

Groundwater Purification Using Gamma Irradiation under Oxidation and Reduction Conditions

Mohamed M. El-Toony (✉ malnoni@kku.edu.sa)

Egyptian Atomic Energy Authority

Ahmed H. Rajab

Ghada A. Eid

Nabial M. Maziad

Egyptian Atomic Energy Authority

Research Article

Keywords: gamma irradiation, groundwater, purification, drinking water

Posted Date: June 3rd, 2022

DOI: <https://doi.org/10.21203/rs.3.rs-1673089/v1>

License:  This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Additional Declarations: No competing interests reported.

Groundwater Purification Using Gamma Irradiation under Oxidation and Reduction Conditions

Mohmamed M.El-Toony^{1,3*}, Ahmed H. Rajab¹, Ghada A Eid², Nabila M.

Maziad³

1-King Khaled Univ., Tohama branch, Chemistry dept., Abha, Kingdom Saudi Arabia, phone: +966582114618, E-mail: malnoni@kku.edu.sa, 2- King khaled Univ., Tohama branch, Physics dept., Abha, Kingdom Saudi Arabia, 3- National Center for radiation research and Technology, Nasr city, Cairo, Egypt.

Abstract

Gamma irradiation was applied for the elimination of different pollutants in groundwater. Two techniques of irradiation have been studied. The first technique, irradiation-reduction, resulted in un-soluble metals forming aggregations, such as cadmium, mercury, and lead, which can be separated out of the solution. Different parameters, such as different hydroxyl scavengers and different gasses, were used for water de-aeration. Metal ion removal yields were 99.4%, 97.8%, and 96.9%, for Cd²⁺, Hg²⁺, and Pb²⁺ respectively at the best-studied conditions. The second technique was irradiation coupled with ozonization which performed organics degradation. The procedure can reduce the values of turbidity, chemical oxygen demand (COD), biological oxygen demand (BOD), total organic carbon (TOC), and total dissolved solids (TDS). The bacterial colony counts, and rotavirus, have diminished. A constant value of COD/BOD ratios at different purification steps was about 1.2. For the sake of conferment, this methodology of degradation of a simulated organic detergent and antibacterial such as triclosan has been studied. Degradation of triclosan, using reduction techniques, produced fragments dangerous to human health which were ensured by high values of COD and TOC. These fragments were completely degraded using the two techniques (reduction followed by oxidation) which were conducted to attain the least COD and TOC values. The

two techniques of irradiation proved to be successful method for people highly sensitive to pollutants in water consumed.

Keywords; gamma irradiation; groundwater; purification; drinking water.

1. Introduction

Water polluted by heavy metals is a serious problem for humans and deserves a great deal of research to eliminate it. Among heavy metals, people identify lead, cadmium, and mercury as some of the worst pollutants for human beings. It has been reported that metals, even in small quantities, can damage some vital organs of living organisms and cause dangerous illnesses in humans (Landrigan et al., 2002; Navas-Acien et al., 2007; Cruz-Olivaresa et al., 2018). Gamma radiation is a known technique for reducing some metal ions in aqueous organic systems to metal ions in unstable oxidation states and further reduction of certain metal ions to insoluble metal atoms (Ershov and Sukhov, 1990; Johnston, 1989; Chaychian et al., 1998; Malkov and Belani, 1991; Al-Sheikhley et al., 1995).

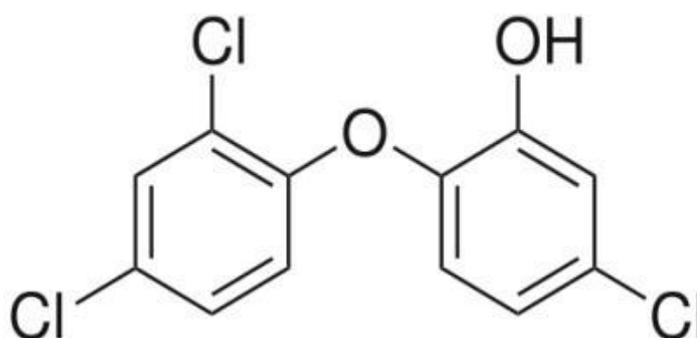
The role of organic substances such as aliphatic alcohols was applied to scavenge the hydroxyl radicals and create a reduction condition. The role of the solvated electrons in effecting desired transformations of some problematic species should be emphasized. Water purification-based gamma irradiation is mainly performed via the indirect effects of irradiation. The radical species resulting from water radiolysis can be reacted subsequently with the groundwater contaminants (Wojnárovits and Takács, 2014).

The androgynous irradiation process with its nearly equal amounts of oxidizing and reducing intermediates is much more efficient in the removal of organic compounds. This method has high penetration, is environmentally

friendly, with neither toxic chemicals added nor residual radioactivity being produced in water after treatment (He et al., 2014).

The applied irradiation doses created nitrite and hydrogen peroxide above the limit values for drinking water (Gehring et al., 1992a). To overcome this problem radiation-coupled ozone is recommended (radiation under oxidation conditions) (Gehring et al., 1992b; 1993). Ozone coupled irradiation can remove all the residual pollutants in wastewater; it may eliminate the dose rate effect for the remediation of the contaminated water (Gehring et al., 1995).

The use of pharmaceutical products such as triclosan (TN) creates more of their concentration in municipal wastewater treatment plants.



Triclosan molecular structure

The TN contamination in water results in a change to aquatic ecosystems as it is harmful to aquatic species (Johansson et al., 2014; Ding et al., 2018), and human health (Olaniyan et al., 2019). This pollutant is widespread in many water sources, including groundwater, due to the difficulty of eliminating them by traditional methods, and they are only partially degraded by radiation under reduction conditions (Ebele et al., 2017; [Dhillon et al., 2015](#); Dann et al. 2011). The researchers made extra efforts in order to create smart methods for the TN complete removal in wastewater.

Gamma radiation under reduction conditions degrades TN in water, while hazardous intermediate such as chlorinated phenols were created (which is considered a carcinogenic material) (Canosa et al., 2005). The results focus on the removal efficiency of TN in the combined irradiation and sorption treatment process, which reached as much as 97%, depending on the absorbed dose (Wang et al., 2017). Wang et al., (2018) have studied a final degradation of TN using an irradiation coupled-oxidation method by using ozone which complemented the existing metal oxide (Wang et al., 2018; Matzek et al., 2016).

The hazardous metals (that were precipitated by oxidation into metal oxide), organic pollutants, and some parameters such as chemical oxygen demand (COD), biological oxygen demand (BOD), and total organic carbon (TOC) have been significantly managed by implanted irradiation systems (Guo and Shen, 2014).

Groundwater irradiation processing is successfully eliminated all of the low-level contaminants and has potential application for bacterial cell disinfection using the two aforementioned conditions to attain highly purified water.

This work, which includes gamma irradiation, is applied for groundwater purification. Through reduction conditions, the understudied metal ions (Hg^{2+} , Cd^{2+} , Pb^{2+}) were reduced to insoluble metal atom form and can be easily separated. Through oxidation conditions, the radiation-oxidation coupled ozonation caused the degradation of organics. The turbidity, COD, BOD, and TOC are purified to create acceptable values for human use. Irradiation-disinfection of bacterial cells and rotavirus is successfully performed for real

groundwater. To ascertain which of the typical conditions of radiation reduction followed by oxidation are the best for producing pure water, complete degradation of triclosan has been studied. Highly purified water can be attained using gamma irradiation proving to be appropriate for consumption for elderly patients and highly sensitive people water.

2. Experimental

2.1. Sampling site

The source of the tested groundwater was a deep well in Muhayel Aseer, KSA.

