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Caffeine degradation in water by gamma irradiation, ozonation and ozonation/gamma irradiation

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Abstract. Aqueous solutions of caffeine were treated with ozone and gamma irradiation. The amounts of remaining caffeine were determined after solid phase extraction as a function of absorbed dose and ozonation time. In addition to this, some important parameters such as inorganic ions, chemical oxygen demand (COD) dissolved oxygen and total acidity changes were followed. Caffeine (50 ppm) is found to be completely decomposed at 3.0 kGy and 1.2 kGy doses in the absence of H_2O_2 and in 1.20 mM H_2O_2 solutions, respectively. In the case of gamma irradiation after ozonation, 50 ppm caffeine was removed at 0.2 kGy when the solution was ozonized for 100 s at a rate of 10 g O_3 h^{-1} in 400 mL 50 ppm paracetamol solution.

Key words: caffeine • effect of ozone • radiolytic decomposition • advanced oxidation process (AOPs) • caffeine decomposition • COD change

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Introduction

Caffeine (3,7-dihydro-1,3,7-trimethyl-1H-purine-2,6--dione) is a natural purine compound and present in most drinks such as tea, coffee and cola nuts. The high consumption of these beverages focused most researchers on caffeine behaviour in aquatic media. Coffee and tea plants are the major sources of caffeine in which caffeine varies between 1 and 4% by weight [1, 2]. Caffeine is also an environmental problem for soil and water supplies [3–5]. Coffee and tea pulps, obtained when processing of tea and coffee, are disposed to the soil and discharged into the ground and underground water sources. These pulps contain some nutritional compounds such as carbohydrates, proteins [6] and some anti-nutritional factors such as caffeine and polyphenols which decrease the quality of nutritional value of the coffee pulp [7]. Caffeine also affects the quality of sleep [8, 9] and have negative affects on the health of the human beings reported in the literature. Caffeine decomposition is important for the health of the living organisms and environmental aspects because of its adverse effects. Conventional methods of caffeine removal are water decaffeination (caffeine is extracted to water then to solvent) solvent

extraction and supercritical carbondioxide extraction [10]. Organic chlorinated solvents or mixtures of these solvents are used for the extraction of caffeine from water and pulps [11] but organic chlorinated solvents are also another problem for the environment if not used properly and discarded carefully. Solubility of caffeine in water is 1.992 g/100 mL water at 24°C [12] relatively higher than most of the organic compounds and has to be removed from water.

Conventional water treatment methods include mechanical removal, filtration and activated sludge. These methods are not destructive technologies as irradiation treatment [13–17] for removal of some water soluble natural and industrial compounds like caffeine. Radiation technology has some advantages over the ones which are no radioactivity production during treatment, no waste, safe for personnel, environment and general public, economically competetive and with high efficiency. High-energy irradiation of water generates hydrated electrons (e_{aq}^-), hydroxyl radicals ($^\bullet OH$) and hydrogen radicals ($H^\bullet$) in water that interact with a wide range of pollutants [14, 18]. The interaction processes include decomposition of organic compounds, decolourization of dyes, redox reactions and other chemical reactions in addition to disinfection.

OH radical is the most powerful oxidant known to occur in water and hydrated electrons e_{aq}^- is the most powerful reductant formed during water radiolysis. Processes which generate hydroxyl free radicals to decompose pollutants effectively are referred as "Advanced Oxidation Processes" (AOPs) [19].

Ozone is also another powerful oxidizing agent which is used for drinking water and waste water treatment on a technical scale [20–23]. Decomposition of organic solutes with ozone follows two paths which are direct oxidation through the attack of ozone at the electron rich site of the solute and indirect oxidation that ozone produces hydroxyl radicals after radiolysis or photolysis. These radicals exhibit little solute selectivity and react very rapidly with organic and inorganic solutes.

When ozonized solution is exposed to high-energy radiation, the yield of hydroxyl free radicals is higher than each system alone because of two origins for hydroxyl free radicals, one of them is from water radiolysis and the other is from ozone decomposition during water radiolysis [13]. Some research groups studied and explained the reaction of ozone with radiolysis products of water [2, 20, 24–26].

Chemical oxygen demand (COD) is one of the important parameters for the aquatic environment. When it is not possible to detect the compounds and their amounts in aquatic samples, this method gives results about the degree of mineralization of organic wastes in waters.

Toxicity end points for aqueous solutions of caffeine were investigated with *Ceriodaphnia dubia*, *Pimephales promelas* and *Charaxes dilutus* by means of 48 h LC$_{50}$, 7-day LC$_{50}$ and 7-day LC$_{25}$ and reported as caffeine is not a threat for freshwater organisms with its current presence in the aquatic environment [27].

Radiolytic removal of caffeine is not being of interest in the literature with a great concern. In this study, caffeine, one of the most important natural and industrial pollutants is selected as a target compound because of its diverse effects on the human health and environment. To remove caffeine from water completely, irradiation and ozonation methods and their combinations are used. The main objective of this study is to examine the effect of gamma irradiation on the decomposition of aqueous caffeine and the synergic effects of hydrogen peroxide and preliminary ozonation of caffeine solutions. Hydrogen peroxide concentration was 1.20 mM which is the optimum condition for effective degradation of 50 ppm caffeine solution determined experimentally. Preliminary ozonized solutions were irradiated at 0.2 kGy irradiation dose and the results were compared with only ozonized caffeine solutions. Irradiation dose was selected as 0.2 kGy to examine the effect of gamma irradiation in the presence of ozone even if at low irradiation doses. The remaining caffeine and possible intermediates after treatment were observed with GC/MS and ion chromatography. Methyl ester of 2,4-DP is used as an internal standard for chromatographic quantitative analysis of caffeine. This novelty is useful for monitoring both 2,4-DP, which is a widely used herbicide still present in natural waters, after conversion of 2,4-DP to methyl ester (internal standard) and caffeine (a natural compound) in GC/MS conditions used.

