for biological systems. Xe_2 excilamp emits in the vacuum UV range, which allows destroying even the most persistent organic molecules, as well as generating ozone, enhancing water disinfection. UVB-04 irradiator (UV-B, 280-315 nm) can play an important role in photodynamic processes. In our study, we will compare the effects of the above UV radiations for the paracetamol degradation in water and select the optimal strategy for the treatment of contaminated water environments.

The aim of the work is to study the influence of UV and e-beam irradiation on the total phenolic content (TPC) after paracetamol transformation using Folin-Ciocalteu reagent, UV-Vis and fluorescence spectroscopy, cathodoluminescence and thin layer chromatography methods.

Materials and Methods

Chemicals and Reagents

The object of the study was paracetamol with a guaranteed purity of 99%, which was purchased from Central Drug House (P) Ltd. Co. (CAS. 103-90-2, New Delhi, India). Distilled water was obtained in a VOC-Parkand Ri Osoт Merck (MILLIPORE) Milli-Q (Darmstadt, Germany) water purification system. To obtain a matrix solution of paracetamol at a concentration of 1 mM, a dry sample weighing 30.23 mg was dissolved in 200 ml of distilled water with the use an ultrasonic stirrer at a temperature of

40 °C for 2 hours.

To determine TPC in the mixture of paracetamol transformation products, Folin-Ciocalteu reagent synthesized by Central Drug House (P) Ltd. Co. (No. 251567.1609, Pan Reac Applichem, New Delhi, India) was used. An aqueous Na_2CO_3 (CAS 497-19-8, 99.5-100.5%, CDH, New Delhi, India) solution with a soda ash3 content of 20 % was prepared immediately before the experiment. Gallic acid with a guaranteed purity of at least 98% purchased from the commercial company DIAM (CAS 149-91-7, D149917.0100, New Delhi, India) was used as a standard for the calibration curve.

Instruments and Apparatus

The absorption spectra of aqueous paracetamol solutions before and after irradiation were recorded on VARIAN Cary 5000 UV-VIS-NIR (AgilentTech Co., USA-Netherlands-Australia) and Shimadzu UV-1700 (Shimadzu Inc., Kyoto, Japan) spectrophotometers at room temperature in the range from 200 to 800 nm. To record the absorption and fluorescence spectra and determine the TPC before and after irradiation with e-beams, the solution was always diluted with distilled water by 10 times. Fluorescence spectra were obtained using a VARIAN Cary Eclipse spectrofluorimeter (AgilentTech Co., USA-Netherlands-Australia). A quartz cuvette with an optical path length of 1 cm was used for measurements.

Photoreactors

Stationary Photoreactor

A stationary reactor was assembled to study the effect of UV radiation of different wavelengths and powers on paracetamol solutions. The setup included a UV source, a magnetic stirrer, and a beaker with a paracetamol solution (Supplementary materials, Figure S1). A KrCl excilamp with an emission wavelength of 222 nm and a bactericidal UV irradiator (UVb-04) emitting in the wavelength range from 180 to 275 nm were used as UV sources [24]. An aqueous paracetamol solution with a volume of 90 ml and a paracetamol concentration of 0.05 mM was irradiated in glass beakers with a diameter of 4.6 cm at room temperature. The distance from the UV radiation outlet window to the surface of the solution was 4 cm. The control irradiation times were 0, 1, 2, 4, 8, 16, 32, 64, and 128 minutes. To keep the solution volume constant, 2 beakers were irradiated simultaneously. To carry out the analysis, an aliquot was taken from the test beaker and, at the same time, the same amount was added from the second beaker with control solution.

Flow Photoreactor

In a flow photoreactor, the solution was irradiated with a vacuum-ultraviolet Xe_2 excilamp, emitting at a wavelength of 172 nm (Supplementary materials, Figure S2) [24]. For irradiation, an aqueous paracetamol solution with a volume of 500 mL and a drug concentration of 0.05 mM was taken. The control time was 0, 1, 2, 4, 8, 16, 32, 64 and 128 min. For analysis, samples (2 mL) were taken from the flask, and 2 ml of the control solution were added to it to maintain the volume of the studied solution. The radiation energy densities of the UV sources have been calculated previously [25] and their values are given in the Supplementary material in Table S1.

e-beam Irradiation

The irradiation was carried out using a vertical electron beam from a RADAN-300 generator installed in the quantum electronics laboratory (Institute of Electrophysics, Ural Branch of the Russian Academy of Sciences, Yekaterinburg, Russia) [26]. The experimental setup for studying the effect of an electron beam on solutions and solids is described in detail in [27-29]. The paracetamol solutions with a volume of 1 mL and a drug concentration of C = 1 mM were irradiated by pulsed electron beams with a pulse duration of 2 ns, an average electron energy of 170 keV, a current density of 130 A/cm^2, and an energy density in an e-beam pulse of 44.2 mJ/cm^2. The number of irradiation pulses with a repetition rate of 1 Hz varied from 50 to 3200. The irradiated samples were diluted with distilled water to reduce the paracetamol concentration to 0.1 mM enabling the recording of absorption and fluorescence spectra.