2.2. Materials

Ampoules made of Pyrex glass were used in the series of experiments. They were filled with metal (Cd^{2+} , Hg^{2+} , and Pb^{2+} with purities of 99% ,99% and 98% respectively) sulfates solution. All of the simulated wastewater and real groundwater have been irradiated. The use of 75 cm³ volume ampoules was performed and, subjected to ⁶⁰Co gamma rays. Examination of the solution concentration and a specified dose rate was performed. Before radiation exposure, the studied solutions were infused with either hydrogen (H_2) or nitrogen (N_2) at a low rate of 100 cm³/min, which permitted the solutions to be made and kept saturated with the gas. Aldrich Co., England, has supplied the chemical reagents (metal sulfates, and alcohols). The purities of methyl, ethyl, and propyl alcohols were 99.8, 99.5, and 99.7% respectively. The two applied gases were purchased from Egypt for industrial gas Co., Egypt (Fujita et al., 1997).

The TN was purchased from Supelco as a pharmaceutical secondary standard, certified reference material, with cas number: 3380-34-5, formula: $C_{12}H_7Cl_3O_2$, and molecular weight: 289.54.

After irradiation exposure, the solution was centrifuged for 6 min at a speed of 11,000 RPM. The centrifuged water was filtered with a Millipore filter (HAWP 04700, 0.45 mm pore size) to separate suspended substances produced in the solution. The clear solution was then transferred to a screw cap glass bottle to be analyzed by atomic absorption for measuring the concentration of the studied metal ions. This method can measure both lab and real groundwater (Gehring et al., 1993).

2.3. Inorganic Measurements.

2.3.1. Cations

10 ml samples were collected to be analyzed by an atomic absorption spectrophotometer (AAs) (Unicam, Solaar 939, England). The instrument consists of a graphite tube, D2-background correction, electrothermal atomizer PU 9390, PI computer, Software (Win3.11), and a power supply.

The AAs can measure cadmium, mercury, and lead in very low concentrations (in the range of PPB) with confidence of about 99% for the studied concentrations.

2.3.2. Total Organic Carbon Measurement

The groundwater studied was sampled for TOC, in high-density polyethylene (HDPE) bottles that had been treated with 1.2M HNO_3 for 2 h followed by rinsing with deionized water. The TOC samples were immediately acidified to reduce the pH to ~ 2 and stored at low temperatures for analysis.

The N₂ and H₂ gases bubbled the acidified samples to purge the carbon dioxide, followed by the analysis (TOC) with a high temperature (680 °C) catalytic oxidation method. Then the TOC was measured using an Apollo 9000, while the TOC Analyzer with an NDIR detector (Teledyne Tekmar, Ohio, USA) has applied. The certified reference material, procured from Analytik Jena, was used for calibration (Al-Said et al., 2018).

2.3.3. COD, BOD, and Microbial Count Evaluation

The 10 mL samples were taken and centrifuged for 6 min at the speed of 11,000 RPM. Then the relevant parameters of the polluted water were observed and recorded to evaluate the polluted water after irradiation coupled with ozonation. In this process, a UV/ visible spectrograph was obtained using the CARY 50 UV/visible Spectrometer. COD was detected with Spectroquant NOVA 30 according to its manual, and BOD was detected according to the standard methods reported by Chen et al., (2003).

Bacterial Investigation:

Approximately, 100 ml of the water samples were cultured on the readily available and suitable agar. All the samples were examined after 24 h of storage at 37 °C, wherein a binocular microscope was used for bacterial assessment (Ledergerber et al., 2003, El-Toony et al., 2019).

The resultant bacterial colonies were counted with colony counting equipment (Colony counter Stuart-SC6PLUS, England), in order to adequately evaluate such infections (Vandepitte et al., 2003, El-Toony et al., 2019).

2.4. Triclosan Degradation

A High-performance liquid chromatography (Agilent 1200 Series, Agilent, USA) with a C18 reverse-phase column (5 mm, 4.6 x 150 mm) was

used to measure TN's concentration. The diode array detector (DAD), set to 200 ± 10 nm, was used as a detector. The flow rate was controlled at 1 mL min^{-1} while it was kept at $30 \text{ }^\circ\text{C}$. The applied solvent was water/acetonitrile with a ratio of 70:30 respectively while the latter was raised to 90% after 3 mins. This ratio then reached the original ratio after 3 mins of operation. The injected volume was 50 mL while the retention time for TN is 6 mins.

The TN's intermediates, such as chlorophenol, dichlorophenol, and benzene, were identified using HPLC-MS with the previously described column coupled to a Shimadzu 2010EV mass spectrometer with ESI ion source (LC-MS 2010, Columbia, USA). This instrument was accompanied by a photodiode array (PDA) as a detector, while the injected solvent volume was 30 mL (Wang et al., 2019).

The Cl^- concentration was measured by an Ion Chromatography (Dionex ICS-2100, California, USA) with Dionex RFICTM IonPac AS 14 analytical column (4 x 250 mm). The rate of flow was 1.0 mL/min , and the effluent was a mixture of Na_2CO_3 (3.5 mM) and NaHCO_3 (1.0 mM) while the injected volume was 25 ml (Wang et al., 2017).

Gamma irradiation

The dose rate used was 1.76 kGy/h . The dose rate to water in the center of the sample holder of a Canadian Gamma Cell was calibrated by the National Physical Laboratory (NPL) in the UK using the alanine dosimetry system according to the standard ISO/ASTM 51261(2004) (Abdel-Hady et al., 2013; Abdel-Hady & El-Toony 2015).

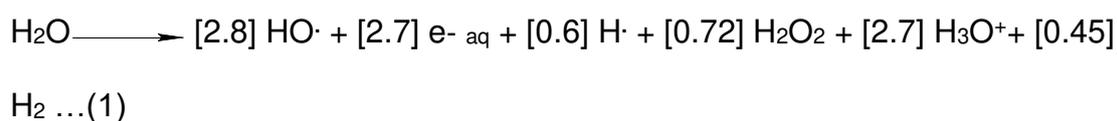
3. Results and Discussion

3.1. Metal Ion Removal by Gamma Irradiation

Fig. 1 shows the removal of metal ions such as Cd^{2+} , Hg^{2+} , and Pb^{2+} . The percentages of removal were 98%, 95%, and 94% for Cd^{2+} , Hg^{2+} , and Pb^{2+} respectively, while the initial concentrations were 50 mmole/L (at lab scale). There is an affinity of gamma irradiation towards the studied metal ions. The Cd^{2+} has the greatest affinity towards irradiation, followed by Hg^{2+} , while the Pb^{2+} has the least affinity. There are many parameters that affected the metal-irradiation affinities, such as atomic weight, ionic radii, and ionic charges (Faur-Brasquet et al., 2002).

The actual samples of groundwater have the same behavior while the metal ions being studied have lower values of removal yield. This may be due to many interference pollutants that have a serious role in decreasing the irradiation potential towards the studied metal ions. These results agreed with those that have been attained by Zhang et al., (2015).

Irradiation of water with ionizing radiation leads to the production of both reducing and oxidizing species.

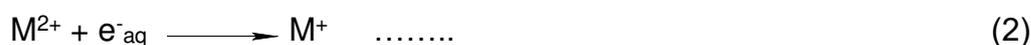


The values in square brackets in Eq. (1) indicate the number of molecules formed when an energy of 100 eV is absorbed, i.e., the average radiation-chemical yield of the process (G-value) at a pH range of 6.0–8.5 in an air-free medium (Zhang et al., 2016; Le Caër, 2011).

The active radiation species in water are e^-_{aq} , $\text{OH}\cdot$, H_3O^+ , H_2 , $\text{H}\cdot$, and H_2O_2 (Buxton, 1987). The ionizing radiation treatment of aqueous waste containing hazardous metal salts is intended to be reduced into insoluble products. Reduction by e^-_{aq} and $\text{H}\cdot$ may be very efficient; however, re-oxidation by $\text{OH}\cdot$

and H₂O₂ have avoided by the addition of an OH scavenger (Chaychian et al., 1998; Al-Sheikhly et al. 1995).