Experimental

Materials

Caffeine, (from Aldrich, 99% purity), 2,4-dichlorophenoxypropionic acid (2,4-DP) as internal standard after conversion to methyl ester, (from Aldrich, 95% purity) were used without further purification. Stock standard solutions of caffeine and methyl ester of 2,4-DP were freshly prepared before injection and were mixed or diluted (if necessary) to prepare the adjusted amounts and stored in a refrigerator (4°C). Solvents: n-hexane (95% purity), methanol (99.5% purity), acetone (99%) were supplied from Merck. Dichloromethane, used as the solvent of caffeine were obtained from Fluka (99.9%). For ion chromatography, possible acid standards oxalic acid dihydrate (99%), acetic acid (99.7%) and formic acid were obtained from Sigma-Aldrich and BDH, respectively. Nitrite and nitrate standards are from Dionex seven anion standard II. Sodium carbonate used as mobile phase for ion chromatography is obtained from Dionex, 0.5 M sodium carbonate is diluted to 10 mM with deionized water. The chemicals used in the tests of formaldehyde and total acid yield are, formaldehyde (37%), acetylacetone (98%), ammonium acetate (98%), sodium hydroxide (97%) which were obtained from Merck, BDH, Sigma-Aldrich and Merck, respectively. Hydrogen peroxide (35%) is purchased from Riedel-de Haen. Chemicals for COD analysis are potassium dichromate ($\geq 99.5\%$), sulphuric acid (95–98%), silver sulphate, mercury(II) sulphate ($\geq 99.0\%$) are from Merck, ammonium iron(II) sulphate hexahydrate (Mohr salt) is from Riedel de-Haen, the constituents of ferroin indicator; 1,10-phenanthroline ($\geq 99.5\%$) and iron(II) sulphate pentahydrate ($\geq 99\%$) are from Merck and Riedel de-Haen, respectively. Potassium hydrogen phthalate ($\geq 99.5\%$) standard as a COD analyte is from Merck. Potassium iodide

(99.6%) for peroxide tests is obtained from Sigma. Sodium chloride and sulphuric acid for Fricke dosimeter are supplied from Merck. All chemicals were used without any further purification.

Gamma irradiation

Aqueous solutions of caffeine were irradiated in 200 mL open pyrex conical flasks without deaeration in a Gammacell 220 type γ-irradiator with a dose rate of 0.056 kGy/h in the presence and absence of ozone or hydrogen peroxide. 50 ppm caffeine solutions were ozonized at desired times and irradiated for 0.2 kGy and irradiated in 1.20 mM hydrogen peroxide. The dose rate of the gamma source was detected with the Fricke method at the beginning of the irradiations.

UV – visible spectroscopy

The absorbance values of unirradiated, irradiated and ozonized 50 ppm caffeine solutions were followed with a Varian Cary 100 model UV-Vis spectrophotometer at the maximum at 272 nm. Formaldehyde tests were examined with a UV-Vis spectrophotometer by recording maximum of complex registered at 412 nm [28] to see whether the formaldehyde is formed.

pH measurements

pH values of caffeine solutions were measured by an ISTEK NeoMet pH-200L model pH meter.

Ion chromatography

The determinations of possible aliphatic acids, nitrate and nitrite ions were performed using DX-3000 Ion Chromatography from Dionex, equipped with an electrochemical ultra anion self regenerating suppressor model ASRS 300, 4 mm, a conductivity detector set at 50 mA and an AG9-HC guard column with an analytical column IonPac AS9-HC, columns – Dionex Ionpac AS9-HC (4 × 250 mm) and AG9-HC (4 × 50 mm) set at 30°C. Cell heater temperature was 35°C. The mobile phase was 10 mM Na_2CO_3 with a flow rate of 1.000 mL/min under a pressure of 1800 psi. Samples and standards were injected with an autosampler Dionex AS-3000 as 20 μL from vials with a cut segment volume of 10 μL, the flush volume was 250 μL and the syringe speed was 4.

GC/MS analysis

The ozonized/irradiated caffeine solutions were analyzed with gas chromatography (GC-3900)/mass spectrometry (Saturn 2100T) system with an ion trap mass spectrometer from Varian Instruments (Sunnyvale, CA, USA) operated in the split mode. For chromatographic separation of caffeine and its intermediates (if any), a VF5-MS (30 m × 0.25 mm i.d.) column with a 0.25 μm film thickness was employed. Ion trap mass spectrom-

eter was operated in the electron ionization (EI) mode. The NIST library was used to detect possible intermediates, and also our own mass library was created with this program. The mobile phase helium (99.99%) was used at a flow-rate of 1 mL·min⁻¹. Caffeine is characterized by GC/MS by means of retention time and mass spectrum as well as the remaining caffeine was analyzed by following the retention time and mass spectrum.

Standards of caffeine solutions and treated samples collected in vials with dichloromethane after solid phase extraction were injected as 1.0 μL manually at a flow rate of 1.0 μL·s⁻¹. Mass spectrometer was calibrated weekly and known amounts of caffeine were injected twice a day to validate the calibration curve. Non-resonant wave form was used during analysis. The transfer line, manifold and trap temperatures were 280, 80 and 210°C, respectively. The analysis was performed with a filament and the multiplier delay was 3.0 min. The automatic gain control (AGC) was activated as an AGC target of 20 000 counts. Electrons were generated under 70 eV energy, while the emission current for ionization was set at 10 μA, and the axial modulation amplitude voltage was 4.0 V.

Extraction of caffeine and possible intermediates

Varian vacuum manifold system was used for solid phase extraction of caffeine and other possible intermediates from water. Varian octadecyl (C18) one way cartridges, end capped, 10 mL cartridge volume with 500 mg sorbent were purchased from Varian. The recovery was observed as higher than 90% for caffeine. Efficiency of the C18 cartridges were increased by eluting 6 mL n-hexane, then 12 mL methanol and 6 mL HPLC grade water, respectively before sample aspiration. 200 mL sample was eluted from the conditioned C18 cartridges with a flow rate of 5 mL/min and after sample aspiration, C18 cartridges were dried by purging nitrogen gas for 25 min. Caffeine and other possible intermediates were eluted to vials with 2.0 mL of dichloromethane.

Derivatization of internal standard 2,4-DP

2,4-DP samples were dissolved in methanol and acidified with concentrated sulphuric acid for catalyzed esterification. The acidified methanol solution is mixed enough for esterification and 10 mL of deionized water was added to this solution with sodium chloride to extract 2,4-DP methyl ester into hexane. Then, a desired amount of 2,4-DP methyl ester is prepared in hexane and mixed with caffeine standards and/or extracted samples from C18 cartridges for GC injections.