Method for determination of Total Phenol Content with Folin-Ciocalteu Reagent

The TPC was measured according to the well-known Folin-Ciocalteu (FC) method [30-34]. The TPC was estimated colorimetrically using a calibration curve, which represents the dependence of the absorption at a wavelength of 765 nm on the concentration of the standard sample in the reaction mixture. The gallic acid in water was used as a standard.

In this work, the FC method was applied in the following modification: before the experiment, the FC reagent was diluted with distilled water in the ratio of 1:10. 1 ml of an aqueous paracetamol solution and 1 mL of the FC reagent were successively mixed (1:10), shaken, kept for 5 minutes, and then 1 ml of an aqueous solution of 20 % Na_2CO_3 was added. The solutions were kept in the dark for 30 minutes. The same procedure with gallic acid was carried out to construct the calibration curve. Solutions at concentrations of 1.7, 3.4, 5.1, 6.8, 8.5, 10.2, 11.9, 13.6, 15.3 μg/mL were prepared in duplicate. The absorbance value for each solution was determined (Supplementary materials, Figure S3a) at 765 nm. All measurements were performed three times. The average absorbance of all series was used to construct the calibration curve (1) (Supplementary materials, Figure S3b). The resulting set of points was approximated by a regression line:

$$Y = 0.0365 + 0.0013 \quad (1)$$

with the determination coefficient $R^2 = 0.99$.

The concentration of gallic acid in each sample was calculated from the regression equation (1) using their absorbance. The results were converted to TPC as milligrams of gallic acid equivalent per gram of dry sample weight (mg GAE/g) using equation (2):

$$TPC\,(mg\ GAE/g) = C_{GA} \times \left(\frac{V}{m}\right) \quad (2)$$

where C_{GA} is the concentration of gallic acid determined from the calibration curve (1) in μg/mL, V is the total volume of the sample in (mL), m is the mass of the test substance (mg).

To establish the effect of the water matrix, a series of aqueous paracetamol solutions with concentrations from 0.01 to 0.1 mM were prepared for reaction with the FC reagent in accordance with the above procedure. After incubation, absorption spectra were recorded in the range of 400-800 nm (Supplementary materials, Figure S4a). Based on the obtained experimental data, the dependence of the absorption intensity at 765 nm on the concentration of paracetamol in water was constructed (Supplementary materials, Figure S4b). This dependence has a linear character in the studied concentration range, which guarantees the accuracy of the results for TPC calculations in solutions after irradiation.

Separation of Paracetamol Transformation Products by Thin Layer Chromatography

The separation of the mixture components after irradiation of paracetamol was carried out by thin layer chromatography (TLC) (Supplementary materials, Figure S5). During separation, the substances form adsorption zones on the sorbent surface in the form of round, elliptical spots or stripes [35]. Silufol brand TLC plates (Kavalier Sázava, Czech Republic) representing a SiO_2 adsorbent layer with an inert inorganic fluorescent indicator F254 on an aluminum substrate were used. The plates thickness was 0.093 μm and the pore size was 60 Å.

In order to determine the TPC after irradiation on thin layer solid-phase paracetamol, a 2.54 cm diameter section of the adsorbent was left on the plate, onto which 100 μl of an ethanol paracetamol solution (paracetamol concentration C = 10 g/l) was applied. To eliminate the "edge effect", the sorbent was removed from the side edges of the plates leaving an uncovered substance areas. After ethanol evaporation, the plates were irradiated. Extraction of paracetamol from the plates was carried out using 2 mL of water. The resulting solution was diluted to a paracetamol concentration of 0.01 g/L. 1 mL of the final solution was taken for performing the reaction with the FC reagent.

To separate paracetamol transformation products after irradiation, the following method was used: 4 μL of an ethanol paracetamol solution (C = 10 g/L) was applied to a 6 6 cm TLC plate using a syringe. For control, the solution was applied to two areas with a distance of ~1.5 cm between them. The irradiation of the plate with the applied paracetamol layer was carried out in a stationary reactor. The distance from the UV source to the plate surface was 4 cm. The eluent was prepared from a mixture of 13 mL chloroform and 0.8 mL ethyl alcohol. The plates with applied drops before of irradiated or non-irradiated paracetamol were placed in a chromatographic chamber with an eluent and covered with a hermetically sealed lid. The plates were kept in the chamber for 10 minutes. After evaporation of the eluent from the plate, the separation of the components was observed under a UV lamp with an operating wavelength of 254 nm.

