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Removal of dissolved organic pollutants from water by gamma-irradiation based advanced oxidation processes (AOPs)

Çözünmüş organik kirleticilerin gama-ışınları temelli ileri oksidasyon yöntemleri (İOY) ile sudan uzaklaştırılması

Review Article

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ABSTRACT

Various organic compounds including textile dyes, pesticides and pharmaceutical compounds were detected in aquatic environment. A large number of studies were examined to remove these types of compounds from water. This paper includes the applications of radiation technology to decompose such organic compounds with various combinations such as ozone and H_2O_2. Changes in amounts of organic pollutants, their intermediates, toxicity, decoloration and Chemical Oxygen Demand (COD)-Biological Oxygen demand (BOD) with irradiation dose were followed. The results showed that gamma irradiation based water treatment technologies are effective for the water treatment even in drinking water.

Key Words
Gamma-irradiation, organic pollutants, advanced oxidation processes, radiolytic degradation.

ÖZET

Doğal sulu ortamlarda tekstil boyaları, pestisitler ve farmasötik bileşikler gibi birçok organik bileşik saptanmıştır. Sudan bu tür yapıların uzaklaştırılması için birçok çalışma yapılmıştır. Bu çalışma radyasyon teknolojisinin ozon ve H_2O_2 gibi çeşitli kombinasyonlarla bir araya getirilerek yapılan uygulamaları içermektedir. Organik kirleticilerin, ara ürünlerin, toksiste, renk giderimi ve Kimyasal Oksijen İhtiyacı (COD)-Biyolojik Oksijen İhtiyacı (BOD) değerlerinin ışınlama dozuyla değişimi incelenmiştir.

Anahtar Kelimeler
Gama-ışınlaması, organik kirleticiler, ileri oksidasyon yöntemleri, radyolitik bozunma.

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INTRODUCTION

Water is one of the most important foodstuffs for human beings and all living systems. It is a great concern in recent years to keep water resorces clean. A rapid devolopment of industrial applications becomes a great problem for water supplies by charging the waste chemicals. These wastes include solvents such as chlorinated aromatic compounds, pharmaceutical agents, pesticides and others. Pharmaceuticals can reach waters also by domestic ways, but pesticides reach water from farms and agricultural activities in more amounts than others. Pesticides and their aromatic intermediates in the environment are more toxic than most of the other organic wastes. Because of their widespread use, pesticides can be present in drinking water. Persistent organic pesticides, although some of them are restricted or banned, can still be found in drinking water [1]. World Health Organization (WHO) derived water guidelines for some pesticides [1,2,3]. The other major problem for the environment is textile dyes. They strongly change the color of the wastewater. Their complex structure resist on biodegradation for a long time, the degradation intermediates are still toxic that include mostly phenolic compounds. These toxic organic compounds and their intermediates should be urgently removed from water with an effective method.

Conventional water treatment methods include filtration, adsorption, ion-exchange are not effective for some of the organic compounds and these processes change only the phase of the pollutants. Chlorination is more effective than methods given above but it results to the formation of chlorinated organic compounds as well as chloroform. There are a number of methods for water purification which are biological processes, photoinduced oxidation, photocatalytic treatment, thermal oxidation Fenton Processes, electrochemical treatment, solar and ultrasonic treatment, ozonation and radiation technology. Radiation Technology is the most effective way to remove organic pollutatnts from water. It is named as clean method that no chemicals are added into the medium. Radiation technology has some advantages over ones which are no radioactivity production during treatment, no waste, safe for personel, environment and general public, economically competetive and high efficiency. High-energy irradiation of water generates hydrated electrons (e^-_{aq}), hydroxyl radicals (•OH) and hydrogen radicals (H•) in water that interact with a wide range of pollutants [4,5]. Main products of water radiolysis are:

$H_2O \rightsquigarrow {}^{\cdot}H, e^-_{aq}, {}^{\cdot}OH, H_2, H_2O_2, H_3O^+ OH^-$ [6].

In the presence of oxygen, water radiolysis products follow the reactions; (1)-(6).

Ozone is a powerful ozidizing agent used on a technical scale for purification of drinking and wastewater [14-17]. Ozone may react with solutes either by direct oxidation by attacking on the electron rich site or by unselective attacking of hydroxyl radicals formed after ozonation. Hydroxyl free radicals can also react with ozone to produce oxygen and hydroperoxyl radicals [18]. Reactions of ozone in water are given reactions (7)-(16).

Advanced oxidation processes (AOPs) are referred as methods to generate hydroxyl free radicals for the subsequent use of pollutant decomposition [23]. AOPs are characterized by the production of highly oxidative hydroxyl radical at ambient temperatures for oxidative destruction of organic compounds which can ultimately lead to complete minerilization with the formation of CO_2, H_2O and mineral acids.

$$\text{Organic pollutants} + \text{AOPs} \rightarrow CO_2 + H_2O + \text{mineral acids}$$

A wide range of AOPs have been developed for the treatment of aqueous waste streams with a single treatment process or by combinations of ozonation, UV irradiation with or without catalysts such as TiO_2, ultrasonic irradiation, electron beam irradiation, gamma-ray irradiation, Fenton processes and hydrogen peroxide. AOPs fundamentally rely on the production of large fluxes of hydroxyl radicals which in the presence of complementary oxidants (e.g. ozone, H_2O_2) or upon extended treatment can bring about (in favorable cases) complete minerilization of organic matter. Hydroxyl radicals can oxidize a variety of organic materials and are central to the