Ozone generator

Ozone was generated from atmospheric air by a prototype corona discharge generator (OPAL OGL-20, Turkey) with a production rate of 10 g O_3 h⁻¹. 400 ml 50 ppm caffeine solutions were ozonized in a 500 mL cylindirical pyrex reactor by bubbling the ozone/air mixture through a sinterized glass filter (pore size 50–80 mm)

at various ozonation times which were analyzed directly or transferred to pyrex bottles for irradiation.

Formaldehyde tests

Formaldehyde tests were performed by the Hantzsch method [28]. The formation of formaldehyde is controlled spectrophotometrically at λ_{max} = 412 nm by means of a calibration curve.

Determination of total acid yield

The total acid yield was measured after treatment with the titrimetric method by using 0.01 M NaOH, which is standardized against 0.01 M oxalic acid.

Determination of dissolved oxygen

WTW Microprocessor Oxi 3000 Oxygen Meter, which includes the membrane-type dissolved oxygen electrodes using a galvanic cell, was used to measure dissolved oxygen. The working electrode uses a noble metal (Ag), and the opposite electrode uses a base metal (Pb).

COD analysis

Behrotest® TRS 200 model COD instrument with a pyrex bottle set, heater and water bath was used for COD analysis which is based on an open reflux method [29]. After hydrogen peroxide test (iodometric), 50 mL of samples were transferred in pyrex bottles, heated at 155°C for 2 h with potassium dichromate, sulphuric acid, silver sulphate and mercury(II) sulphate. After cooling, the bottles are filled with water up to 100 mL and titrated with dilute Mohr salt for the change in ferroin indicator. Blank COD is determined with deionized water as the same procedure. COD value of potassium hydrogen phthalate (KHP) was checked with the same procedure to verify the method and standards.

Results and discussion

Caffeine, a target compound was irradiated under different conditions, including 1.20 mM hydrogen peroxide concentration, which is the optimum concentration of hydrogen peroxide to be used in this study. The amount of hydrogen peroxide was optimized for various hydrogen peroxide concentrations (0.6, 1.20, 1.80 and 2.40 mM) for 50 ppm caffeine solution and 0.5 kGy irradiation dose with a dose rate of 0.056 kGy/h. The amount of hydrogen peroxide lower than 1.20 mM is not enough to degrade caffeine efficiently in water. Similarly, a higher amount of hydrogen peroxide scavenges hydroxyl radicals with a rate constant k (20°C) = 3.1 × 10^{10} M^{-1}·s^{-1}. The reactions of hydrogen peroxide in irradiated aqueous solution are [30]

(1) $e^-_{aq} + H_2O_2 \rightarrow {}^\bullet OH$ k = 2.4 × 10^{10} (20°C)

(2) $H^\bullet + H_2O_2 \rightarrow {}^\bullet OH + H_2O$ k = 1.5 × 10^7 (20°C)

(3) ${}^\bullet OH + H_2O_2 \rightarrow HO_2^\bullet + H_2O$ k = 3.1 × 10^{10} (20°C)

(4) $2HO_2^\bullet + H_2O_2 \rightarrow HO_2^\bullet + O$
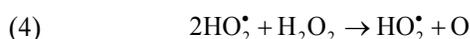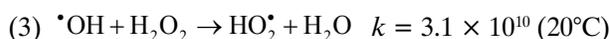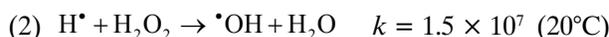
The total effect of the last two reactions are

(5) $2{}^\bullet HO + H_2O_2 \rightarrow O_2 + 2H_2O$
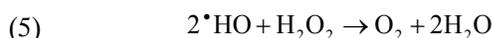
Reactions in water when exposed to ionizing radiation in the presence of oxygen are the following

(6) $H_2O \rightsquigarrow {}^\bullet H, e^-_{aq}, {}^\bullet OH, H_2, H_2O_2, H_3O^+, OH^-$ [31]

(7) ${}^\bullet H + O_2 \rightarrow HO_2^\bullet$ k = 1.9 × 10^{10} L·mol^{-1}·s^{-1} [31, 32]
                   k = 1.2 × 10^{10} L·mol^{-1}·s^{-1} [33]

(8) $e^-_{aq} + O_2 \rightarrow O_2^{\bullet-}$ k = 2 × 10^{10} L·mol^{-1}·s^{-1} [31, 34]
                   k = 1.9 × 10^{10} L·mol^{-1}·s^{-1} [33]

(9) $HO_2^\bullet \rightleftharpoons H^+ + O_2^{\bullet-}$ pK = 4.8 [35, 36]

(10) $HO_2^\bullet + O_2^{\bullet-} \rightarrow H_2O_2 + O_2$
                   k = 1.2 × 10^{10} L·mol^{-1}·s^{-1} [35]
                   k = 9.7 × 10^7 L·mol^{-1}·s^{-1} [37]

(11) $HO_2^\bullet + HO_2^\bullet \xrightarrow{2H^+} H_2O_2 + O_2$
                   k = 3.7 × 10^6 L·mol^{-1}·s^{-1} [36]
                   k = 8.3 × 10^7 L·mol^{-1}·s^{-1} [37]