The position of each moving zone on a TLC plate is characterized by the value of retention factor R_f (Cai 2014). Since measurement of this value in practice is challenging, R_f is determined experimentally as the ratio of the distance *l* traveled by the substance from the sample application point to the center of the spot to the distance *L* traveled by the eluent from the starting line its front line in the same time (Supplementary materials, Figure S6).

Results and Discussion

Pulsed Cathodoluminescence Spectrum of Paracetamol in Water

The cathodoluminescence spectra of the aqueous paracetamol solution were recorded in the range from 350 to 900 nm (Figure 1). In the spectrum of pulsed cathodoluminescence of the aqueous paracetamol solution, no new bands appear when compared with the background glow (Figure 1, black curve). This indicates that the aqueous paracetamol solution does not luminesce in the range of 350÷900 nm when irradiated with electrons. This glow belongs to the radiation of the air environment above the solution.

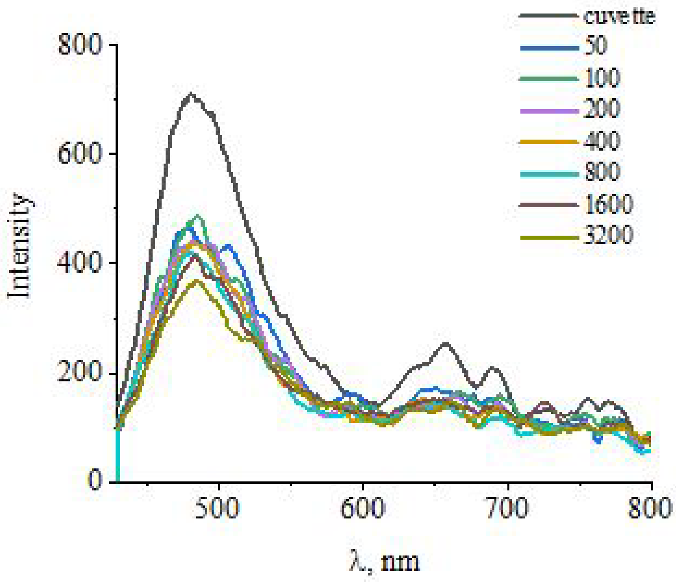

Figure 1: Pulsed cathodoluminescence spectra of an aqueous solution of paracetamol (C = 1 mM). The numbers in the figure indicate the number of e-beam pulses

With an increase in the number of e-beam irradiation pulses from 50 to 3200, a decrease in the intensity of the bands in the region of 480 and 650 nm was recorded (Figure 1), associated with the absorption of air radiation by an aqueous solution of paracetamol. An increase in the number of irradiation pulses is accompanied by a weakening of the intensity of the air spectral lines, which indicates that there is an effective transformation of paracetamol in water after the e-beam exposure.

The absorbed dose was estimated using the formula (x):

$$D = \frac{E}{\rho S d_e} \quad (3)$$

where E is the energy absorbed by the substance. Since the proportion of paracetamol in the solution is small, ρ=1 g/cm^3 is the density of water; S=1 cm^2 is the unit irradiation area, de is the penetration depth of electrons with an energy of 170 keV into water and was about 300 µm. For one pulse of the electron beam at an energy density of 44.2 J/cm^2, the absorbed dose was about 10 kGy.

Study of Paracetamol Transformation in Water by UV and E-Beam Radiation Using Absorption Spectroscopy

As a result of exposure to UV radiation, the initial compound dissociates, forming various photoproducts. With increasing irradiation time, the photoproducts accumulate, interact with each other, and undergo transformation. The changes that occur in the solution during irradiation are well illustrated by the absorption spectra of paracetamol in water (Supplementary materials, Figure S7). After irradiation with KrCl excilamp for up to 8 min, the absorption at a wavelength of 243 nm slightly increases (Figure 2a, black curve). Then it slightly decreases, which is the result of the transformation of the initial compound (Figure S7a). In the region of 280 nm, an absorption band appears in the form of an inflection. The intensity of this band is observed to increase with the irradiation time (Figure 2b, black curve), indicating the accumulation of the formed photoproduct. An increase in absorption intensity at wavelength of 380 nm is also recorded, which corresponds to the accumulation of the photoproduct (Figure 2c, black curve).

The absorption data has shown that the efficiency of phototransformation is influenced by the radiation source. Therefore, depending on the chosen exposure souse photoproducts of different nature may be formed. This is confirmed by the observed changes in the absorption spectra after irradiation of an aqueous solution of paracetamol with a UVb-04 lamp (Supplementary materials, Figure S7b). After irradiation with a UVb-04 lamp for up to 128 min, an increase in absorption intensity in the 380 nm region was recorded (Figure 2c, red curve). This indicates the accumulation of the final photoproduct.