${}^{\cdot}H + O_2 \longrightarrow HO_2^{\cdot}$	$k = 1.9 \times 10^{10}$ L mol^{-1} s^{-1} $k = 1.2 \times 10^{10}$ L mol^{-1} s^{-1}	[6-8]	(1)
$e^-_{aq} + O_2 \longrightarrow O_2^{\cdot -}$	$k = 2 \times 10^{10}$ L mol^{-1} s^{-1} $k = 1.9 \times 10^{10}$ L mol^{-1} s^{-1}	[6,8,9]	(2)
$HO_2^{\cdot} \overset{H^+}{\rightleftharpoons} H^+ + O_2^{\cdot -}$	pK =4.8	[10,11]	(3)
$HO_2^{\cdot} + O_2^{\cdot -} \longrightarrow H_2O_2 + O_2$	$k = 1.2 \times 10^{10}$ L mol^{-1} s^{-1} $k = 9.7 \times 10^{7}$ L mol^{-1} s^{-1}	[11,12]	(4)
$HO_2^{\cdot} + HO_2^{\cdot} \xrightarrow{2H^+} H_2O_2 + O_2$	$k = 3.7 \times 10^{6}$ L mol^{-1} s^{-1} $k = 8.3 \times 10^{7}$ L mol^{-1} s^{-1}	[10,12]	(5)
$O_2^{\cdot -} + O_2^{\cdot -} \xrightarrow{2H^+} H_2O_2 + O_2^{\cdot}$	$2k < 10$ L mol^{-1} s^{-1} 2k = no reaction	[10,13]	(6)

$O_3 + OH^- \longrightarrow HO_2^- + O_2$	$k = 7 \times 10^{1}$ L mol^{-1} s^{-1}	[19]	(7)
$O_3 + HO_2^- \longrightarrow HO_2^{\cdot} + O_3^{\cdot -}$	$k = 2.2 \times 10^{6}$ L mol^{-1} s^{-1}	[19]	(8)
$O_3 + O_2^{\cdot -} \longrightarrow O_3^{\cdot -} + O_2$	$k = (1.6 \pm 0.2) \times 10^{9}$ L mol^{-1} s^{-1}	[20]	(9)
$O_3^{\cdot -} + H^+ \longrightarrow HO_3^{\cdot}$	$k = (5.2 \pm 0.6) \times 10^{10}$ L mol^{-1} s^{-1}	[21]	(10)
$HO_3^{\cdot} \longrightarrow O_3^{\cdot -} + H^+$	$k = (3.7 \pm 0.3) \times 10^{4}$ s^{-1}	[21]	(11)
$HO_3^{\cdot} \longrightarrow HO^{\cdot} + O_2$	$k = (1.009 \pm 0.06) \times 10^{5}$ L mol^{-1} s^{-1}	[21]	(12)
$O_3 + HO^{\cdot} \longrightarrow HO_4^{\cdot}$	$k = 2 \times 10^{9}$ L mol^{-1} s^{-1}	[22]	(13)
$HO_4^{\cdot} \longrightarrow HO_2^{\cdot} + O_2$	$k = (2.8 \pm 0.3) \times 10^{4}$ L mol^{-1} s^{-1}	[22]	(14)
$HO_4^{\cdot} + HO_4^{\cdot} \longrightarrow H_2O_2 + 2O_3$	$k = 5 \times 10^{9}$ L mol^{-1} s^{-1}	[22]	(15)
$HO_4^{\cdot} + HO_3^{\cdot} \longrightarrow H_2O_2 + O_3 + O_2$	$k = 5 \times 10^{9}$ L mol^{-1} s^{-1}	[22]	(16)

application of AOPs for treatment of pollutants in water. In this review, the synergic effect of ozone and H_2O_2 on gamma-irradiation are discussed and the reactions of these AOPs system are given below. Reactions of ozone in water when exposed to high energy rays (gamma irradiation):

Propagation [18]

$$O_3 + O_2^- \rightarrow O_3^- + O_2 \qquad (17)$$
$$O_3^- + H^+ \rightarrow \cdot OH + O_2 \qquad (18)$$
$$\cdot OH + O_3 \rightarrow HO_2\cdot + O_2 \qquad (19)$$
$$HO_2\cdot \rightarrow H^+ + O_2^- \qquad (20)$$

Termination [18]

$$HO_2\cdot + \cdot OH \rightarrow H_2O + O_2 \qquad (21)$$

(Dominant at low pH)

$$\cdot OH + \cdot OH \rightarrow {}_2O_2 \qquad (22)$$

(Dominant at pH >4)