The metal ions such as Pb²⁺, Cd²⁺, and Hg²⁺ can be rapidly reduced. The reduction mechanism can be summarized as the following (Fujita et al., 1998):



The M⁺ produced undergoes disproportionation



The concentrations of groundwater's metal ions were 0.08 mole/L, 0.04 mole/L and 0.02 mole/L for Pb²⁺, Cd²⁺ and Hg²⁺ respectively.

The M⁺ can react more rapidly with hydrogen atoms than M²⁺ via an intermediate product (MH⁺) which in turn dissociates into M.



Figure 1: Effect of gamma irradiation on precipitation of metal ions (Cd²⁺, Hg²⁺, and Pb²⁺) for lab and groundwater samples.

3.2. Removal of Metal Ions by Gamma Irradiation Using De-aeration and Hydroxyl Scavenging

3.2.1. Hydroxyl Scavengers' Addition

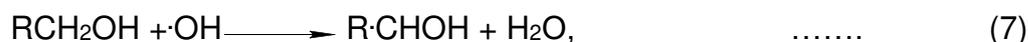
Many hydroxyl scavengers such as methanol, ethanol, and isopropanol were applied for exclusion of the studied metals as is tabulated in table (1).

Table (1): Effect of gamma-irradiation couple de-aeration, and hydroxyl scavenger on metal ions removal

Hydroxyl scavengers have a very important role in avoiding the metals' oxidation with different states as in the following reaction (Fujita et al., 1998):



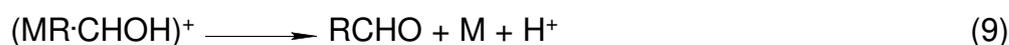
In the presence of an aliphatic alcohol such as methanol, ethanol, and isopropanol, the following reaction can be carried out (Chaychian et al., 1998):



Metal ions (M^{2+}) can react with previous reactions, resulting in slower rates compared to M^+ as in the following:



The $(MR\cdot CHO H)^+$ is dissociated into an undissolved metal form as in the following:



Methanol has the most powerful effect to scavenge hydroxyl which exceeds the metal removal to 99% for Cd^{2+} , 97% Hg^{2+} , and 96% for Pb^{2+} . Ethanol is less effective than methanol for OH scavenging; the isopropanol was the least effective, while the ethanol is the safest for human consumption. These results may be due to less alkyl length (the most mobile and fastest one) which has high efficiency in scavenging the hydroxyl. The metal ions studied in lab samples and groundwater have the same behavior while the latter has a smaller removal yield which is the result of the other pollutants interfering with the studied metal ions. These results agree with those attained by Zhang et al., (2015).

3.2.1. Metal Ions Gassing:

The solution's de-aeration appears to be a considered factor in the studied metal removal (Pospisil et al., 2006).

The gassing of the samples has been performed to eliminate the oxygen as it oxidizes the created metals (at low pH) as in the following reaction:



Dissolved O₂ also reacts rapidly with hydrated electrons and hydrogen atoms as in the following reactions (Bao et al., 2014):



While gassing with hydrogen it eliminates the oxygen and facilitates the metal ion reduction as in equations 4 and 5. It represented the most efficient method for the removal of the metal ions under consideration. Nitrogen gassing is less efficient than hydrogen as it has solely role in O₂ exerting out of the samples while the oxygenated air was the least efficient. The groundwater samples have less yield of metal removal than lab samples while it approved in their purification.

3.3. Organic Pollutant Removal, and Microbial Cell Disinfection Using Irradiation Coupled Ozone

Table (2): Effect of gamma irradiation coupled ozonation on groundwater purification.

The treatment of different parameters such as turbidity, TDS, COD, BOD, TOC, bacterial colony counting, and rotavirus detection as a function of gamma irradiation has been tabulated in table 2.

Gamma rays can interact with atoms and molecules to produce the free radicals OH, ⁻O₂, and HO₂ that can damage or modify important components of water pollution. The energy of the ionizing radiation can also be absorbed by water, resulting in the formation of several primary reactive species, such as hydrogen radicals (H[·]), hydrated electrons (e⁻_{aq}), hydroxyl radicals (OH), and less reactive species (H₃O⁺) (Woods and Pikaev, 1994; Jeong et al., 2018).

The hydroxyl radicals more rapidly and strongly attack the organic compounds while they do not differentiate between them (non-selective). The OH interacts with the organics by one of the following possibilities: first, the elimination of H from X-H (X=N, C, S); second by adding to unsaturated organic molecules or by a redox reaction (Josephson, 2018, Ibrahim et al., 2018). The degradation of organics is facilitated in the presence of dissolved oxygen while in the absence of oxygen the degradation is retarded (Zheng et al., 2012; Chu et al., 2015).

Gamma irradiation under reduction conditions has an important role in degrading organics. These findings demonstrate the reduction of turbidity, TOC, COD, and metal ions were precipitated which caused a dramatic decrease in TDS values (Abdou et al., 2011; Guo and Shen, 2014).

Gamma irradiation reduces the bacterial count as was reported by Esmaeili et al. (2018), and as the consequence, the BOD values were reduced.

After centrifugation and filtration, the collected supernatant was ozonated, coupled with irradiation (10 kGy). These coupled processes have a potential role in organic degradation and oxidation of the metal ions which are summarized as the following reaction:

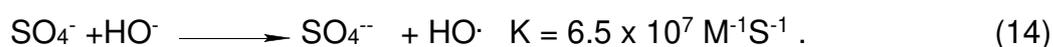


This degradation made the groundwater safe for human consumption. Many inorganic anions such as carbonate, bicarbonate, and organics can also be degraded (Chaychian et al., 1998; Cuba et al., 2012). The nitrite has also eliminated in the presence of a hydroxyl scavenger (Gehring et al., 1992a).

Moreover, the significance of the reduction in the radiation dose requirement by the combined ozone/irradiation treatments is considered. This

process (radiation-coupled ozonation) has a role in the removal of the studied metal ions as they are oxidized into insoluble metal oxides, which cause the decrease in TDS. The traces of metal ions remaining in water samples can catalytically decompose the remaining organic compound pollutants (Nawrocki, 2013; Huang et al., 2017). The COD and TOC values' were markedly managed. The ratios of COD/BOD were constant before and after the different studied techniques of water treatment, which were about 2.2. These results agreed with the results obtained by Chen et al., (2003). The advanced oxidation processes (AOPs) with gamma irradiation is an effective technology for removing persistent organic pollutants using HO· (Wang et al., 2016; Liu et al., 2014; Zhang et al., 2018).

Gamma irradiation is known to play an important role in the destruction of pathogenic microorganisms (bacterial cells and virus) (Simone-Finstrom et al., 2018; Shin et al., 2018). Radiation can produce various reactive molecular species and free radicals, including methoxy ($\cdot\text{CH}_3\text{O}$), hydroxyalkyl ($\cdot\text{CH}_2\text{OH}$), hydrogen ($\cdot\text{H}$), superoxide anions ($\cdot\text{O}_2^-$), and peroxy ($\cdot\text{OOH}$) radicals, as well as the hydroxyl ion (OH^-) (Butt and Qureshi, 2008). For the above-mentioned reasons, bacterial colony counts have dramatically decreased while the rotavirus is deactivated and their detection turned to a negative result. The presence of inorganic anions such as sulfate may be present as a pollutant in groundwater and has an important role in organic degradation as it enhances HO· production as the following reaction (Chen et al., 2015):



These findings caused a decrease in turbidity, COD, and BOD values. Based on the above-mentioned reasons, the groundwater irradiated subjected

to reduction followed by oxidation resulted in highly purified water that is safely applied in drinking and medical applications for the elderly, infants, and pollutant-sensitive people.