A Xe_2 excilamp was chosen because it emits photons with shorter wavelength and its radiation energy density is higher than those for the KrCl and UVb-04 lamps (Supplementary materials, Table S1). Therefore, a significant transformation of paracetamol was recorded (Supplementary materials, Figure S7c, Figure 2, blue curve). The bands at wavelengths of 194, 243 and 280 nm in the absorption spectrum were chosen to be analytical. In the absorption spectra after e-beam irradiation, a decrease in intensity at these wavelengths was observed (Figure S7d, Figure 2, green curve). No new bands were recorded in the absorption spectra, but after 3200 e-beam pulses, the band at 194 nm broadened and its intensity increased. This may be a result of accumulation of the final product of paracetamol transformation (Supplementary materials, Figure S7d, Figure 2, green curve).

Analysis of changes in the absorption spectra of irradiated paracetamol in water (Figure 2) showed that in the region of 243 nm a drop in the absorption intensity is recorded for all exposure sources, including UV radiation and e-beam. This indicates that paracetamol decomposes (Figure 2a). Under the action of KrCl and UVb-04 lamps, accumulation of a photoproduct absorbing in the region of 280 nm was recorded (Figure 2b, black and red curves). Only after irradiation with a UVb-04 lamp the final photoproduct absorbing in the region of 380 nm is manifested in the paracetamol solution (Figure 2c, red curve). Under the action of Xe_2 excilamp radiation, intense formation of photoproducts absorbing in the region of 380 nm is recorded after 2 min of irradiation (Figure 2c, blue curve). And after 60 min of Xe_2 irradiation there was an absorption increase in the region of 280 and 380 nm (Figure 2b and 2c, blue curve). Efficient transformation of paracetamol in water (its conversion was 93 %) and its photoproducts was achieved after 128 min of Xe_2 excilamp irradiation in a flow photoreactor. After 53 min of e-beam irradiation (Figure 2, green curve) the conversion of paracetamol was 92%. Moreover, the formation of transformation products absorbing in other spectral regions was not registered.

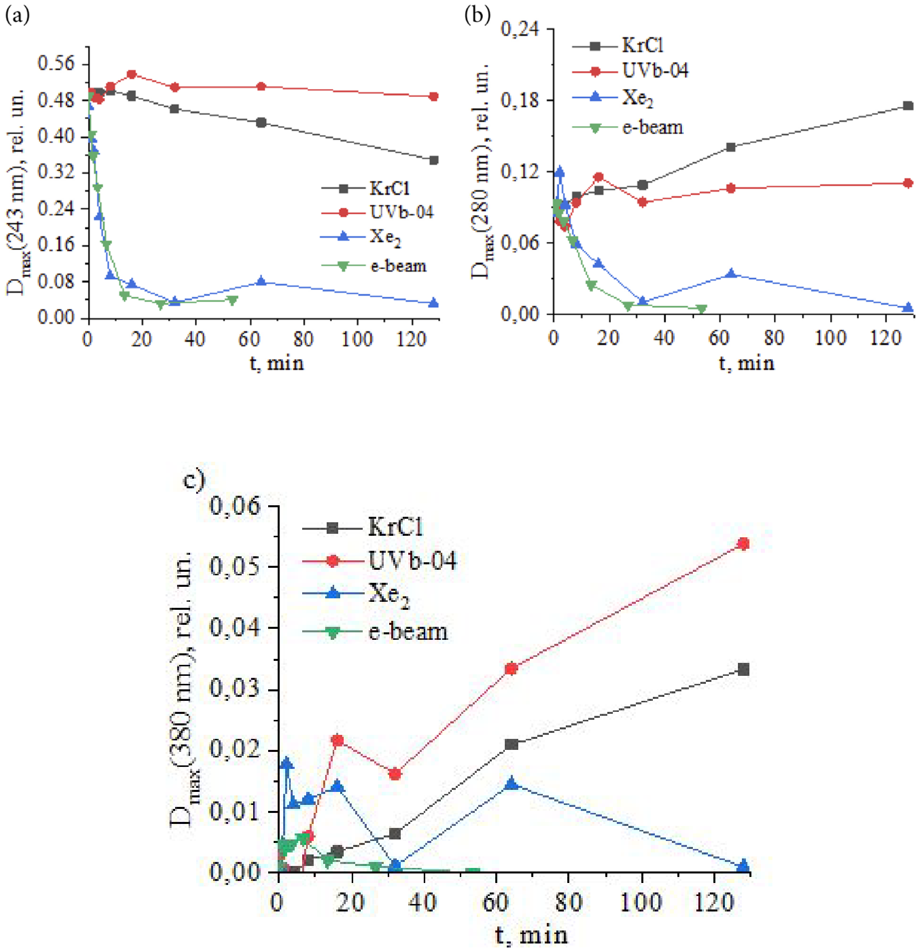

Figure 2: Change in absorbance at different wavelengths depending on time and radiation source: 243 nm (a), 280 nm (b) and 380 nm (c)

Study of Paracetamol Transformation in Water by UV and E-Beam Irradiation Using Fluorescence Spectroscopy

Fluorescence spectra data obtained for the paracetamol transformed in water under UV and e-beam exposure is shown in the product formation diagram (Figure 3).