H_2O_2 is another hydroxyl radical generator in water when exposed to gamma-irradiation. The amount of hydrogen peroxide should not be under an optimum amount, in addition to this, also higher amount of hydrogen peroxide is not effective to degrade dissolved organic compounds from water since it 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: [24]

$$e^-_{aq} + H_2O_2 \rightarrow \cdot OH + OH^- \quad k = 2.4 \times 10^{10}\ (20^{\circ}C) \qquad (23)$$
$$H\cdot + H_2O_2 \rightarrow \cdot OH + H_2O \quad k = 1.5 \times 10^{7}\ (20^{\circ}C) \qquad (24)$$
$$\cdot OH + H_2O_2 \rightarrow HO_2\cdot + H_2O \quad k = 3.1 \times 10^{10}\ (20^{\circ}C) \qquad (25)$$
$$2HO_2\cdot \rightarrow H_2O_2 + O_2$$

The total effect of last two reactions are;

$$2\cdot OH + H_2O_2 \rightarrow O_2 + 2H_2O \qquad (26)$$

Pesticides

Chloropehenoxy herbicides

As mentioned before, pesticides are widely used in agricultural activities and farms, results in dragging of huge amounts of molecular pesticides into the ground and surface waters,

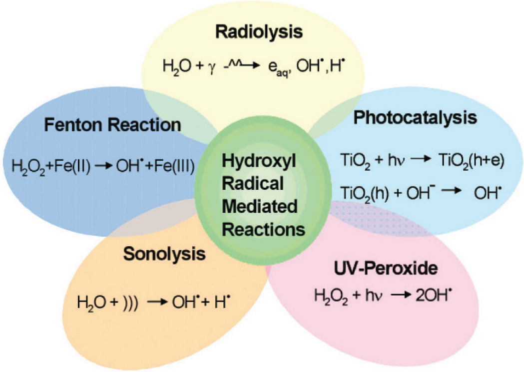


Figure 1. Examples of advanced oxidation processes employing hydroxyl radical [23].

as well as drinking water. Organochlorinated pesticides (OCPs) have been used for agricultural purposes for decades and they are distributed to control algae in lakes, canals, across the globe, even in pristine regions, such as Antarctica. Their chemical properties such as high lipophilicity, bioaccumulation potential, long half-life in the environment, and potential to long-range transport are the main reasons for their persistence in the environment. They are among the most prevalent contaminants and can be found in water [25,26], soil [27,28], or food [29,30] even decades after being banned. These compounds are primarily applied to the foliage of crops and weeds and their metabolism in plants has been extensively studied. The persistence and degradation of the phenoxyalkonoic acids in the soil environment has also been the subject of detailed study since these compounds reach the soil both during application and by transfer from plants to the soil by rainwater [31].

Phenoxy herbicides have been commercially available and are the most widely used family of herbicides worlwide. 2,4-dichlorophenoxyacetic acid (2,4-D), the most common of the phenoxy herbicides, is one of the best studied agricultural chemicals. Several phenoxy acids have been used as herbicides, including 2,4,5-trichlorophenoxyacetic acid (2,4,5-T), 4-(2,4-dichlorophenoxy) butyric acid (2,4-DB), 2-(2,4-dichlorophenoxy)propionic acid (2,4-DP), 2-(2-methyl-4-chlorophenoxy)- propionic acid (MCPP), 2-methyl-4-chlorophenoxyacetic acid (MCPA) and 2-(2,4,5-trichloro phenoxy)propionic acid (2,4,5-TP), with the most commonly and widely used herbicide being 2,4-D. 2,4,5-T and 2,4,5-TP are no longer manufactured or sold [32].

For over 50 years, 2,4-D has been the most commonly and widely used herbicide throughout the world. When applied to plants, 2,4-D is absorbed through the roots and leaves within 4 to 6 hours and is distributed in the plant via the phloem [33]. In addition, 2,4-D affects plant metabolism, which leads to interference with food transport. 2,4-D is primarily used as a herbicide in agriculture, forestry and lawn care practices, with the majority (>60%) of the total usage in the United States being reported for use as weed control in agriculture [34]. To a lesser extent, 2,4-D is used as a growth regulator on various crops ranging from potatoes to citrus fruits [35].

Researchers focused on degradation of mostly phenolic compounds and some chlorophenoxy herbicides, but all stages of degradation was not followed. In a laboratory scale experiments, 50 ppm 2,4-D was ozonized upto 20 min. ozonation time.

8.33 g/L (20 min.) ozone treatment is necessary to remove 50 ppm 2,4-D from 400 ml aqueous solution. The amount of necessary ozone decreases to 4.87 g/L (13 min.) when the solution is 0.2 kGy irradiated under gamma-rays with a dose rate of 0.07 kGy/h. Residual herbicide was followed with GC-MS programmed upon EPA methods after derivatization to methyl ester in methyl alcohol. Solid phase extraction (SPE) method is used to extract residual herbicide and its phenolic intermediates into the organic solvent. Some phenolic intermediates was observed with GC-MS, mainly 2,4-dichlorophenol (2,4-DCP). Although, 4-Chlorophenol (4-CP) was observed as an radiolysis intermediate of 2,4-D, it was not observed in the presence of ozone. Formation of 2,4-DCP was observed with ozonation but further ozonation results in the decomposition of 2,4-DCP. Ozone assisted with gamma irradiation results in the formation of 2,4-DCP in more amount although it is completely removed in shorter ozonation times/gamma irradiation. G_i values (number of decomposed molecules per 100 eV absorbed energy) for ozonized and ozonized/0.2 kGy irradiated 50 pppm 2,4-D samples are 1.48 and 2.81, respectively. It is clear with G values that combination of ozone with gamma irradiation is more effective. Amounts of aliphatic acids (oxalic, acetic and formic), splited chloride ions, total acidity, dissolved oxygen, formlaldehyde and pH were followed. Amounts of formic acid, formaldehyde, acetic acid was increased with ozonation time but further ozonation decomposed these aliphatic groups. Oxalic acid amount increased with ozonation time since it is the one of the last stage before minerilization. Splitted chloride ion ratio to 2,4-D is higher for ozonized/0.2 kGy irradiated 50 ppm 2,4-D sample in all stages. Decomposition of ozone to oxygen results in the increase of dissolved oxygen amount. Amount of dissolved oxygen for irradiated aqueous 50 ppm 2,4-D samples were lower since radiolysis products of water consume dissolved oxygen. Total acidity increased and pH decreased with ozonation and further ozonation caused no changes in total acidity although there is a slight decrease in pH. Change in pH depends on the strength of the formed acids in each stage [36].