3.4. Triclosan Degradation Using Typical Proposed Irradiation Conditions:

Rastogi et al., (2009) reported that ethanol has applied in organic degradation as a scavenger of radicals. The reaction rate constant of ethanol with hydroxyl radical was $109 \text{ M}^{-1}\text{s}^{-1}$ (Buxton et al., 1988). The degradation of TN by gamma irradiation, coupled with a hydroxyl scavenger, has been recommended (Schemeling et al., 1998). Fig. (2) shows the increase of TN degradation with an increasing irradiation dose until 30 kGy, while by increasing the dose value, more or less degradation has been conducted. By increasing TN concentration (10-50 PPM) a decrease in the degradation yield has been performed with very small limits which did not exceed 3%.

Fig. (2): Degradation of different concentrations of triclosan at different gamma irradiation doses, coupled with a hydroxyl scavenger (ethanol).

Fig. (3) illustrates the degradation of TN by gamma irradiation under reduction conditions (presence of OH scavenger) which conducts degradation up to 66%, while it increased to 100% (complete degradation) with an extra 10 kGy under oxidation condition (ozonation).

Fig. (3): Degradation of 50 PPM of triclosan at different gamma irradiation doses under reduction condition to 30 kGy and oxidation conditions from 30-50 kGy.

Many intermediate products were identified and their molecular structures were defined. The TN degradation pathway in reduction and

oxidation conditions was expressed in Fig. 4. The degradation of TN to chlorophenol and dichlorophenol at reduction condition is approximately performed. During reduction conditions the medium is enriched with H (eq. 9) which has a basic role in hydroxylation at 10 kGy, and dehydroxylation and dechlorination at 30 kGy (Schemeling et al., 1998). Under oxidation conditions the dechlorination and dehydroxylation were the main degradation pathway of the TN. The dechlorination was mainly due to electron transfer caused by the O radicals (Anipsitakis et al., 2006; Wang et al., 2011). In addition, electron transfer can form carbon-centered radicals in the benzene ring, which induced hydroxylation in the benzene ring ([Bandala et al., 2007](#)). In this study the formation of hydroxyl radicals could be due to the oxidation of water molecules via an electron transfer process (Duan et al., 2016). Under the combined action of ozone, hydroxyl radicals, and singlet oxygen, the intermediate products were further oxidized to carbon dioxide and water (Ibrahim et al., 2018).

Fig. (4): Scheme of triclosan degradation in reduction and oxidation conditions coupled with gamma irradiation.

By increasing the irradiation doses of the TN's solution, the pH value is decreased especially at the end of this process. After irradiation at 10 kGy, 20 kGy, 30 kGy, and 40 kGy doses, the resulted pH were 6.4, 6.1, 5.9, 5.7 and 5.5, respectively. The decrease in pH was attributed to the formation of organic acids during the irradiation process (Wang et al., 2017). The content of TOC decreased to 3.3 mg/L, 2.8 mg/L, 2.5 mg/L, 2.2 mg/L and 1.8 mg/L, respectively, corresponding to the dose of 10 kGy, 20 kGy, 30 kGy, and 40 kGy.

Chemical oxygen demand (COD) decreased with irradiation dose gradually until 30 kGy, after which it dramatically dropped off up to 40 kGy as is seen in Fig. 5.

Fig. (5): Removal of COD (mg/L) at different irradiation doses, under reduction and oxidation conditions.

The simulated wastewater with TN showed a small increase in COD with irradiation up to 30 kGy which is due to the resulting chlorophenol and dichlorofenol which are more hazardous for alive organisms than un-degraded TN. The TN's COD is completely diminished to the accepted level in water at 40 kGy coupled with ozonation due to the finally degradation of TN to CO₂ and H₂O.

Conclusion

This work aims to attain a highly purified water that can be used as drinking water for the elderly, infants, and sensitive humans, and can be successfully applied in medical applications. Gamma irradiation was used for the elimination of different pollutants in actual groundwater. Irradiation based reduction caused insoluble metal forms can be easily separated out of the water samples. Some important parameters have been studied such as different hydroxyl scavengers and different gases for water de-aeration. The maximum limit of metal exclusion yields were 99.4 for Cd²⁺, 97.8 for Hg²⁺, and 96.9, for Pb²⁺ at the best-studied conditions. Irradiation based oxidation coupled with ozonation resulted in the degradation of organics. Many impacts had reduced values, such as turbidity, TDS, COD, BOD, and TOC. Irradiation caused the sterilization of bacterial cells and rotavirus from the studied groundwater. Degradation of triclosan has been carried out in order to ensure the coupled

methods of irradiation under oxidation, and reduction conditions, are an optimum technique to attain highly purified water. Degradation of tn has been resulted in di- and chlorphenols at 10 kGy, while de-chlorination and de-hydroxylation have occurred at 30 kGy. Finally tn has been degraded to carbon dioxide and water by 40 kGy coupled with ozonation. These techniques proved to be successful for groundwater purification and can be safely applied for human consumption purposes.

Acknowledgement The authors would like to thank King Khalid University for funding this work under a number of RGP.1/394/42.

Conflict of Interest Statement: None

References

- Abdel-Hady, E. E., El-Toony, M. M., M.O. Abdel-Hamed, 2013. Grafting of glycidyl methacrylate/styrene onto polyvinylidene fluoride membranes for proton exchange fuel cell, *Electrochim Acta* 103, 32-37.
- Abdel-Hady, E. E., El-Toony, M. M., 2015. Grafting of vinyl pyrrolidone styrene onto ethylene/ chlorotrifluoroethylene membrane for proton exchange membrane fuel cell, *Electrochim Acta* 176, 472–479.
- Abdou, L. A. W., Hakeim, O. A., Mahmoud, M. S., El-Naggar, A. M., 2011. Comparative study between the efficiency of electron beam and gamma irradiation for treatment of dye solutions. *Chem. Eng.* 168, 752–758.
- Al-Said T., Naqvi S. W. A., Al-Yamani, F., Goncharov, A., Fernandes, L., 2018. High total organic carbon in surface waters of the northern Arabian Gulf: Implications for the oxygen minimum zone of the Arabian Sea. *Marine Pollut. Bull.* 129, 35–42.
- Al-Sheikhly, M., Chaychian, M., McLaughlin, W. L., 1995. Radiation-initiated

removal of heavy metals from water. *Trans. Am. Nucl. Soc.* 72, 128–130.

Anipsitakis, G.P., Dionysiou, D.D., Gonzalez, M.A., 2006. Cobalt-mediated activation of peroxymonosulfate and sulfate radical attack on phenolic compounds. Implications of chloride ions, *Environ. Sci. Technol.* 40, 1000–1007.

Bandala, E.R., Peláez, M.A., Dionysiou, D.D., Gelover, S., Garcia, J., D. [Macías, J., 2007](#). Degradation of 2,4-dichlorophenoxyacetic acid (2,4-D) using cobalt-peroxymonosulfate in Fenton-like process, *J. Photochem. Photobiol. A* 186 357–363.

Bao, Q., Chen, L., Tian, J., Wang, J., 2014. Degradation of 2-mercaptobenzothiazole in aqueous solution by gamma irradiation. *Radiat. Phys. Chem.* 103, 198–202.

Butt, S., Qureshi, R. N., 2008. Gamma radiolytic degradation of flouranthene and monitoring of radiolytic products using GC-MS and HPLC. *Radiat. Phys. Chem.* 77, 768–774.

Buxton, G. V., 1987. Radiation chemistry of the liquid state. 1. Water and homogeneous aqueous solutions. In: Farataziz, Rodgers, M.A. (Eds.), *Radiat. Chem. Principles Applicat.* VCH, New York, 321-376.

Buxton, G.V., Greenstock, C.L., Helman, W.P., Ross, A.B., 1988. Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals ($\cdot\text{OH}/\cdot\text{O}^-$ in aqueous solution, *J. Phys. Chem. Ref. Data* 17, 513–886.

Canosa, P., Morales, S., Rodriguez, I., Rubi, E., Cela, R., Gomez, M., 2005.