The study of fluorescence spectra after exposure to UV sources was conducted for the range from 300 to 550 nm. The product fluorescing in the 370 nm region accumulates and remains in solution after 128 min of irradiation with a UVb-04 lamp (Figure 3, pink columns). The product fluorescing in the region of 425 nm accumulates up to 8 min of irradiation with a KrCl lamp (Figure 3, green columns). Then the fluorescence intensity decreases, which indicates the decay of this photoproduct. Irradiation with a Xe_2 excilamp also leads to the appearance and accumulation of a photoproduct fluorescing in the region of 430 nm (Figure 3, blue columns). It is worth noting that the same product with fluorescence at 430 nm is most likely accumulates and transforms after both the Xe_2 excilamp radiation and the e-beam irradiation.

The fluorescence excitation spectra of aqueous solutions of paracetamol before and after UV radiation and e-beam exposure are shown in Figure 3. The data analysis shows that the compound, which is a product of paracetamol transformation after KrCl irradiation and fluoresces with a band of about 425 nm, absorbs in the region of 235, 290 and 330 (inflection) nm. In aqueous solution of paracetamol being exposed to a Xe_2 excilamp radiation and e-beam, there is the formation of a compound responsible for the fluorescent band in the region of 430 nm and the absorption bands at 230, 340 and 380 (inflection) nm.

The absence of luminescence in irradiated solutions does not necessarily indicate complete degradation of paracetamol. Rather, it indicates a change in its molecular structure, resulting in a loss of luminescence. Intermediate degradation products may be formed that do not luminesce but are still present in the solution. Additional analytical methods such as chromatography or mass spectrometry are needed to confirm complete degradation.

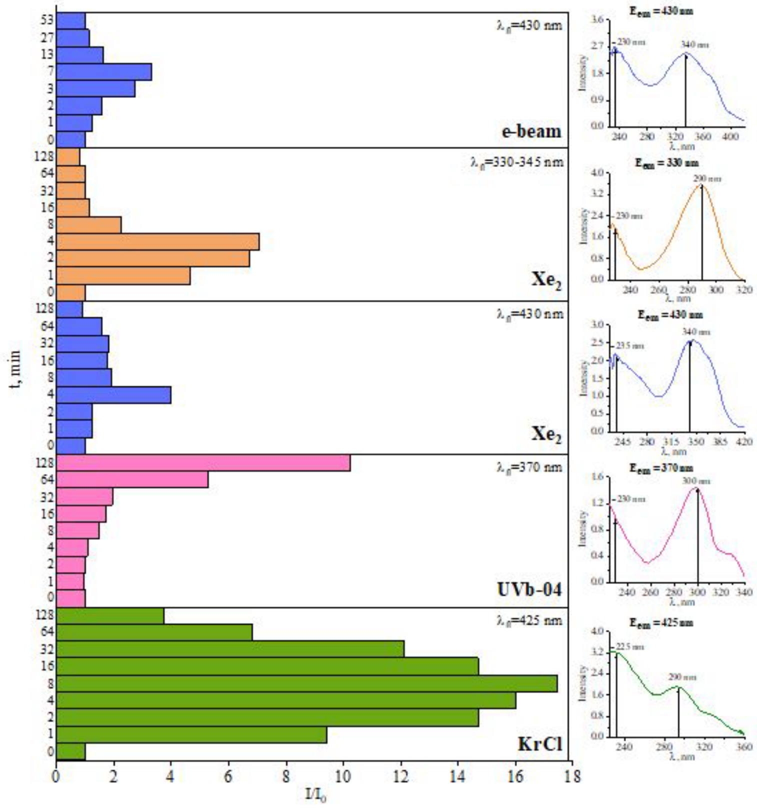

Figure 3: Diagram of the formation of fluorescent photoproducts depending on the source and time (t, min) of irradiation. λ_{fl} is the wavelength in nm of the fluorescence band maximum; I is the intensity of the fluorescence band of the transformation paracetamol product; I_0 is the fluorescence intensity of an aqueous paracetamol solution before irradiation. On the right are the fluorescence excitation spectra of the aqueous paracetamol solutions after irradiation at different emission wavelength

After an aqueous paracetamol solutions has been exposed to a Xe_2 excilamp radiation, the fluorescent band in the region of 330-345 nm (Figure 3, orange columns) appears due to in the presence of the compound with absorption at 230 and 290 nm. The fluorescent band in the region of 370 nm (Figure 3, pink columns) after UVb-04 exposure to an aqueous solution of paracetamol is formed by a compound with absorption at 230, 300 and 330 (inflection) nm.