(12) $O_2^{\bullet-} + O_2^{\bullet-} \xrightarrow{2H^+} H_2O_2 + O_2^\bullet$
                   $2k$ < 10 L·mol^{-1}·s^{-1} [36]
                   $2k$ = no reaction   [38]
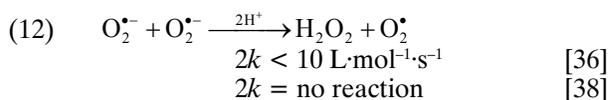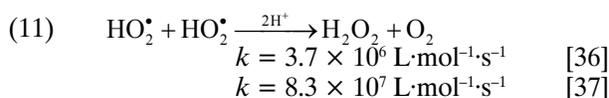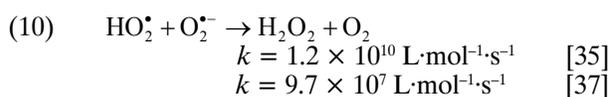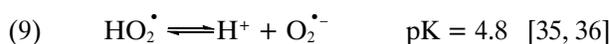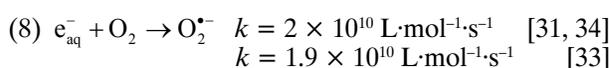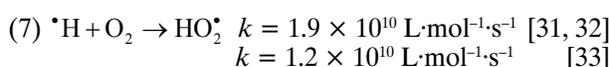
Figure 1 shows the change in UV-Vis spectra of irradiated and unirradiated 50 ppm caffeine solutions and percent decrease in absorbance at 272 nm [39] with irradiation dose. Hydroxyl radicals from hydrogen peroxide play an important role in the decomposition of caffeine. The absorbance at 272 nm disappeared completely at a 1.0 kGy irradiation dose in the presence of 1.20 mM H_2O_2, although it is at 1.5 kGy without H_2O_2. The addition of hydrogen peroxide (finally 1.20 mM) to unirradiated 50 ppm caffeine solution resulted in a decrease in the absorbance from 2.451 to 2.366 (almost 3.5% of decrease in absorbance).

Figure 2 shows the change in UV-Vis spectra of ozonized and ozonized/0.2 kGy irradiated 50 ppm caffeine solutions. Absorbance at 272 nm disappears readily with preliminary ozonation before irradiation since there are two strong hydroxyl radical sources – ozone and gamma irradiation. 0.2 kGy irradiation of ozonized solutions enhances the degradation efficiency of caffeine solutions.

Reactions and rate constants of these reactions of ozone and ozonolysis products in water are investigated by some authors and data are added to the literature [17, 40–42].

Reactions of ozone in irradiated water are:

– Propagation [24]

(13) $O_3 + O_2^- \rightarrow O_3^- + O_2$
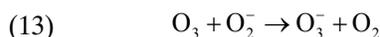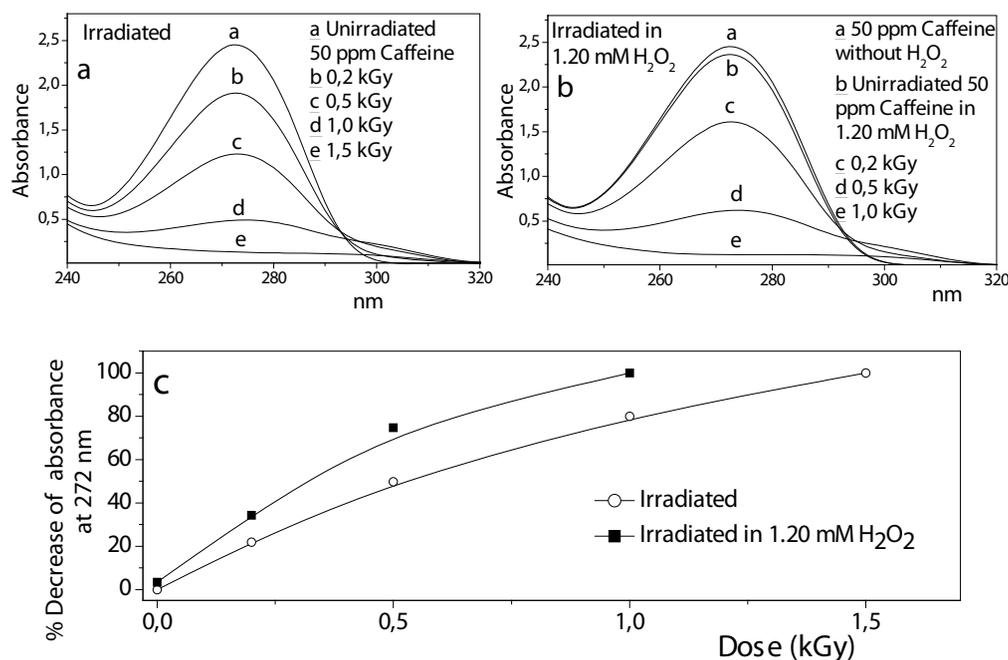
Fig. 1. Variation of the decrease of absorbance of 50 ppm caffeine as a function of irradiation dose at 272 nm (a) irradiated in free H_2O_2, (b) irradiated in 1.20 mM H_2O_2; (c) percent decrease in absorbance value.

(14) $$O_3^- + H^+ \rightarrow {}^\bullet OH + O_2$$

(15) $${}^\bullet OH + O_3 \rightarrow HO_2^\bullet + O_2$$

(16) $$HO_2^\bullet \rightarrow H^+ + O_2^-$$

– Termination [24]