Effect of hydrogen peroxide on degradation of 2,4-D is also followed. As discussed above, the amount of used hydrogen peroxide should be optimized experimentally. Previous experiments showed that 1.20 mM H_2O_2 is optimal concentration for the degradation of 50 ppm 2,4-D. 1.20 mM H_2O_2 decreases the irradiation dose from 3.0 kGy to 2.0 kGy for aqueous 50 ppm 2,4-D. 0.8 ppm 2,4-D is decomposed to 2,4-DCP as aromatic intermediate in the presence of 1.20 mM H_2O_2 without irradiation. G_i values for degradation of 2,4-D in the presence and absence of 1.20 mM H_2O_2 are 1.42 and 2.72, respectively. The main aromatic intermediate, 2,4-DCP completely removed at 3.0 kGy and 4.5 kGy irradiation doses in 1.20 mM H_2O_2 and H_2O_2 free solutions, respectively although the amount of formed 2,4-DCP is higher in the presence of H_2O_2. 4-CP, another aromatic degradation intermediate was observed in lower amounts than 2,4-DCP (nearly 25 times lower). 4-CP is intermediate of both 2,4-D and 2,4-DCP. It is completely removed from water at lower irradiation doses in the presence of H_2O_2. 4-CP was not observed as aromatic intermediate in the presence of ozone. This may be because of the attack of ozone on double bonds of 2,4-D and 2,4-DCP to produce aliphatic organic compounds.. Chloride ions splitted completely at lower irradiation doses in the absence of H_2O_2. Oxygen is consumed with irradiation dose up to 0.6 kGy and the amount of dissolved oxygen is constant for further irradiation doses. Addition of 1.20 mM H_2O_2 into 200 ml 50 ppm 2,4-D solution decreases dissolved oxygen from 3.54 mg/L to 2.95 mg/L because of the oxidation of 2,4-D. As expected, total acidity increases with irradiation dose with higher yield in the presence of H_2O_2 although pH change is similar for both conditions. Addition of 1.20 mM H_2O_2 decreases pH value with an increase in total acidity slightly [37].

Organophosphorous insecticides

Parathion (O,O-diethyl-O-4-nitro-phenyl thiophosphate) was a highly used organophosphorous insecticide in agricultural applications in past decades; now it can be detected in surface and groundwaters in the concentration level of ng/L to μg/L with the highest level up to 0.1 mg/L [38,39]. Solubility of parathion in water is 24 mg/L [40] and it is classified as an acutely toxic pesticide [41]. Major of degradation pathways of parathion are hydrolysis, microbial degradation and photolysis in the environment [42]. Parathion is stable in dry soil for long periods and may be converted to highly toxic paraoxon and related compounds [43]. Reaction of parathion with ozone in aqueous solution also results in formation of parathion [44].

Parathion is preliminary ozonized for 0.5 minutes with a rate of 30 g/h and irradiated up to 4 kGy with a dose rate of 0.87 kGy/h. For complete decomposition of parathion, 4 kGy irradiation dose is necessary although short ozonation time (0.5 min) reduces irradiation dose to 1 kGy for complete removal of parathion. Paraoxon and p-nitrophenol formation is favored with preliminary ozonation before irradiation. Irradiation of parathion produces paraoxon at lower amounts, and p-aminophenol was observed for when parathion is only irradiated. Further irradiation decomposed both intermediates. In the case of ozonation combined with constant irradiation (0.2 kGy), ozone was passed through the 15 ppm aqueous parathion samples for different time periods upto 5 min before irradiation. It was observed that ozonation/irradiation enhances the degradation of parathion Intermediates, paraoxon amount is higher for the only ozonized samples although no p-amino phenol for only ozonized samples. P-nitrophenol was observed only for ozonized samples which can also be formed as a product of hydroxyl radical attack on paraoxon. Other radical degradation products of parathion such as acetic acid, formic acid and inorganic ions were determined with ion chromatography. Acetic acid and formic acid amounts are lower in the case of combined processes of ozone and irradiation. Observation of inorganic species are the strong evidence for degradation of insecticide parathion. Effects of irradiation dose and time of ozonation on formation of inorganic ions such as sulfate, phosphate, nitrate and nitrite were followed. Concentrations of sulfate for 0.5 min. ozonized/irradiated samples were higher than samples only irradiated. The opposite effcet was observed for the formation of phosphate. There is no additional effect on the amount of nitrite and nitrate ions after 4 kGy irradiation dose. Generally, it was observed that irradiation carried out in addition to ozonation does not significantly affect the formation or decomposition of inorganic ions. Decomposition of parathion and formation of paraoxon and p-nitrophenol were also investigated in the presence of common radical scavengers (carbonate, nitrate and humic acid) which can react with some radicals. 15 ppm parathion samples containing 50 ppm each scavenger is prepared seperately. These scavengers did not affect the decomposition level of herbicide parathion below 2 kGy, but, they strongly influence the formation and decomposition of paraoxon and p-nitrophenol with irradiation dose. Toxicity changes of parathion with ozonation and irradiation were followed with Microtox M500 Toxicity Analyzer. Toxicity increases with the processes ozonation combined with irradiation and decreases with further irradiation doses or ozonation times. When parathion solution only ozonized, an increase of toxicity with ozonation time was observed [45].