Aquatic degradation of triclosan and formation of toxic chlorophenols in presence of low concentrations of free chlorine. *Anal. Bioanal. Chem.* 383, 1119-1126.

Chaychian, M., Al-Sheikhly, M., Silverman, J., McLaughlin, W. L., 1998. The mechanisms of removal of heavy metals from water, by ionizing radiation. *Radiat. Phys. Chem.* 53, 145-150.

Chen, H., Zhang, Z. L., Yang, Z. L., Yang, Q., Li, B., Bai, Z. Y., 2015.

Heterogeneous Fenton-like catalytic degradation of 2, 4-dichlorophenoxy acetic acid in water with FeS. *Chem. Eng. J.* 273, 481–489.

Chen, J., Liu, M., Zhang, Li, Zhang, J., Jin, L., 2003. Application of nano TiO₂ towards polluted water treatment combined with electro-photochemical method. *Water Res.* 37, 3815–3820.

Chu, L., Wang, J., Liu, Y., 2015. Degradation of sulfamethazine in sewage sludge mixture by gamma irradiation. *Radiat. Phys. Chem.* 108, 102–105.

Cruz-Olivaresa, J., Barrera-Díaza C. E., Martínez-Barreraa G., Pérez-Alonsoa, C., Roa-Moralesa, G., 2018. Comparative application of an irradiated and non-irradiated calcite-type material to improve the removal of Pb in batch and continuous processes. *J. Environ. Chem. Eng.* 6, 6297–6307.

Čuba, V., Pavelkova´, T., Barta, J., Gbur, T., Vlk, M., Zavadilov, A., Indrei, J., Docekalova´, Z., Pospisil, M., Mucka, V., 2012. Preparation of inorganic crystalline compounds induced by ionizing, UV and laser radiations. *Radiat. Phys. Chem.* 81, 1411–1416.

- Dann, A.B., Hontela, A., 2011. Triclosan: environmental exposure, toxicity and mechanisms of action, *J. Appl. Toxicol.* 31, 285–311.
- Dhillon, G.S., Kaur, S., Pulicharla, R., Brar, S.K., Cledon, M., Verma, M., Surampalli, R.Y., 2015. Triclosan: current status, occurrence, environmental risks and bioaccumulation potential, *Int. J. Environ. Res. Public Health* 12, 5657–5684.
- Ding, T., Lin, K., Yang, M., Bao, L., Li, J., Yang, B., Gan, J., 2018. Biodegradation of triclosan in diatom *Navicula* sp.: kinetics, transformation products, toxicity evaluation and the effects of pH and potassium permanganate, *J. Hazard. Mater.* 344, 200–209.
- Duan, X., Su, C., Zhou, L., Sun, H., Suvorova, A., Odedairo, T., Zhu, Z., Shao, Z., Wang, S., 2016. Surface controlled generation of reactive radicals from persulfate by carbocatalysis on nanodiamonds, *Appl. Catal. B* 194, 7–15.
- Ebele, A.J., Abou-Elwafa Abdallah, M., Harrad, S., 2017. Pharmaceuticals and personal care products (PPCPs) in the freshwater aquatic environment, *Emerg. Contam.* 3, 1–16.
- El-Toony, M. M., Eid, Gh., Algarni, H., 2019. Estimation of hazardous materials in water and their toxicity levels in Mahayel Aseer, Kingdom of Saudi Arabia (KSA), *Environ. Monit. Assess.* 191,779.
- Ershov, B.G., Sukhov, N. L., 1990. A pulse radiolysis study of the process of the colloidal metal formation in aqueous solutions. *Radiat. Phys. Chem.* 36, 93-97.
- Esmaeili, S., Barzegar, M., Sahari, M. A., Berengi-Ardestani, S., 2018. Effect of gamma irradiation under various atmospheres of packaging on the

- microbial and physicochemical properties of turmeric powder. *Radiat. Phys. Chem.* 148, 60–67.
- Faur-Brasquet, C., Kadirvelu, K., Le Cloirec, P., 2002. Removal of metal ions from aqueous solution by adsorption onto activated carbon cloths: Adsorption competition with organic matter, *Carbon* 40(13):2387-2392
- Fujita, N., Matsuura, C., Hiroishi, D., Saigo, K., 1998. Radiation-induced precipitation of nickel ion in aqueous solution saturated with hydrogen gas. *Radiat. Phys. Chem.* 53, 603-609.
- Fujita, N., Matsuura, C., Hiroishi, D., Saigo, K., Kiyokawa, H., Hatashita, M., 1997. Radiation-assisted regeneration of waste liquor from electroless plating process. *Bull. Nippon Bunri. Univ.*
- Gehring, P., Eschweiler, H., Szinovatz, W., 1992a. Clean-up of polluted groundwater by radiation-induced oxidation. *Proc. Sp. Applicat. Isotopes Radiat. Conservat. Environ. Karlsruhe*, 203-205. IAEA, Viena.
- Gehring, P., Proksch, E., Eschwiler, H., Szinovatz, W., 1992b. Remediation of Groundwater Polluted with Chlorinated Ethylenes by Ozone-electron Beam Irradiation Treatment. *Appl. Radiat. Isotopes* 42, 1107-1115.
- Gehring, P., Eschweiler, H., Fiedler, H., 1995. Ozone-electron beam treatment for groundwater remediation. *Radiat. Phys. Chem.* 46 (4-6), 1075-1078.
- Gehring, P., Eschweiler, H., Szinovatz, W., Steiner, F. R., Sonneck, G.,

1993. Radiation-induced OH radical generation and its use for groundwater remediation. *Radiat. Phys. Chem.* 42, 711-714.
- Guo, F., Shen, H., 2014. Study of gamma irradiation-induced effects on organic pollutants and suspended solids in coking wastewater, *Desal. water treat.* 52 (10-12), 1850-1854.
- Gyeong, H. J., Jae-Hyeon, C., Cheorun, Jo, Sungbeom, L., Seung, S. L., Hyoung-Woo, B., Byung, Y. C., Tae, H. K., 2018. Gamma irradiation-assisted degradation of rosmarinic acid and evaluation of structures and anti-adipogenic properties. *Food Chem.* 258, 181–188.
- He, S. J., Wang, J. L., Ye, L. F., Zhang, Y. X., Yu, J., 2014. Removal of diclofenac from surface water by electron beam irradiation combined with a biological aerated filter. *Radiat. Phys. Chem.* 105, 104–108.
- Huang, H., Lu, H., Zhan, Y., Liu, G., Feng, Q., Huang, H., Wu, M., Ye, X., 2017. VUV photo-oxidation of gaseous benzene combined with ozone-assisted catalytic oxidation: Effect on transition metal catalyst. *Appl. Surf. Sci.* 391, 662–667.
- Ibrahim, K. E. A., Elbashir, A. A., Ahmed, M. M. O., Şolpan, D., 2018. Radiolytic degradation of Carbofuran by using Gamma and Gamma/hydrogen peroxide Processes. *Radiat. Phys. Chem.* 153, 251-257.
- Johansson, C.H., Janmar, L., Backhaus, T., 2014. Triclosan causes toxic effects to algae in marine biofilms, but does not inhibit the metabolic activity of marine biofilm bacteria, *Mar. Pollut. Bull.* 84, 208–212.
- Johnston, F. J., 1989. Radiolytic reductions of Ag(I), Cu(II), Hg(II) and Pb(II) in

aqueous-ethanol systems and the effect of colloidal sulfur. *Radiat. Phys. Chem.* 33, 113-118.

Josephson, V. C., 2018. Preservation of food by ionizing radiation. CRC Press. Landrigan, Ph. J., Schechter, C., B., Lipton, J., M., Fahs M.C., Schwartz, J., 2002. Environmental pollutants and disease in American children: estimates of morbidity, mortality, and costs for lead poisoning, asthma, cancer, and developmental disabilities. *Environ. Health Perspect.* 110 (7), 721–728.