TPC in Aqueous Paracetamol Solution after UV and E-Beam Irradiation

The structure of the paracetamol molecule includes a phenol fragment. For this reason, it is logical to assume that the transformation products of paracetamol can also be phenol derivatives. Indeed, the authors [36, 27] showed using radiolytic and UV experiments that the hydroxyl radical effectively destroys paracetamol molecules to hydroxylated derivatives.

The absorption spectra of irradiated and non-irradiated aqueous paracetamol solutions with a FC reagent are given in Supplementary materials, Figure S8. The TPC values in mg GAE/g are presented in Supplementary materials, Table S2. Based on the data obtained, a diagram of the TPC change in aqueous paracetamol solutions depending on the time and source of irradiation was constructed (Figure 4).

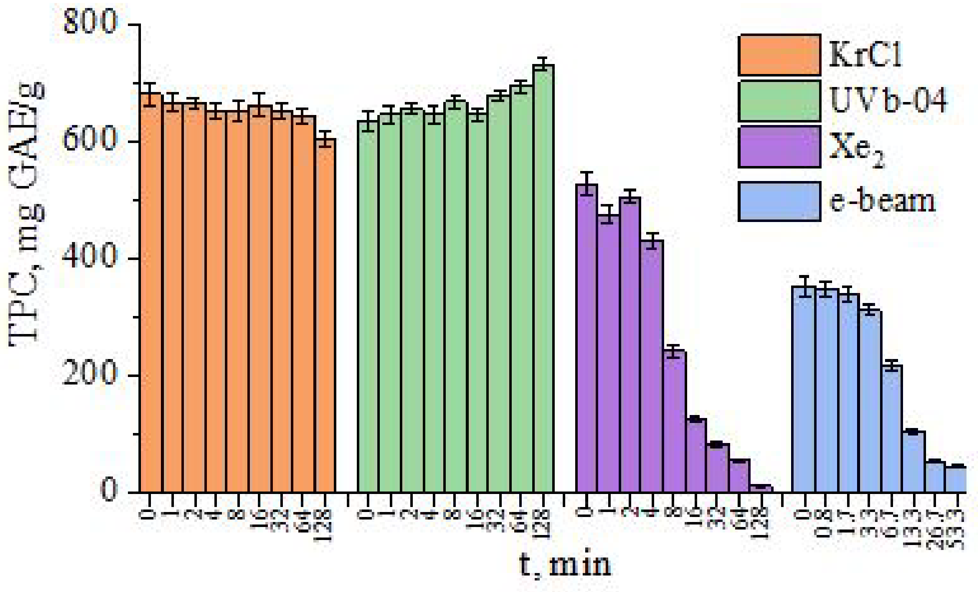

Figure 4: The TPC in aqueous solutions of paracetamol depending on time and source of irradiation

Figure 4 shows that the effective loss of paracetamol transformation products with phenolic structure occurred after irradiation with a Xe_2 excilamp and e-beams (Figure 4, purple and blue columns). After 53 min of e-beam irradiation, TPC decreased by 8 times (Figure 4, blue column). After irradiation with a UVb-04 lamp, TPC increased by ~100 mg GAE/g from TPC value for the control solution (Figure 4, green column). According to the data (Figure 4, orange column), after irradiation with a KrCl excilamp, TPC changed almost insignificantly and remained at the level of 603.78 ± 12.23 mg GAE/g. Radiation of a Xe_2 excilamp turned out to be quite effective for photolysis of paracetamol in water. After 128 min of irradiation with a Xe_2 excilamp, the TPC decreased by 54 times to a level of 9.76 ± 0.82 mg GAE/g and turned out to be minimal compared to other sources (Figure 4).

Analysis of Paracetamol Transformation Products after Irradiation with A Uvb-04 Lamp Using Thin Layer Chromatography

When plates for TLC coated with an ethanol paracetamol solution with a volume of 4 L (paracetamol concentration 1 g/L) were irradiated with a UVb-04, the formation of 5 photoproducts was detected (Figure 5). The products were formed at different time intervals. This indicates several phototransformation pathways. For a more in-depth analysis of the formation of paracetamol transformation products, through the TCL method the R_f retention coefficient values were calculated for each of the detected photoproducts (Figure 5b). The R_f values allowed us to estimate the degree of separation and the number of photoproduct types on the TCL plate.