Pharmaceutical Compounds

Pharmacetical drugs including antiflammatories, analgesics, lipid regulators, betablockers, antiepilectics, antibiotics and estrogens are detected recently in surface and groundwatwaters as well as drinking water in μg/L levels [46-58]. The potential effects of these pharmaceutiacals on environment and living organisms are recently gained a great concern. Adverse effects of these pharmaceutical pollutants include aquatic toxicity, endocrine distruption and genotoxicity [59,60] have hazardous effects on human health. The presence of these compounds in drinking water may result some chronic problems for human beings as well as other living organisms [56]. Direct disposal to domestic waste, excretion by living organisms and industrial applications during drug manufacturing are the main sources of these drugs to reach surface, underground and waste waters [61,62].

Dichlofenac

Dichlofenac, is a nonsteroidal antiinflammatory drug, used to reduce pain and infflammation. In aquatic environment, dichlofenac is one of the most detected pharmaceutical compound [63]. Its presence in wastewaters has been reported [64,65]. Its diverse effects were observed at very low concentrations for different organisms in livers and kidneys [63,66]. Recent studies have shown that conventional water treatment processes can not remove most of the persistent pharmaceutical compounds completely from water [56,67,68]. This reduction in literature can be eliminated with effective advanced oxidation processes [69-71].

50 ppm dichlofenac solution is irradiated under gamma irradiation with a Gamma Chamber with a dose rate of 8.0 kGy/h in a Winkler bottles in different conditions to investigate the effect of various radiolysis products of water. Amount of dichlofenac in concentrations was recorded with HPLC. It was determined that the necessary dose is 4 kGy for aerated solution while it is 1 kGy if saturated with N_2O. The deareation of solution by saturation with argon and irradiation in the presence of tert-butanol implies the degradation of 50 ppm dichlofenac between 0.5-3 kGy irradiation doses, whereas there is no effect above 3 kGy. The hydroxyl radical scavengers nitrate, carbonate and humic acid at 50 ppm level did not affect the decomposition of DCF in anyway. The main species for the decomposition of dichlofenac is expected to be hydroxyl radicals and the reaction of dichlofenac with hydroxyl radical was examined with pulse radiolysis studies. This reaction was observed in N_2O saturated solution at pH 5.6 to transform hydrated electrons, an efficient reductant, to an efficinet oxidant hydroxyl radicals. Pulse radiolysis studies showed that hydroxyl radicals adduct to the two aromatic rings of dichlofenac. The overall rate constant of hydroxyl radicals reaction with dichlofenac was found as $1.24 \pm 0.02 \times 10^{10}$ M s^{-1}. Toxicity measurements for dichlofenac solutions were followed with Microtox test based on bioluminescent marine bacterium Vibro fisheri as the test organism. Toxicity tests were examined up to 5 kGy for 50 ppm aerated dichlofenac solutions after irradiation. An increase in toxicity

was observed especially in the range of 0.5-0.8 kGy irradiation dose that corresponds to 50-60% dichlofenac decomposition. At 3.5 kGy, where complete decomposition of dichlofenac was observed, 33% decrease in toxicity was determined.