Le Caër, S., 2011. Water radiolysis: influence of oxide surfaces on H₂ production under ionizing radiation. *Water* 3 (1), 235–253.

Ledergerber, U., Regula, G., Stephan, R., Danuser, J., Bissing, B., & Stark, K. D. C., 2003. Risk factors for antibiotics resistance in *Campylobacter* spp. Isolated from raw poultry meat in Switzerland. *BMC Public Health*, 3, 39–46.

Liu, Y. K., Hu, J., Wang, J. L. 2014. Fe²⁺ enhancing sulfamethazine degradation in aqueous solution by gamma irradiation. *Radiat. Phys. Chem.* 96, 81–87.

Malkov, A. V., Beloni, J., 1991. Radiation-induced reduction of divalent mercury in the presence of other metal ions. *J. General Chem. USSR* 61, 2449-2452.

Matzek, L.W, Carter, K.E., 2016. Activated persulfate for organic chemical degradation: a review, *Chemosphere* 151, 158–178.

Navas-Acien, A., Guallar, E., Silbergeld, E. K., Rothenberg, S. J., 2007. Lead exposure and cardiovascular disease-a systematic review, *Environ. Health Perspect.* 115 (3), 472–482.

- Nawrocki, J., 2013. Catalytic ozonation in water-controversies and questions. Discussion paper. *Appl. Catal. B: Environ.* 142, 465–471.
- Pospisil, M., Cuba, V., Mucka V., Drtinova, B., 2006. Radiation removal of lead from aqueous solutions—effects of various sorbents and nitrous oxide. *Radiat. Phys. Chem.* 75, 403–407.
- Rastogi, A. Al-Abed, S.R., Dionysiou, D.D., Sulfate radical-based ferrous–peroxymonosulfate oxidative system for PCBs degradation in aqueous and sediment systems, *Appl. Catal. B* 85 (2009 a) 171–179.
- Rastogi, S.K., Satyanarayan, P.V.V., Ravishankar, D. Tripathi, S. 2009 b. A study on oxidative stress and antioxidant status of agricultural workers exposed to organophosphorus insecticides during spraying, *Ind J occupation environ med.* 13: (3), 131-134..
- Schemeling, D. Poster, D., Chaychian, M., Penta, P., MaChlaughlin, W., Silverman, J., Al-Sheikhly, M. 1998. Application of ionizing radiation to the remediation of materials contaminated with heavy metals and poly chlorinated biphenyls' *Radiat. Phys. Chem.* 52, 371-377.
- Shin, Y. P., Myung-Sub, C., Sang-Do, Ha, 2018. Combined effect of sodium hypochlorite and gamma-irradiation for the control of *Vibrio vulnificus* in fresh oyster and clam. *LWT - Food Sci. Technol.* 91, 568–572.
- Simone-Finstrom M., Aronstein, K., Goblirsch, M., Rinkevich, F., de Guzman, L., 2018. Gamma irradiation inactivates honey bee fungal, microsporidian, and viral pathogens and parasites. *J. Invertebr. Pathol.* 153, 57–64.
- Vandepitte, J., Verhaegen, J., Engbaek, K., Rohner, P., Piot, P., & Heuck, C.

- C. (2003). Basic laboratory procedures in clinical microbiology (2nd ed.). Geneva:World Health Organization.
- Wang, J. L., Chu, L. B., 2016. Irradiation treatment of pharmaceutical and personal care products (PPCPs) in water and wastewater: an overview. *Radiat. Phys. Chem.* 125, 56–64.
- Wang, S, Yin, Y, Wang, J, 2017. Enhanced biodegradation of triclosan by means of gamma irradiation, *Chemosphere* 167,406-414.
- Wang, Z., Yuan, R., Guo, Y., Xu, L., Liu, J., 2011. Effects of chloride ions on bleaching of azodyes by Co^{2+} /oxone reagent: kinetic analysis, *J. Hazard. Mater.* 190,1083–1087.
- Wang, J.L., Wang, S.Z., 2018. Activation of persulfate (PS) and peroxymonosulfate (PMS) and application for the degradation of emerging contaminants, *Chem. Eng. J.* 334, 1502–1517.
- Wojnárovits, L., Takács, E., 2014. Rate coefficients of hydroxyl radical reactions with pesticide molecules and related compounds: A review. *Radiat. Phys.Chem.* 96, 120-134.
- Woods, R. J., Pikaev, A. K., 1994. *Appl Radiat Chem: Radiation Processing*, John Wiley and Sons, New York.
- Zhang, Z., Yang, Qi, Wang, J., 2016. Degradation of trimethoprim by gamma irradiation in the presence of persulfate. *Radiat. Phys. Chem.* 127, 85–91.
- Zhang, J., Zhang, G., Cai, D., Wu, Z., 2015. Immediate remediation of heavy metal (Cr(VI)) contaminated soil by high energy electron beam irradiation. *J. Hazard. Mat.* 285, 208–211.
- Zheng, B., Zheng, Z., Zhang, J., Luo, X., Liu, Q., Wang, J., Zhao, Y., 2012.

The removal of *Microcystis aeruginosa* in water by gamma-ray irradiation. *Separat. Purificat. Technol.* 85, 165–170.

Author contributions:

- **Mohamed M. El-Toony** designed the work, follow the experiments, and writes the article.
- **Ahmed H. Rajab** does some experiments, draw some figure.
- **Ghada A. Eid** makes some calculations, make some physics view, review the work.
- **Nabila M. Mazid** makes a revision.