(17) $HO_2^\bullet \rightarrow {}^\bullet OH \rightarrow H_2O + O_2$ (dominant at low pH)
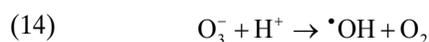
(18) ${}^\bullet OH + {}^\bullet OH \rightarrow H_2O_2$ (dominant at pH > 4)
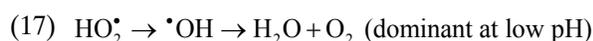
UV-Vis spectra of treated caffeine solutions give some information about decomposition of caffeine for comparison in each condition. The details in degradation of caffeine after treatment were followed by recording with GC/MS analysis. Intermediates after irradiation and/or ozonation could not be detected with GC/MS as well as only degradation of caffeine was followed. The gas chromatogram and mass spectrum of caffeine are given in Fig. 3 with an internal standard (methyl ester of 2,4-DP) for quantitative analysis. In Fig. 3, the most abundant ion in MS spectrum was observed as 194, molecular ion (M^+) of caffeine. The disappearance of isocyanate group ($CH_3N=C=O$) and carbon monoxide ($C=O$) gives a new fragmentation product with m/z 109 $(M-85)^+$ [43]. Other fragmentation products, 67 $(M-127)^+$ and 55 $(M-139)^+$ and structures
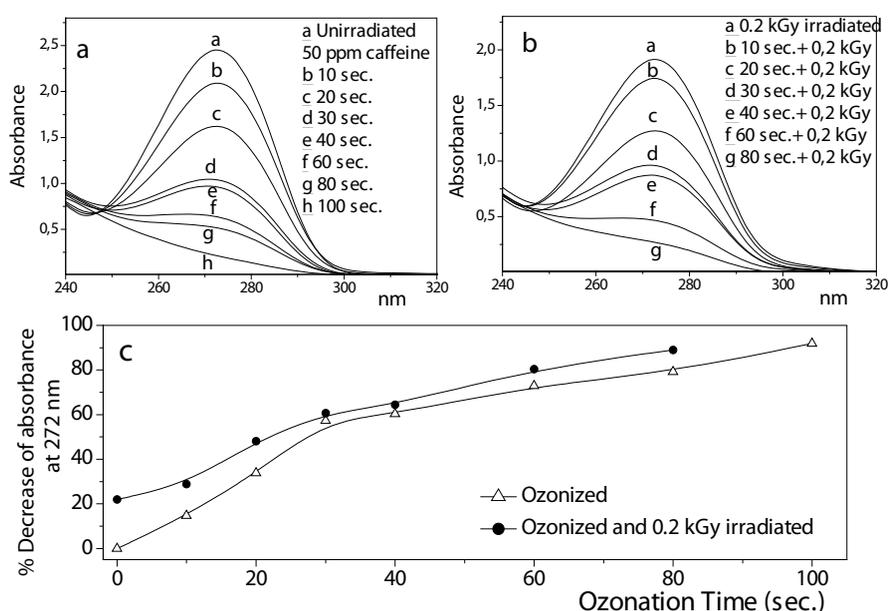
Fig. 2. Variation of the decrease of absorbance of 50 ppm caffeine as a function of ozonation time at 272 nm (a) ozonized without irradiation, (b) ozonized and irradiated for 0.2 kGy; (c) percent decrease in absorbance value.
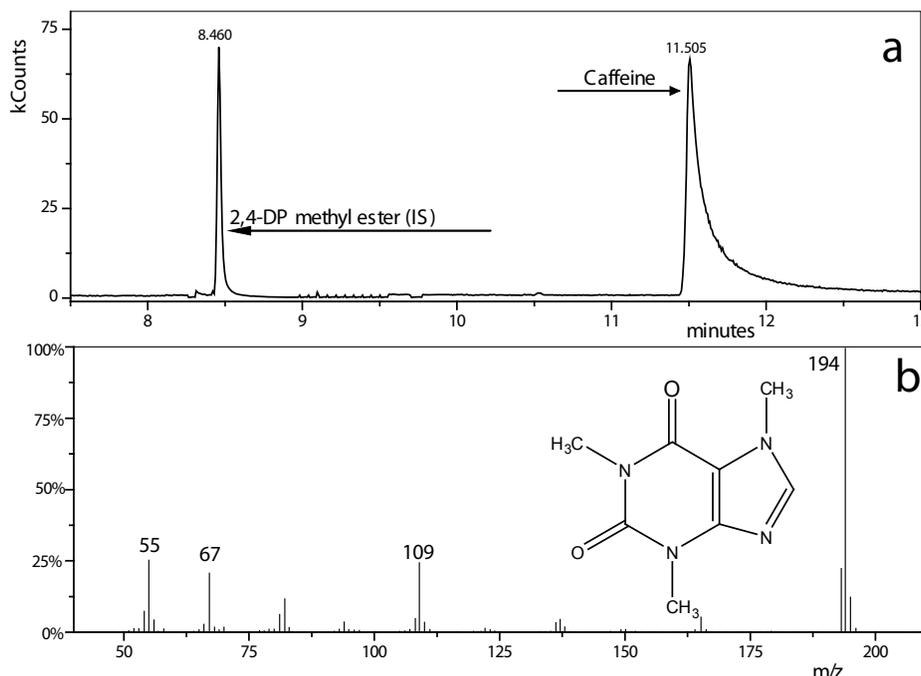
Fig. 3. (a) Gas chromatogram of caffeine (25 ppm) and 2,4-DP methyl ester as IS (20 ppm), (b) mass spectrum of caffeine.

of these possible fragmentation products are given in Table 1. Figure 4 gives the amount of remaining caffeine for gamma-hydrogen peroxide and gamma-ozone systems. It is clearly observed that the combination of hydrogen peroxide with gamma irradiation and the combination of ozonation with gamma irradiation enhances the degradation of caffeine. G_i values are 3.7 and 6.6 for irradiated samples in H_2O_2 free and in 1.20 mM H_2O_2 solutions, respectively. G values give the efficiency of degradation and the value of G_i for samples irradiated in 1.20 mM H_2O_2 is nearly two times of only irradiated caffeine. (G value is the number of molecules decomposed per 100 eV absorbed energy. G_i value is the initial G value). 50 ppm caffeine in aqueous solutions were

Table 1. Possible fragmentation products of caffeine in the mass spectrum

m/z	Fragmentation product or structure
194 (M$^+$) (Caffeine molecular ion)	
109 (M-85)$^+$ (Loss of methyl isocyanate group and carbonyl group)	
67 (M-127)$^+$	
55 (M-139)$^+$	

decomposed at earlier ozonation times when 0.2 kGy irradiated. 0.2 kGy irradiation of 50 ppm aqueous caffeine solution reduced the ozonation time from 120 to 80 min to remove caffeine. Spectroscopic results (Fig. 2) supports the effect of gamma irradiation on ozonation. For both results, it is obvious that the combination of these two oxidation processes give a high efficiency for degradation of 50 ppm aqueous caffeine solution. Reactions of caffeine with hydroxyl radical was investigated by electron spin resonance (ESR) spin trapping which reports that caffeine is an effective OH radical scavenger with a rate constant of $5.9 \times 10^9\,M^{-1}\cdot s^{-1}$ [44]. Effective decomposition of caffeine in combined processes rather than only ozonation or gamma irradiation is due to this high rate reaction constant of caffeine with OH radicals. The addition of 1.20 mM hydrogen peroxide caused the decomposition of nearly 10% of 50 ppm caffeine without irradiation according to GC/MS results. It is suggested that the oxidation of caffeine by H_2O_2 and oxygen free radicals is at the nucleophilic C-8 position of the imidazole ring [45].