Paracetamol

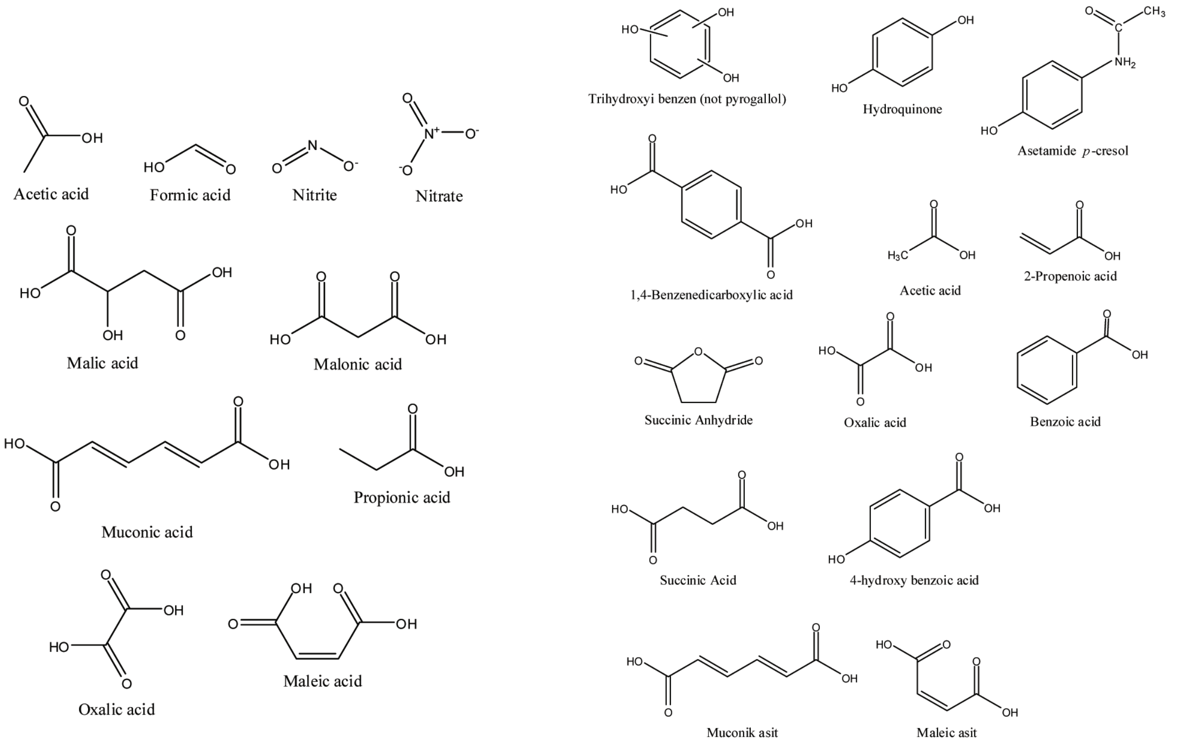
Paracetamol (N-(4-hydroxyphenyl)acetamide) is a common widely used analgesic for humans and animals. At the beginning of 2000, the paracetamol was ranked as one of the top three drugs produced with an amount of more than 400 tons per year [72] . This drug has been reported in European sewage efluents up to 6 μg/L [73] and up to 10 μg/L in USA natural water supplies [51]. Paracetamol is synthesized by acetylation of p-aminophenol and acetic anhydride, hence, it may be hydrolyzed to p-aminophenol depending on tempereture and pH of media [74]. p-aminophenol is suspected to cause nephrotoxicity and teratogenicity [75].

Aqueous 50 ppm paracetamol is prepared with the pH value of 6.41 in pyrex glasses. The experiment was examined for samples exposed to gamma-irradiation in the presence and absence of ozone. Aqueous samples were irradiated in ^{60}Co-gamma source with a dose rate of 0.03 kGy/h in open pyrex bottles. Ozonation of aqueous samples were performed with a rate of 10 g O_3/h for 400 ml sample in pyrex bottles. Amount of paracetamol and its aromatic/organic intermediates were detected with GC-MS injection after derivatization of carboxyl and hydroxyl groups to silyl derivatization as trimethyl silane (TMS) with N-methyl-N-trimethylsilyltrifluoroacetamide (MSTFA). Aliphatic carboxylic acids were determined with ion chromatography. Complete removal of paracetamol from aqueous solution is achieved after 5 kGy irradiation dose with G_i value of 1.36 although 0.5 min preliminary ozonation reduced irradiation dose to 3 kGy with G_i value of 1.66. One of the most important intermediate, hydroquinone was observed at all stages of irradiation doses and its observed amount is lower in the presence of ozone. Hydroquinone is completely removed from water at 4 kGy in the presence of ozone in which ozone lowered the irradiation dose for 2 kGy. Decrease of pH was efficient with irradiation in the presence of ozone. As expected, dissolved oxygen is consumed when reacted with radiolysis products. In the presence of ozone, excess ozone is decomposed to oxygen but still decreases with irradiation. Amount of aliphatic acids under investigation are acetic acid, formic acid and oxalic acid. Their amounts were steadily increasing with irradiation dose. Most important parameters which are evidence of minerilization, nitrate and nitrite amounts were followed and found as about the ratio of [2/1] as [nitrate (ppm)/nitrite (ppm)]. Amount of both ions increases with irradiation in the presence of ozone although it is constant after 2.5 kGy. Formaldehyde amount increases with irradiation, but a decrease was observed after 4 kGy in the presence of ozone. Some detected radioysis products of paracetamol are summarized in Figures (2-4). From Figures (2-4), it is clear that combination of ozone with gamma irradiation is very effective for the removal of paracetamol with its toxic intermediates from water.