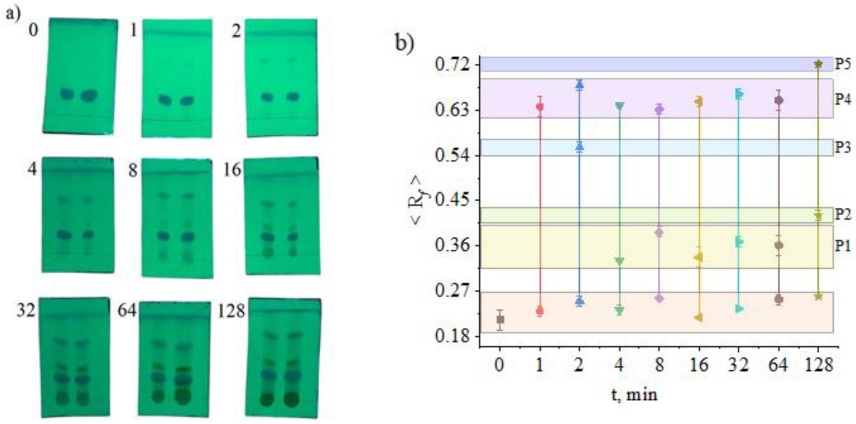

Figure 5: TLC plates with applied paracetamol at C = 10 g/l before and after irradiation with a UVb-04 lamp (a) and the formation of paracetamol phototransformation products (b). The number near the plate corresponds to the irradiation time in min. The eluent was a mixture of chloroform:ethanol in a ratio of 13:0.8

The product 1 (P1) with $R_f = 0.348 \pm 0.033$ is formed at the early stages of irradiation at about 4 min. This indicates that P1 has similar properties to the original paracetamol with $R_f = 0.232 \pm 0.042$, but with some changes in polarity, which may indicate the nature of the initial phototransformation reactions. Accumulation of product 2 with $R_f = 0.421 \pm 0.01$ (P2, Figure 5c) was recorded only after 128 min of irradiation. This indicates that a longer exposure is necessary for the formation of P2. P2 probably has a higher polarity compared to paracetamol or it has a complex structure, for example, dimeric or oligomeric. The product 3 (P3) with $R_f = 0.556 \pm 0.01$ was recorded at about 2 min of irradiation with a UVb-04 lamp (Figure 5c). This may be an intermediate product that is quickly transformed into a more stable compound. The accumulation of product 4 (P4) with $R_f = 0.647 \pm 0.02$ occurred during the period from 1 to 64 minutes of irradiation exposure. The R_f indicates the presence of functional groups that are formed as a result of photochemical reactions, such as hydroxylation. The product 5 (P5) with $R_f = 0.722 \pm 0.02$ remains after 128 min of irradiation, which may indicate the final stage of phototransformation, in other words, when paracetamol was transformed into the final stable compound.

Analysis of TPC and Final Products of Paracetamol Transformation by Thin Layer Chromatography after UV And E-Beam Irradiation

TPC and final products of paracetamol transformation after irradiation with different sources were compared. For this purpose, 100 μL of paracetamol solution in ethanol (C = 10 g/L) were applied to TLC plates on a surface area with a diameter of 2.54 cm and the alcohol was allowed to evaporate. The plates were then exposed to UV and e-beam irradiation for 128 min, 100 and 1600 pulses, respectively. After that, the solution obtained through elution from the TLC plate were analyzed (Figure 6a) and the R_f values for the paracetamol transformation products were calculated depending on the irradiation time and the increase in the number of irradiation pulses. Under exposure to a UVb-04 irradiator, three final products of paracetamol transformation were showed to be formed (Figure 6a, P1, P6 and P7).

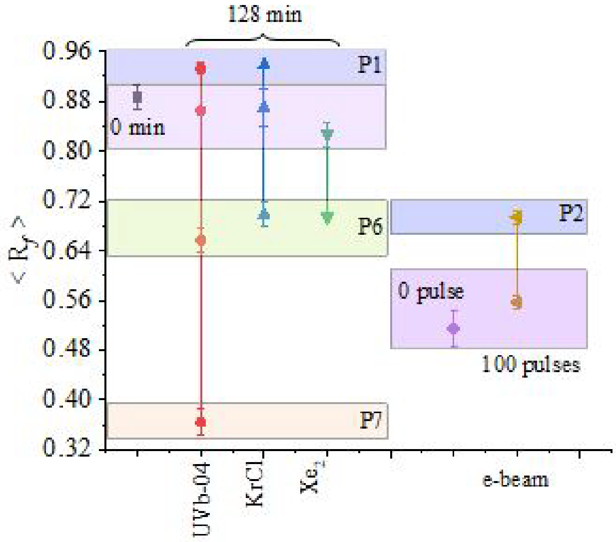

Figure 6 The formation of paracetamol transformation products eluted from a TLC plate being exposed to UV and e-beam irradiation. The eluent for the samples was a mixture of chloroform:ethanol in a ratio of 10:2

After irradiation with a KrCl excilamp there were two final photoproducts (Figure 6a, P1 and P6). At the same time after 128 min of irradiation with a Xe_2 excilamp only one photoproduct P6 remained on the plate (Figure 6a). After the e-beam irradiation there was a transformation product P2 (Figure 6a) on the TLC plate.