Figure 5 gives the change in acidity of caffeine solutions with irradiation and ozonation. Acidity of the solution increases with irradiation and the addition of 1.20 mM H_2O_2 increases the total acidity of the solution. The reason for this result is the decomposition of caffeine to weak acidic groups more effectively with additional OH radicals from H_2O_2 [46]. Total acidity of the ozonized samples are increasing with ozonation times, because of oxidation of ozonolysis products, although irradiation of ozonized samples decreases the total acidity of the caffeine solutions. Some researchers detected acidic groups during ozonation of aqueous caffeine [47] as a consequence of the reaction of caffeine with OH radicals [9]. Irradiation after ozonation can enhance the degradation of formed acids and the total acidity can be reduced. Gamma irradiation of preliminary ozonized caffeine solutions decomposed readily without formation of any major acidic groups. The
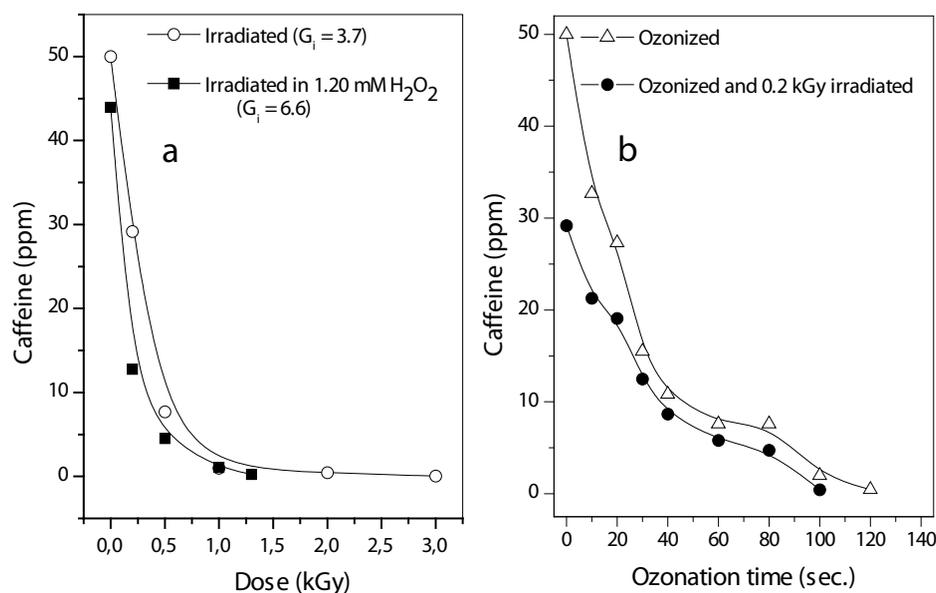
Fig. 4. Change in the amount of remaining caffeine in the treated aqueous samples as a function of (a) irradiation dose and (b) ozonation time. Analytical results were performed by GC/MS.
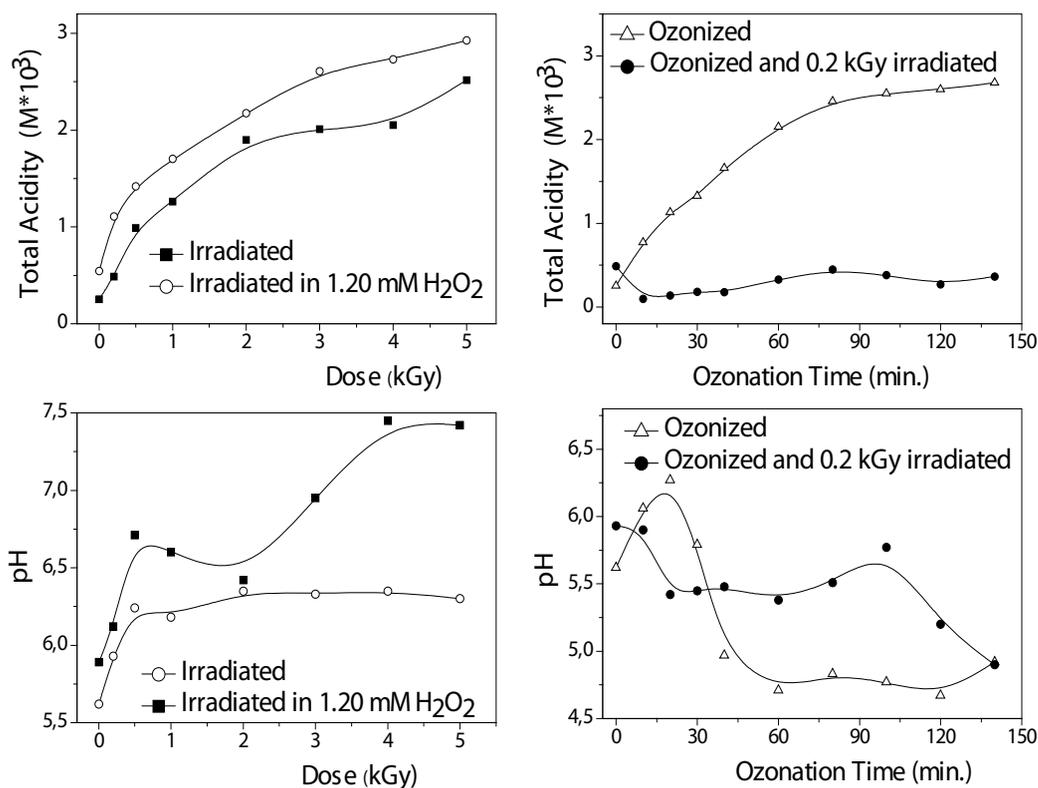
Fig. 5. Change in acidity and pH of caffeine solution (50 ppm) as a function of irradiation dose and ozonation time.

other effect can be the conversion of possible NH_4^+ ions to NH_3; hydrogen on ammonium ions can react with hydroxyl radicals ($NH_4^+...OH$) to form ammonia and water [48]. The other suggestion for acidity with irradiation in the presence of ozone can be due to the formation of less amount of NH_4^+ ions, for only ozonation without irradiation rather than NH_4^+ ions, some weak acids may contribute to acidity. pH results are not in the trend of total acidity, because of the strength of formed weak acids. Ratio of concentration of NH_4^+ to concentration of NH_3 can affect the pH value of the solutions.