Textile Dyes

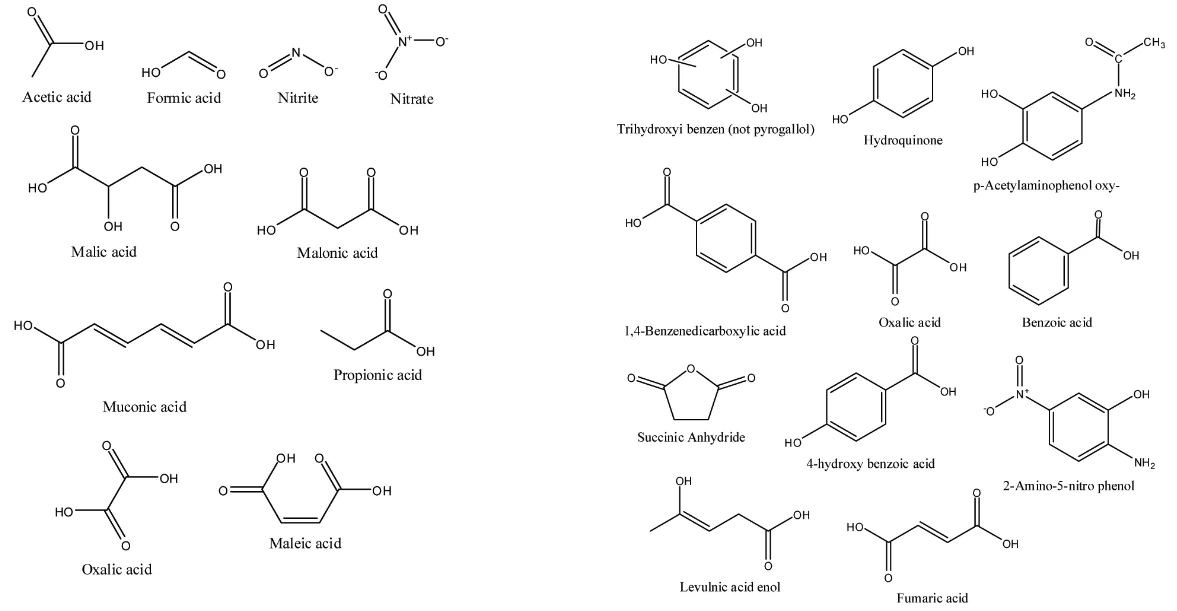
Textile industries are the major sources of textile dyes in wastewater that changes the color highly. Water soluble reactive azo dyes concentrations in wastewaters of textile industries are in the range of 10-10000 ppm depending on the process and structure of the dyes [76]. Nearly 30% of dyestuffs do not attach to the fabric that directly discharged into the wastewater [77-79]. BOD_5/COD ratio is important for the remediation of such colored contaminants since a high value corresponds that conventional methods is not enough for the removal of such structures [80,81]. The most important criteria for the use of textile dyes are their stability to light and microbial attack [82]. Textile dyes in wastewater are non-biodegradable [83,84] and they cause huge problems for living organisms because of high toxicity and stable structure. Most colored compounds undergo decomposition or color change when exposed to ionizing radiation [85]. Apollofix dyes are one of the most important class of synthetic organic dyes in textile industry, as well as, common industrial pollutants in Turkey [86]. Effect of gamma irradiation on two apollofix dyes, apollofix yellow (AY) and apollofix red (AR) were examined.

Dye solutions were prepared in the range of (0.050-0.200) g/L. Solutions were irradiated between 1.0-8.0 kGy irradiation dose with a rate of 0.14 kgy/h. Absorption bands were recorded for both dyes in UV and visible regions. The decrease of absorbance at 534 nm and 424 nm were followed to investigate decomposition for AR and AY, respectively. COD and BOD_5 changes



IC **GC/MS**

Figure 2. Intermediates of paracetamol after gamma-irradiation observed with IC and GC/MS.



IC **GC/MS**

Figure 3. Intermediates of paracetamol after ozonation observed with IC and GC/MS.