Figures

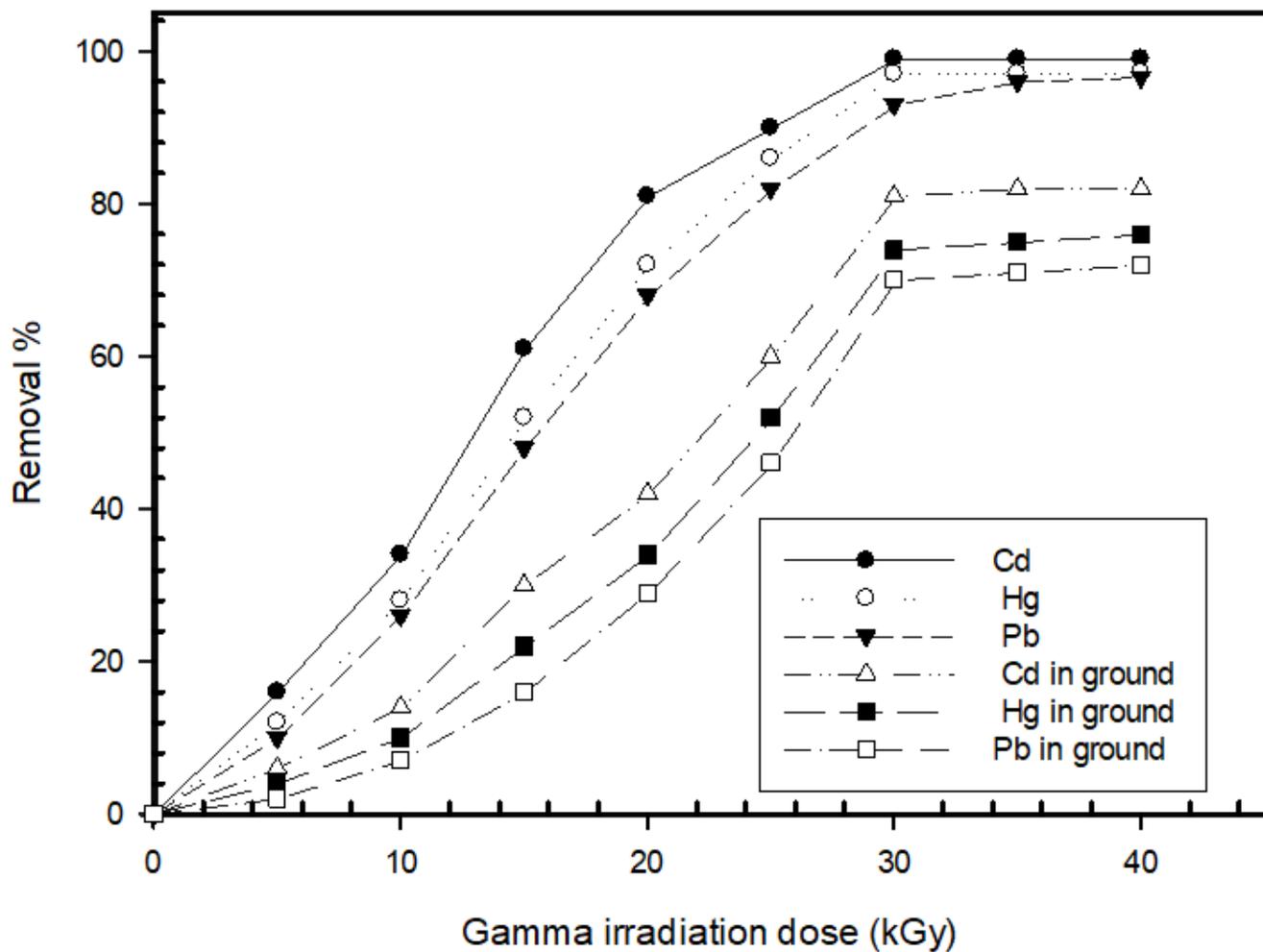


Figure 1

Effect of gamma irradiation on precipitation of metal ions (Cd^{2+} , Hg^{2+} , and Pb^{2+}) for lab and groundwater samples.

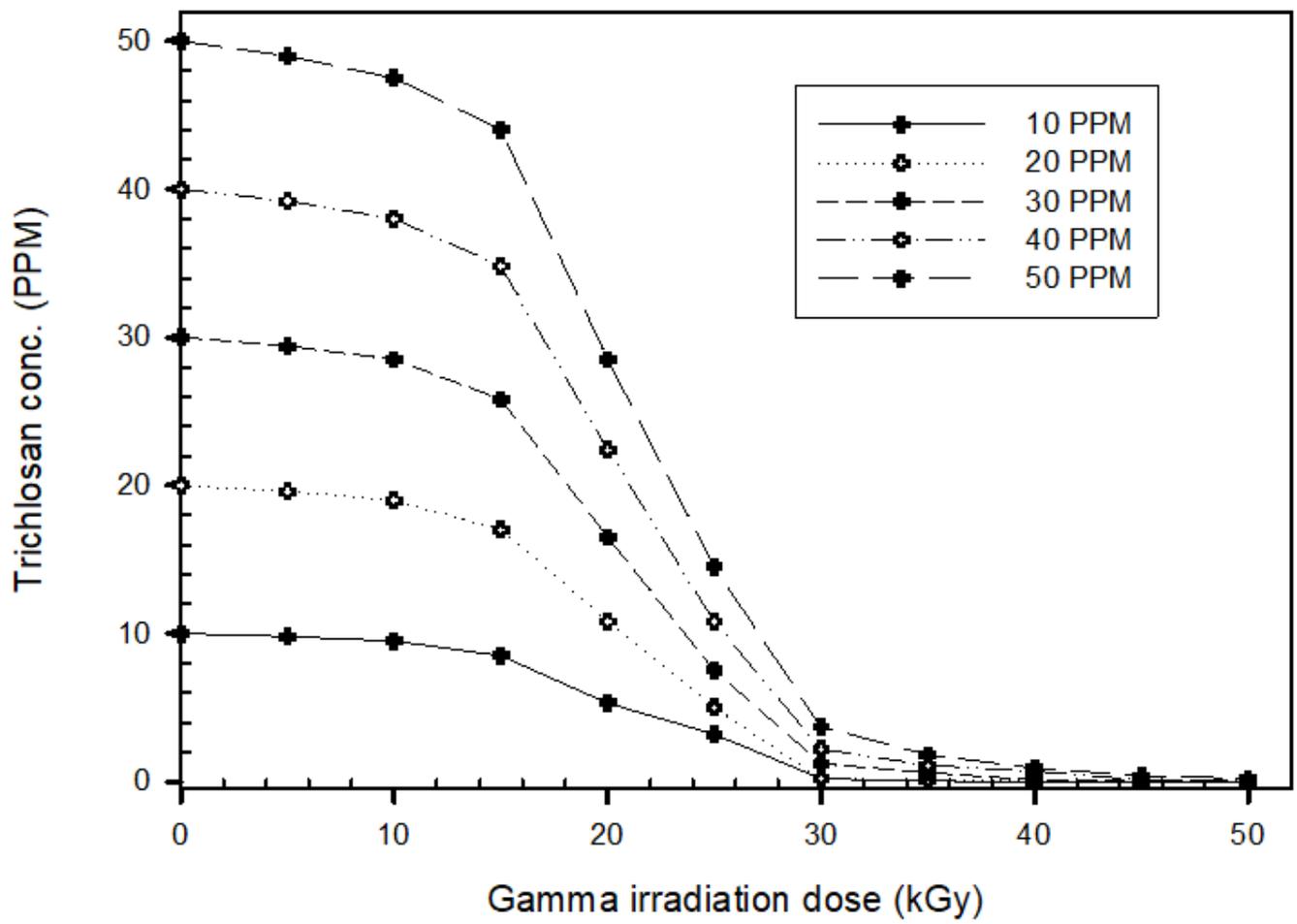


Figure 2

Degradation of different concentrations of triclosan at different gamma irradiation doses, coupled with a hydroxyl scavenger (ethanol).