The amount of dissolved oxygen during irradiation/ozonation are given in Fig. 6. Dissolved oxygen, one of the important parameter for irradiated aqueous solutions consumed during irradiation and formed during ozonation of samples [49]. G_i values of oxygen consumption were found as 1.58 and 0.94 by irradiated in the absence and presence of 1.20 mM H_2O_2, respectively. Consumption of oxygen for irradiated H_2O_2-free solution was found to be higher with respect to G_i values since additional oxygen may be introduced to the solution by decomposition of excess H_2O_2 in 1.20 mM H_2O_2 solutions. Oxygen-based effective radicals may be consumed more in H_2O_2 free
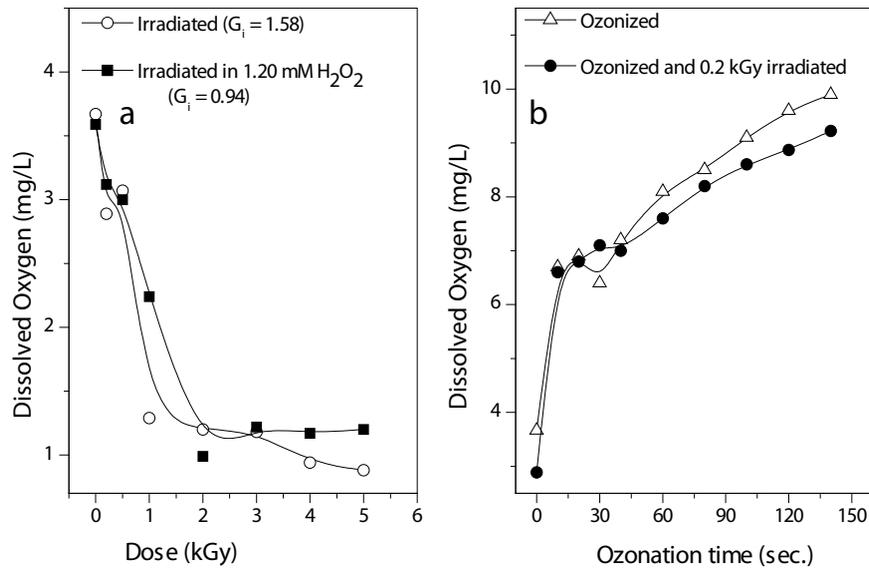
Fig. 6. Change in amounts of dissolved oxygen for caffeine solutions (50 ppm) as a function of (a) irradiation dose and (b) ozonation time.
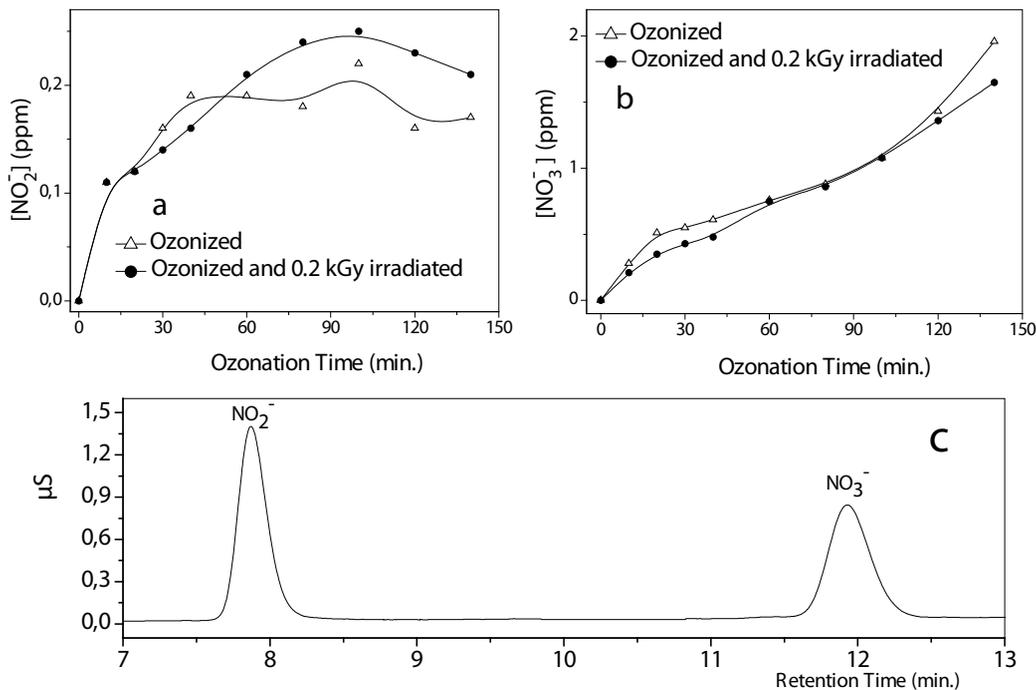
Fig. 7. Changes in the amounts of (a) $[NO_2^-]$ and (b) $[NO_3^-]$ with ozonation and ozonation/0.2 kGy irradiation dose with an (c) ion chromatogram of 0.5 ppm standard for each of them. Retention times in ion chromatogram are 7870 and 11 930 min for $[NO_2^-]$ and $[NO_3^-]$, respectively.

solutions although there is a competition between OH radicals and oxygen based radicals in solutions irradiated in H_2O_2 [30].

Figure 7 gives the amounts of nitrite and nitrate ions formed in ozonized caffeine samples. Retention times of nitrite and nitrate anions were determined by using the standards. Ozonation is a powerful method to oxidize organic and inorganic ions as ammonia and ammonium are readily converted to nitrite and nitrate ions. There is no important difference for the amounts of nitrate ions in ozonized and ozonized/0.2 kGy irradiated samples. Nitrite is a possible product of ozonation of ammonia and formed nitrite ions are oxidized to nitrate by ozone [50]. Gamma irradiation alone is environmentally friendly

method when compared with ozone since caffeine is decomposed completely without formation of nitrate and toxic nitrite anions.

$$(19) \qquad NH_3 + 3O_3 \rightarrow NO_2^- + 3O_2 + H^+ + H_2O$$

$$(20) \qquad NO_2^- + O_3 \rightarrow NO_3^- + O_2$$
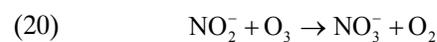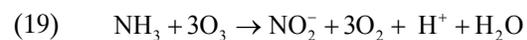
Formaldehyde tests for caffeine samples before/after treatment were performed [28] but it is not observed as an intermediate.

