Suplemento de la Revista Mexicana de Física **4** 011007 (2023) 1–4

Radiation chemistry as a tool in earth science studies

A. Meléndez-López*, J. Cruz-Castañeda, A. Negrón-Mendoza,
S. Ramos-Bernal, A. Heredia, and H.G. Vázquez-López

Instituto de Ciencias Nucleares, Universidad Nacional Autónoma de México,
Circuito Exterior s/n, Ciudad Universitaria, Apartado Postal 70-543, Deleg. Coyoacán, 04510, CDMX, México.
**adriana.melendez@nucleares.unam.mx*

Received 4 November 2022; accepted 21 March 2023

The study of the interaction of gamma radiation with relevant elements on our planet is important for earth sciences in understanding current phenomena the Earth experiences and to suggest solutions, such as the removal of dyes from wastewater. The goal of this work is to show the importance of research results in which the interaction of gamma radiation with organic compounds gives clues to solving current problems by making use of gamma radiation interactions with matter. Our results show that gamma irradiation could be an alternative to the removal of emerging contaminants, a topic of current relevance.

Keywords: Dyes; gamma radiation; earth science.

DOI: https://doi.org/10.31349/SuplRevMexFis.4.011007

1. Introduction

Pollution and contamination of the environment are important issues to tackle. Agronomic methods, economic development, accelerated industrial growth, and urbanization has overall resulted in higher environmental pollution through more release of hazardous wastes, energy expenditure, exhaust emissions from the automobile industry, and emission of toxic gases. *Hazardous waste* is defined as waste that, because of its chemical activity or toxic, explosive, corrosive, or other characteristics, causes danger or likely will cause danger to health or the environment, whether alone or when coming into contact with other waste (LaGrega *et al*., 2010). According to The World Counts, the number of organizations, research institutions, and news services is increasing. In just one generation, the production of manufactured chemicals has increased by 40,000% from 1 million to 400 million tons. Hazardous wastes include dyes eluted from textile industries, toxic heavy metals, pesticides, and polyaromatic hydrocarbons (Borowy, 2019). Dyes (emerging contaminants) are signified as frequent pollutants emitted in significant quantities by industries such as textile, leather, paper, rubber, foodstuffs, and plastics (Thabet *et al*., 2022). About 7×10^7 tons of synthetic dyes are produced annually worldwide, with over 10,000 tons of such dyes used by textile industries (Chandanshive *et al*., 2020). There are various categories of dyes, and some examples are shown in Table I.

Researchers have established that dyes are recalcitrant and refractory pollutants that constitute a significant burden on the environment. Therefore, the toxic effect on wastewater must be understood (Singh *et al.*, 2021). Wastewater is contaminated water that must be treated before it may be transferred into rivers and lakes to prevent further groundwater pollution. Research has been conducted on a wide variety of emerging contaminants as well as industrially related synthetic dyes and dye-containing hazardous pollutants (Khan *et al*., 2022). Guin *et al*., (2014) investigated several advanced oxidation processes, such as gamma irradiation for the treatment of dye wastewater. They found that ionizing radiation was an effective treatment process for dye wastewater at a lower cost. In terms of environmental impact, gamma irradiation technology is capable of reducing the effects of chemical pollution of industrial wastewater in the environment (Verde *et al*., 2015). Today, the increased use of ionizing radiation for treatment purposes is observed because of its well-developed compact design, larger capacity, reliability, and cost-effectiveness (Hossain *et al*., 2018). In this paper, we report the stability of four dyes under gamma radiation to determine the possibility of its use as a treatment in wastewater. As objects, we selected organic dyes on aerated systems, which may be measured using spectrophotometer techniques (UV–vis range).

TABLE I. The most representative dye of different categories, their possible industrial application, and toxicity are shown.

Categories of dyes	The most representative dye	Industrial applications
Acid	Bromothymol blue	Medicine and Textile
Azo	Methyl orange	Textile
Basic	Green malachite	Photographic
Direct	Red 76	Textile
Disperse	Yellow 7	Textile and food
Mordant	Red 19	Textile
Reactive	Red 120	Textile and medicine
Sulphur	Cresol red	Medicine

TABLE II. Organic dyes used in this work.