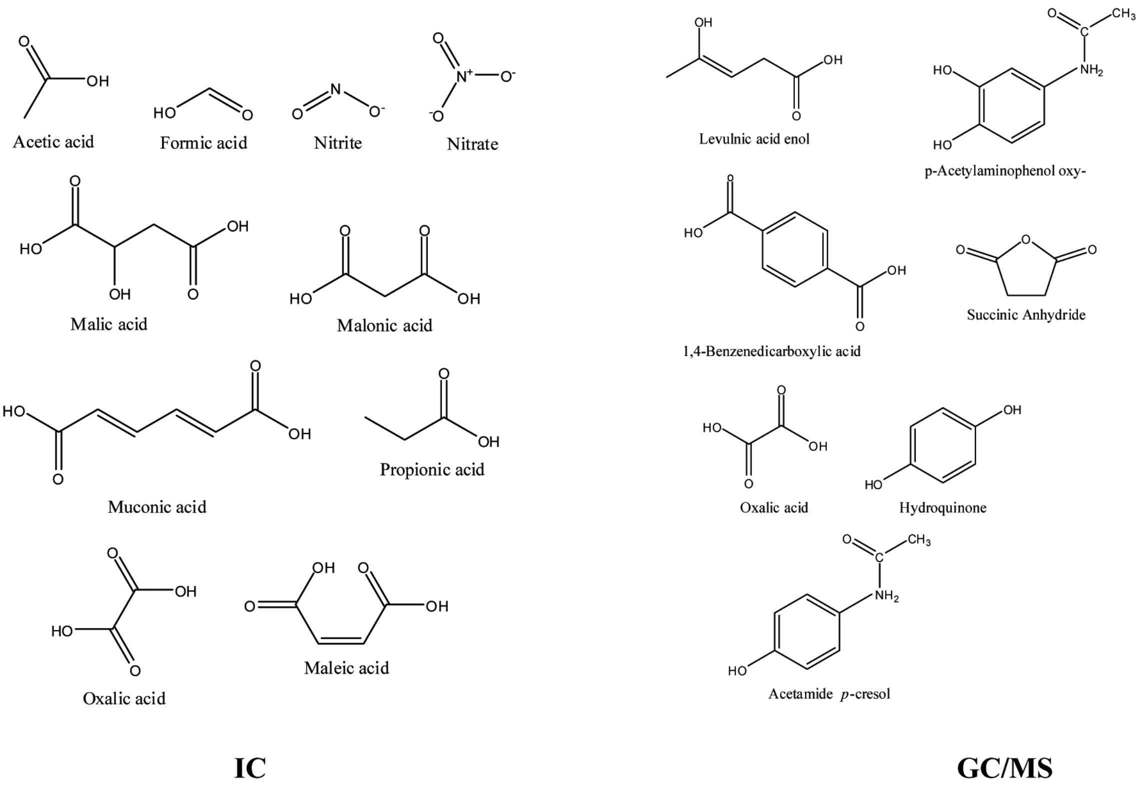


Figure 4. Intermediates of paracetamol after ozonation/irradiation observed with IC and GC/MS.

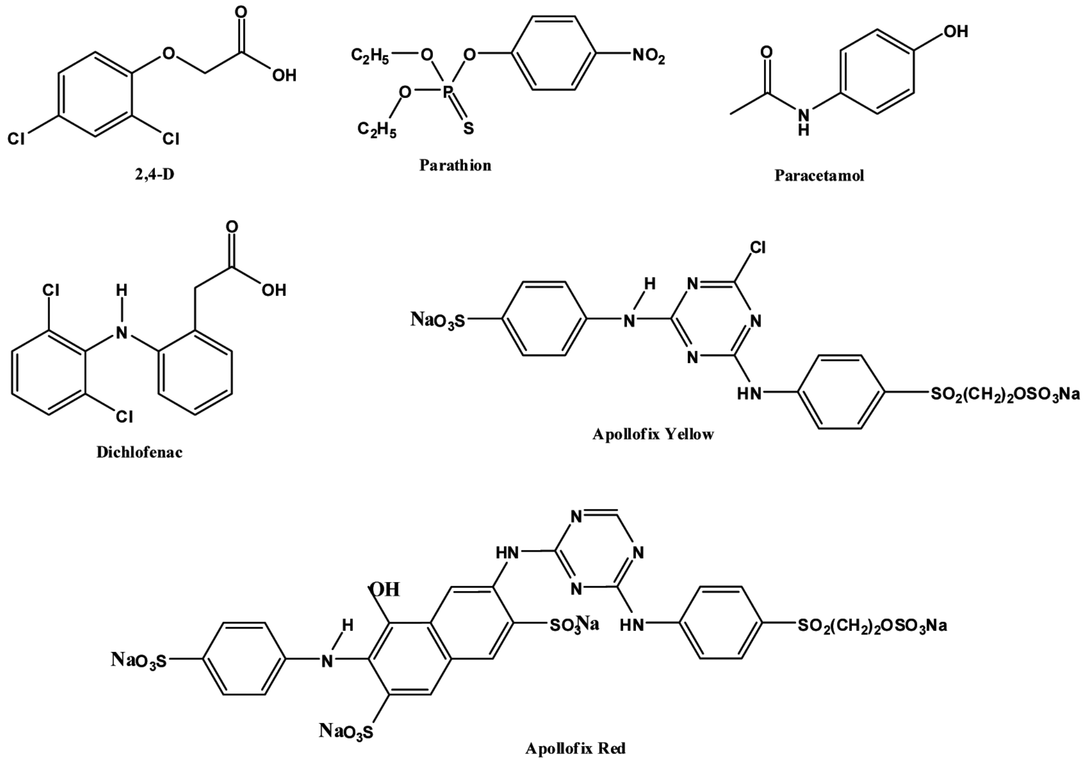


Figure 5. Chemical structures of investigated organic pollutants.

were followed for these dye solutions before after irradiation. For 0.05 g/L dye solutions, absorbance peaks for AR and AY completely disappeared at 2.0 and 1.0 kGy irradiation doses, respectively. At the same irradiation doses, comparatively, degree of decolaration is almost 100% for both dyes. It is observed that decrease of pH of the dye solutions was less sensitive to irradiation in the range of 3.0-8.0 kGy irradiation doses. The optimum concentration of H_2O_2 on degree of decoloaration at 3.0 kGy irradiation dose for both dyes were determined as 1.20 mM. Effect of irradiation dose on COD and BOD values of AR and AY dye solutions were determined. The decrease in COD values of both dye solutions were observed which is more effective in the presence of 1.20 mM H_2O_2. The BOD values of both dye solutions decreased with irradiation dose [86].

Conclusion

Effect of gamma-irradiation on decomposition of pesticides, pharmaceutical compounds and textile dyes were investigated. It is observed that radiation techniques solved environmental problems efficiently. Combination of ionizing radiation with oxidants such as ozone, H_2O_2 improved the removal efficiency. Unselective attack of radiolysis products of water, that include most powerful oxidizing and reducing agents, on organic pollutants makes this technique unique on others. Pesticides, pharmaceutical compounds and textile dyes were compleyely removed from water with their intermediates with gamma irradiation.

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