Table 2 gives the changes of COD values for caffeine after treatment with gamma, ozone, hydrogen peroxide and synergic effects of ozone and hydrogen peroxide on

Table 2. Changes in the COD values of 50 ppm aqueous solutions of caffeine with ozonation and irradiation

Sample	COD value (mg/L)	COD removal (%)	COD removal (%) other than nitrite ions
50 ppm caffeine	46.6	–	–
0.2 kGy irradiated 50 ppm caffeine	21.2	54.3	–
3 kGy irradiated 50 ppm caffeine	12.7	72.6	–
50 ppm caffeine in 1.20 mM H_2O_2	42.4	9.0	–
1.2 kGy irradiated 50 ppm caffeine in 1.20 mM H_2O_2	10.6	77.3	–
120 s ozonized 50 ppm caffeine	8.5	81.8	81.6
100 s ozonized 0.2 kGy irradiated 50 ppm caffeine	4.2	91.0	90.7

gamma irradiation. COD value of potassium hydrogen phthalate standard was determined experimentally in the same conditions as samples and compared with its theoretical value. COD values are interfered from inorganic ions such as halides, nitrite and reduced inorganics [29, 51]. Ammonia and ammonium also interferes COD analysis in the presence of chloride ions [29]. In this study, ammonium and ammonia are possible intermediates for irradiated and ozonized samples, nitrate and nitrite ions were the observed intermediates in the presence of ozone for 50 ppm aqueous solutions of caffeine. Some researchers investigated the effect of ammonia/ammonium on the change of COD values and concluded that ammonia/ammonium is not oxidized when chloride is absent [52]. Nitrite ions are also oxidized by consuming potassium dichromate and increase COD by 1.14 mg per mg of nitrite nitrogen [29]. COD analysis based on potassium dichromate does not interfere from ozone because potassium dichromate is not consumed for the oxidation of ozone [53]. Effect of hydrogen peroxide interference on COD measurements were concluded by some authors [53–55] and each of them reported the corrected experimental COD values as a function of hydrogen peroxide concentration. Although hydrogen peroxide is a strong oxidizer, it acts as a reductant if there is a stronger oxidizing agents such as potassium dichromate. If potassium dichromate is added to the hydrogen peroxide solution acidified with sulphuric acid, a green colour acts due to the formation of Cr^{3+} ions by potassium dichromate reduction [54]. To remove excess hydrogen peroxide that may interfere with COD analysis, samples were hold in an oven for 30 min at 50°C [56] and iodometric tests were followed for residual hydrogen peroxide. It is assumed that heating of the treated caffeine solutions at 50°C had no effect on COD values of the samples [57]. Although nitrite ions are one of the degradation products of caffeine that interferes with potassium dichromate, in Table 2, COD recoveries of intermediates other than nitrite ions are given in which the contribution of nitrite ions to COD data are very low. It is clearly observed that ozonation is a powerful method for the COD removal. For 100 s ozonized/0.2 kGy irradiated 50 ppm aqueous solution of caffeine, the highest removal of COD values were observed. This may be attributed to the mineralization of caffeine to carbon dioxide, water and ammonia [43] in the presence of ozone. Change in total acidity in Fig. 5 correlates this suggestion, the total acidity increases with ozonation although ozonation combined with irradiation causes the total acidity to be almost constant. This suggests that only ozonation still oxidizes some intermediates although ozonation/irradiation

performed mineralization with a yield of more than 90%. COD removal increases with irradiation dose and irradiation in 1.20 mM hydrogen peroxide enhances the COD removal. An addition of 1.20 mM H_2O_2 to 50 ppm caffeine solution caused a COD removal of 9.0%, which is consistent with the decomposition of nearly 10 ppm caffeine in the presence of 1.20 mM hydrogen peroxide. Observation of nitrite and nitrate ions in the presence of ozone is compatible with COD removal values since the presence of these ions are the explanation of mineralization.

Conclusion

Caffeine is one of the important water contaminant existing in water naturally or artificially. Some chemical methods under advanced oxidation processes were performed to remove caffeine from water, but there is not much attention to use gamma irradiation in a part of advanced oxidation processes. In this study, AOPs that include gamma irradiation was performed and caffeine is completely decomposed with high energy radiation and ozonation. Some parameters were followed such as total acidity, pH, nitrite-nitrate anions, dissolved oxygen, COD changes and the determined results were discussed above. The retention times of some aliphatic acids were indicated by using ion chromatography and formaldehyde tests were performed by using a UV-Vis spectrophotometer, for any possibility, all treated caffeine samples were investigated for aliphatic acids and formaldehyde, but none of them were observed. Effect of hydrogen peroxide on irradiation and irradiation on ozonation was investigated for 50 ppm aqueous solution of caffeine both with UV-Vis and GC/MS. It is observed that irradiation in hydrogen peroxide and irradiation after ozonation enhances the degradation of caffeine. Total acidity of the 50 ppm aqueous solution of caffeine increased with irradiation and ozonation although there is no change with ozonation/irradiation. Consumption of oxygen, used for radiolysis reactions, was observed with the change of irradiation dose. Nitrite and nitrate anions, which are the last steps for degradation of caffeine were detected only for ozonized and ozonized/irradiated samples. Gamma irradiation is environmentally suitable method for the decomposition of caffeine because there is no formation of nitrate and toxic nitrite ions during treatment. COD results showed decomposition of 50 ppm aqueous solution of caffeine to its intermediates with a yield of more than 70% when all caffeine is decomposed. Mineralization in the presence of ozone is more effective since COD removals are more than 80% with an

observation of nitrite and nitrate ions with ion chromatography. Irradiation of 50 ppm aqueous solution of caffeine in the presence of 1.20 mM hydrogen peroxide also increased the COD removal (%) values.

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