Dye	Chemical formula	Molecule structure	Toxicity
Green malachite	$C_{23}H_{25}N_2Cl$		Acute, chronic, carcinogenicity, cytotoxicity, genotoxicity, mitochondrial toxicity, mutagenicity, nucleic acid damage (Sabnis, 2010).
Methyl orange	$C_{14}H_{14}N_3O_3Na$		Carcinogenicity, genotoxicity and mutagenicity (Sabnis, 2010).
Cresol red	$C_{21}H_{18}O_5S$		Gastrointestinal corrosive injury, central nervous system, cardiovascular disturbances, renal, and hepatic injury (Andersen, 2006; Doughmi *et al*., 2019).
Bromothymol blue	$C_{27}H_{28}Br_2O_5S$		Gastrointestinal irritation, and respiratory tract irritation (Kumar *et al*., 2022)

2. Experimental

The glassware was treated with a warm mixture (1:1) of nitric and sulfuric acid for 30 minutes, followed by washing with distilled water and, later, was heated in an oven at 250°C overnight to minimize contamination (Draganić & Draganić, 1971). Six mL of dye solutions (2 x 10^{-4} mol L^{-1}) were placed in glass tubes in the presence of oxygen. The water was redistilled according to Spinks and Woods (1990). The dyes studied were green malachite, methyl orange, cresol red, and bromothymol blue (Table II, toxicity is also shown) at room temperature. Glass tubes were irradiated at different doses using a gamma ray source, originated from ^{60}Co (Gamma-beam 651-PT, at the Instituto de Ciencias Nucleares, UNAM). The absorbed doses were between 0 and 40 kGy at a fixed position with a dose rate of 187 Gy/min. The dose rate was determined using the ferrous ammonium sulfate-cupric sulfate dosimeter (Spinks & Woods, 1990). After irradiation, aliquots of dyes were analyzed using a Varian Cary 100 Scan UV-vis spectrophotometer (200–800 nm) and 1 cm quartz cells.

3. Results

3.1. Calibration curves by UV-vis spectrophotometer

The existence of a linear response ($r^2 = 0.99$) in the absorbance change *versus* concentration of solutions was taken as an indication of the extent of the suitability of the analytical technique used (Fig. 1). Using the UV-vis spectrophotometer and Beer's Law, the molar extinction coefficient was calculated for dyes in an aqueous solution (Table III).

Figure 2 shows the plot of the residuary percentage after 40-kGy-absorbed dose at room temperature; as shown, degradation is not an easy task because dyes consist of very stable molecular structures (Table II). Residuary percentage refers to the amount of material that remains without changes after irradiation.

Water decomposition plays a critical role in the radiolysis processes because the free radicals formed are reactive to organic compounds. The products formed by the irradiation of water are shown in Fig. 3. When a dilute aqueous solution of dyes is irradiated, those species participate in degrading dyes. New species and molecular products are formed and could be

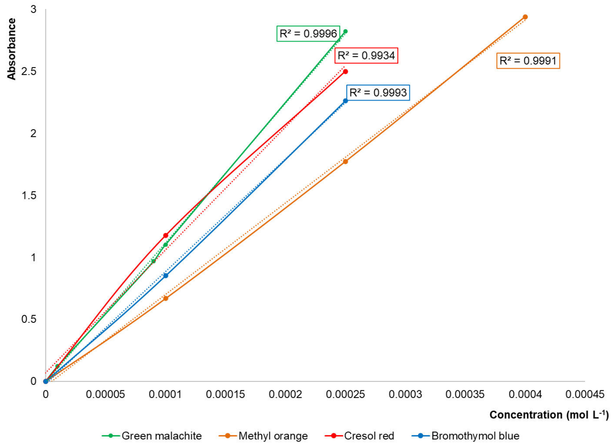

FIGURE 1. Linear response in the absorbance change versus concentration of dye solutions.

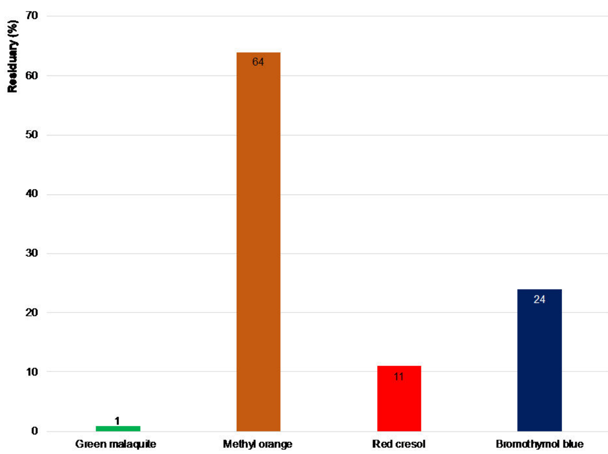

FIGURE 2. Residuary percentage of dyes after irradiated at 40 kGy.