Analysis of paracetamol transformation showed (Figure 6) that with increasing UV or e-beam irradiation time there was an accumulation of products. This indicates that long-term irradiation leads to the decomposition of paracetamol and the formation of aromatic compounds.

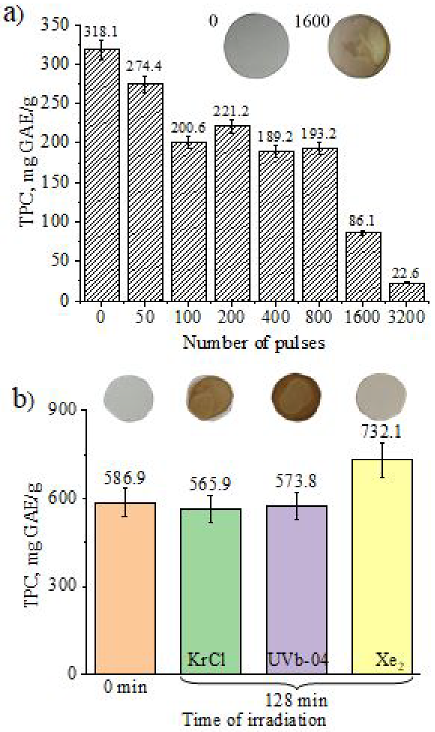

Figure 7: TPC in paracetamol transformation products eluted from the TCL plates with distilled water: from 0 to 3200 pulses e-beam irradiation (a), after 128 min UV irradiation (b). The appearance of the plates before and after irradiation is shown in circles

TPCs in paracetamol transformation products eluted from the TCL plates with distilled water were also obtained. A diagram of the TPC change was plotted for comparison (Figure 7). The appearance of the TLC plates with paracetamol applied before and after irradiation is shown in Figure 7. The change in color of the plates indicates that new compounds have been formed.

The increase in TPC under Xe_2 excilamp irradiation indicates the formation of new phenolic compounds as a result of paracetamol transformation. For example, this may indicate the formation of hydroxylated derivatives of paracetamol. The decrease in TPC under the influence of other UV sources (KrCl and UVb-04 lamps) indicates weak further degradation of phenolic compounds. Under the influence of the e-beams, degradation of both paracetamol and phenolic compounds was recorded. The TPC after e-beam irradiation was reduced by 15 times and it reached 22.6 ± 0.3 mg GAE/g.

Conclusions

This work was devoted to the study of the efficiency of paracetamol transformation in water and applied to TLC plates in its solid state under the action of UV and e-beam irradiation. It was found that in an aqueous solution, the photolysis of paracetamol proceeded most effectively under Xe_2 excilamp radiation with a conversion of 93 %. As a result, the TPC decreased to a level of 9.76 ± 0.82 mg GAE/g after 128 minutes of Xe_2 excilamp irradiation. A similar result was obtained under pulsed e-beam irradiation. However, to achieve an equivalent result, 2 times less exposure time was required, since the e-beam radiation has significantly higher energy density than a Xe_2 excilamp radiation. It was found that the conversion and TPC in the e-beam irradiated aqueous paracetamol solution were 92 % and 42.84 ± 1.63 mg GAE/g, respectively. The highest TPC in an aqueous paracetamol solution (up to 730.85 ± 10.78 mg GAE/g) was recorded after 128 minutes of exposure to UVb-04 lamp radiation.

Analysis of the absorption, fluorescence and fluorescence excitation spectra showed that the composition of the products depends on the selected radiation source. This conclusion is confirmed by the data obtained using the TLC method. The products of paracetamol transformation in the solid state were detected, which were preserved after prolonged irradiation. It was shown that under the action of the e-beam, the degradation of solid-phase paracetamol applied to TCL plates and its transformation products occurred. The decrease in TPC after e-beam irradiation was 15 times to a level of 22.6 ± 0.3 mg GAE/g. The available results suggest that, apparently, after Xe_2 and e-beam treatment, paracetamol that may be present in the treated wastewater will be in the form of residual phenolic compounds. The evidence-based knowledge presented in this paper is useful to support risk analysis processes in the treated wastewater chain to protect human health from exposure to undisposed waste.

CRediT Authorship Contribution Statement

O.N., I.F. and V.S. conceptualized and designed the experiments. E.B., N.B. and A.M. performed the experiment. O.N., I.F., V.S. and E.B. contributed to critical discussion and data interpretation. O.N. acquired fnancial support for this work leading to publication. O.N. and V.S. supervised the whole process and provided with resources and improved intellectual content. O.N., E.B. and N.B. drafted the original manuscript and I.F., V.S. and A.M. reviewed and edited the manuscript. All authors have read and agreed to the published version of the manuscript.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary Materials

https://www.annexpublishers.com/articles/JERC/4102-Supplementary-Materials.pdf

Data Availability

The data that support the findings of this study are available from the corresponding author, upon reasonable request.

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