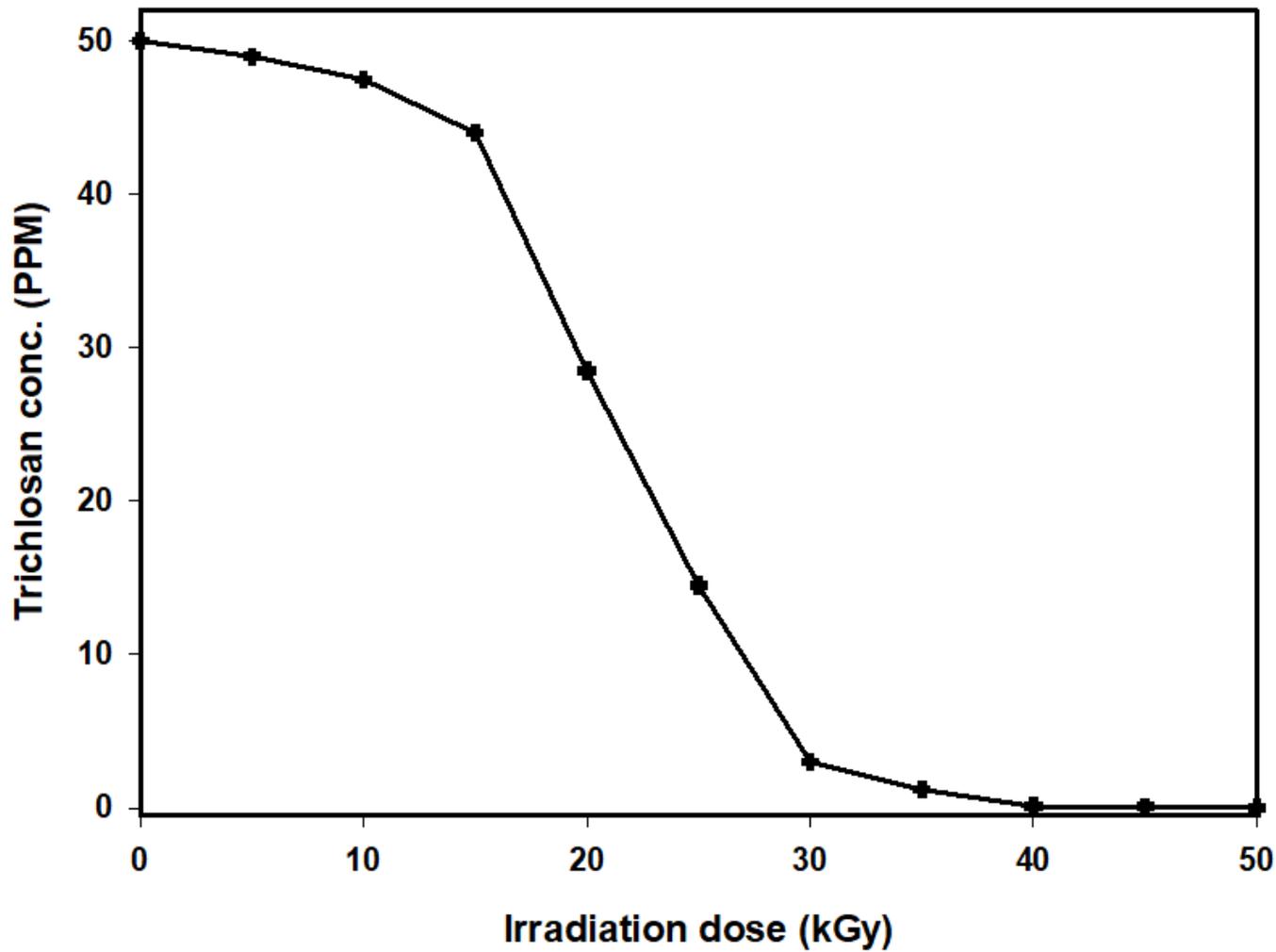


Figure 3

Degradation of 50 PPM of triclosan at different gamma irradiation doses under reduction condition to 30 kGy and oxidation conditions from 30-50 kGy.

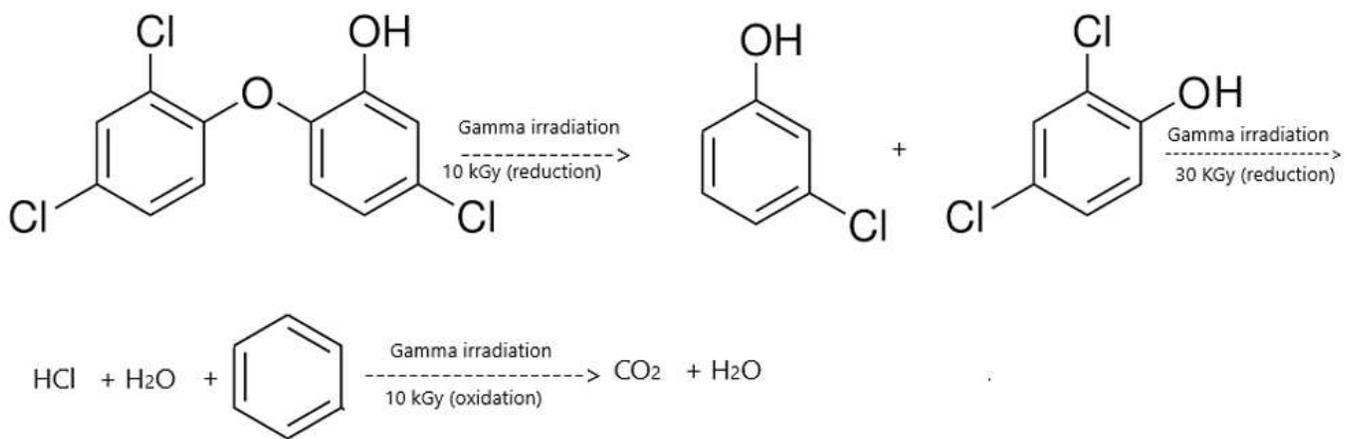


Figure 4

Scheme of triclosan degradation in reduction and oxidation conditions coupled with gamma irradiation.

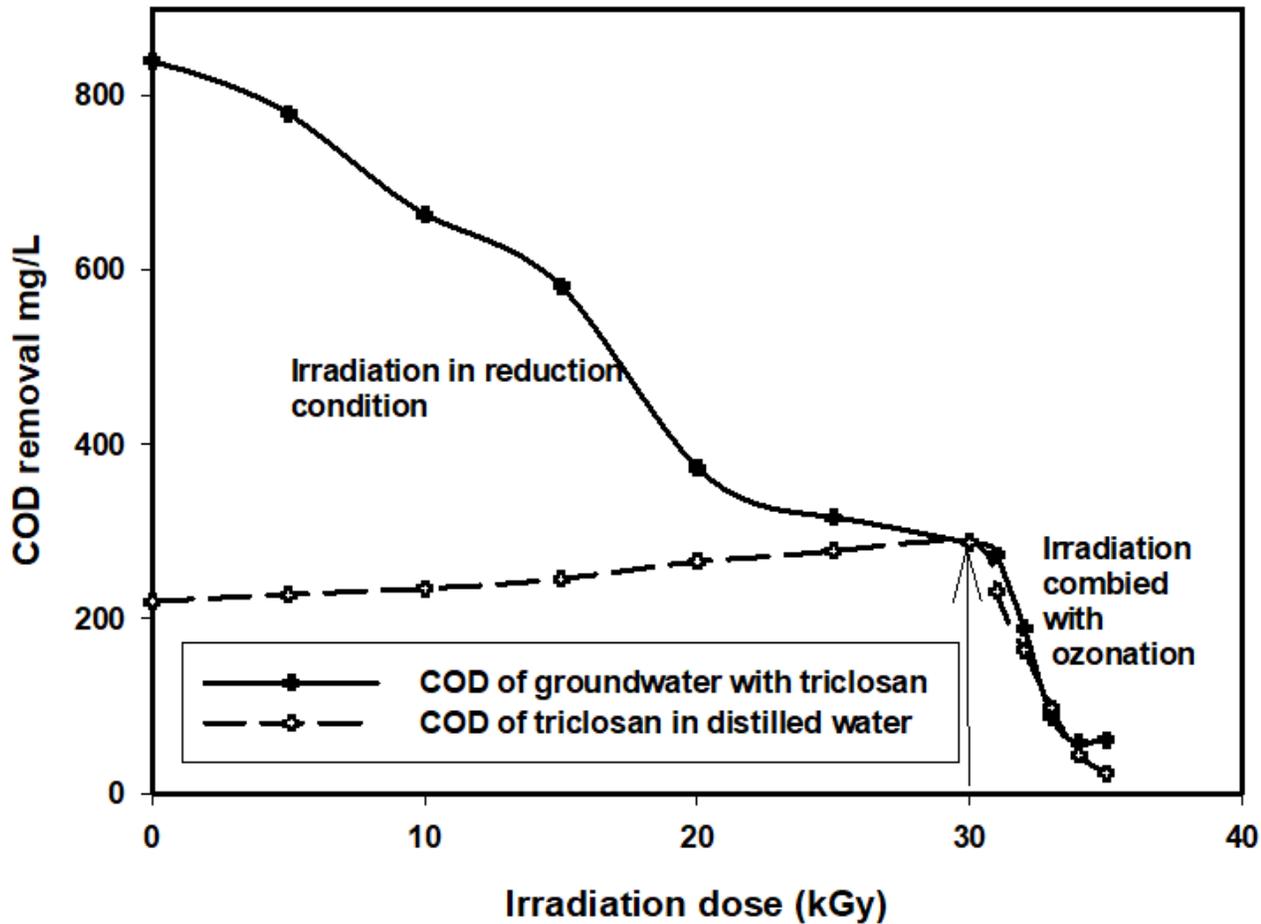


Figure 5

Removal of COD (mg/L) at different irradiation doses, under reduction and oxidation conditions.

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [supplementarymaterials.docx](#)