TABLE III. Linear range data of the absorbance–concentration relationships and molar extinction coefficients of different dye solutions.

Dye	Maximum wavelength (nm)	Molar extinction coefficient (mol L^{-1} cm^{-1})
Green malachite	427	11244
Methyl orange	328	7313
Cresol red	273	13338
Bromothymol blue	328	9072

toxic to the environment, a topic that was not investigated in this work.

The degradation of methyl orange (azo dye) under gamma irradiation was investigated by Chen *et al.*, (2008). They demonstrated that the degradation of methyl orange was significantly accelerated under the oxidative conditions, while its discoloration efficiency was higher under the reductive conditions. They showed that ·OH is more reactive than e-aq for the methyl orange decomposition. N-methylbenzenamine, 4-(dimethylamino) phenol, aniline, 4-hydrazinyl-N, and N-dimethylbenzenamine are the degradation intermediates of methyl orange by gamma irradiation processes. Besides oxidative or reductive conditions in gamma radiolysis, the temperature is another critical variable in the processes, due to the probability of recombination of the primary radicals increasing as the temperature increases. A previous study (Meléndez-López *et al.*, 2018) showed that temperature is important in the degradation rate. When irradiation occurs at 77 K, the degradation of the dyes is lower than at a higher temperature (295 K).

$$H_2O \rightsquigarrow {}^{\bullet}H + {}^{\bullet}OH + e^-_{aq} + H_2 + H_2O_2$$

FIGURE 3. Gamma radiolysis of water.

Methyl orange is categorized as an acute toxicity compound and mutagenic substance (Table II) and is the most stable dye under high doses of gamma radiation in this study. Because it is highly solubilized in the environment, it is very challenging to remove it (Velusamy *et al.*, 2022).

Dyes discharged into the environment cause severe problems, such as limited light penetration into the water because organic dyes absorb and reflect sunlight entering the water, resulting in killing aquatic species, as well as bacteria used to degrade impurities in the water (Attri *et al.*, 2018). For example, methyl orange affects the habitat of aquatic environments and results in the production of various amines under anaerobic conditions (Bashir *et al.*, 2020).

4. Remarks

Gamma irradiation processes could be applied in water remediation due to their effectiveness and are considered an advanced oxidation process (AOPs). Gamma irradiation was chosen in this work because it involves high-quality treatment techniques, low costs, and simplicity. To understand the mechanism of dye decolorization after gamma rays and to optimize the complete degradation, more studies are needed, for example, the study of actual wastewater samples, different pH values, degradation rate constant, and the analysis of the intermediates using different analysis techniques (*e.g.*, Fourier transforming infrared and chromatography-mass spectrometry).

Acknowledgments

This work was supported by project PAPIIT IN114122, CONACYT 319118. The authors express their gratitude to Claudia Camargo for her technical help at the Laboratorio de Evolución Química (ICN-UNAM), José Rangel, Martín Cruz, Enrique Palacios, Javier Gutiérrez Romero, and Benjamín Leal, for the irradiation of the samples. Adriana Meléndez was supported by a CONACYT postdoctoral fellowship. This work was performed at and supported by the

Instituto de Ciencias Nucleares, UNAM. The authors warmly appreciate the comments of the anonymous reviewers, that substantially improved the manuscript.

1. A. Andersen, Final report on the safety assessment of sodium p-chloro-m-cresol, p-chloro-m-cresol, chlorothymol, mixed cresols, m-cresol, o-cresol, p-cresol, isopropyl cresols, thymol, o-cymen-5-ol, and carvacrol. *Int. J. Toxicol.* **25** Suppl 1 (2006) 29, https://doi.org/10.1080/10915810600716653Attri.
2. P. Tochikubo, F. Park, J.H. Choi, E.H. Koga, K. Shiratani, Impact of Gamma rays and DBD plasma treatments on wastewater treatment. Sci. Reports 8 (2018), pp. 1-11. https://doi.org/10.1038/s41598-018-21001-zBashir.
3. I. Lone, F.A. Bhat, R.A. Mir, S.A. Dar, Z.A. Dar, Concerns and threats of contamination on aquatic ecosystems. Bioremediation Biotechnol. *Sustain. Approaches to Pollut. Degrad* (2020) 1, https://doi.org/10.1007/978-3-030-35691-0_1/TABLES/4Borowy.
4. I. Hazardous Waste: The Beginning of International Organizations Addressing a Growing Global Challenge in the 1970s. Worldw. *Waste J. Interdiscip. Stud. 2* (**??**) **11** (2019) 1, https://doi.org/10.5334/WWWJ.39Chandanshive.
5. V. Kadam, S. Rane, N. Jeon, B.H. Jadhav, J. Govindwar, In situ textile wastewater treatment in high rate transpiration system furrows planted with aquatic macrophytes and floating phytobeds. *Chemosphere* **252** (2020) 126513. https://doi.org/10.1016/J.CHEMOSPHERE.2020.126513Chen.
6. Y.P. Liu, S.Y. Yu, H.Q. Yin, H. Li, Radiation-induced degradation of methyl orange in aqueous solutions. *Chemosphere* **72** (2008) 532, https://doi.org/10.1016/J.CHEMOSPHERE.2008.03.054Doughmi.
7. D. Bennis, L. Berrada, A. Derkaoui, A. Shimi, A. Khatouf, Severe ARDS Complicating an Acute Intentional Cresol Poisoning. *Case Reports Crit. Care* (2019). https://doi.org/10.1155/2019/6756352Draganic.
8. Z., Draganicć, I. The radiation chemistry of water. *J. Chem. Educ.* **49** (1971) A494. https://doi.org/10.1021/ed049pA494.2Guin.
9. J.P., Bhardwaj, Y.K., Naik, D.B., Varshney, L. Evaluation of efficiencies of radiolysis, photocatalysis and ozonolysis of modified simulated textile dye waste-water. *RSC Adv.* **4** (2014) 53921, https://doi.org/10.1039/C4RA10304AHossain.
10. K. Maruthi, D. Y. Avasn, N. Lakshmana, K. P. Rawat, K S S. Sarma, Irradiation of wastewater with electron beam is a key to sustainable smart/green cities: a review. *Appl. Water Sci.* **81** (2018) 1, https://doi.org/10.1007/S13201-018-0645-6Khan.
11. S., Naushad, M., Govarthanan, M., Iqbal, J., Alfadul, S.M. Emerging contaminants of high concern for the environment: Current trends and future research. *Environ. Res.* **207** (2022). https://doi.org/10.1016/J.ENVRES.2021.112609Kumar.
12. A., Raorane et al., Synthesis of TiO2, TiO2/PAni, TiO2/PAni/GO Nanomaterials and Photodegradation of Anionic Dyes Rose Bengal and Thymol Blue in Visible Light. *Environ Res.* **216** (2023) 114741. https://doi.org/10.2139/SSRN.4213173LaGrega.
13. M. D., Buckingham, P. L., & Evans, J.C. Hazardous waste management, Second edi. ed. Waveland Press, United States of America, 2010.Meléndez-López, A., Paredes-Arriaga, A., Cruz-Castaneda, J., Negrón-Mendoza, A., Ramos-Bernal, S., Colín-García, M., Heredia, A. Gamma Dosimetry Using Some Dyes in Organic Solvents Solutions at 295 and 77 K. J. *Nucl. Phy. Mat. Sci. Rad. A.* **6** (2018) 87.
14. R.H. Handbook of Biological Dyes and Stains: Synthesis and Industrial Applications. John Wiley / Sons, Inc. United State of America, 2010.Singh, J., Gupta, P., Das, A. *Dyes from Textile Industry Wastewater as Emerging Contaminants in Agricultural Fields* **11** (2021) 109, https://doi.org/10.1007/978-3-030-63249-6_5Spinks.
15. J.W. Woods, An introduction to radiation chemistry. Wiley. United State of America, 1990.Thabet, R.H., Fouad, M.K., El Sherbiny, S.A., Tony, M.A. Identifying optimized conditions for developing dewatered alum sludge-based photocatalyst to immobilize a wide range of dye contamination. *Appl. Water Sci.* **12** (2022) 1, https://doi.org/10.1007/S13201-022-01739-8/TABLES/4Velusamy.
16. K., Periyasamy, S. P.S. Kumar, T. Jayaraj, M. Gokulakrishnan, P. Keerthana, Transformation of aqueous methyl orange to green metabolites using bacterial strains isolated from textile industry effluent. *Environ. Technol. Innov.* **25** (2022) 102126, https://doi.org/10.1016/J.ETI.2021.102126Verde.
17. S.C. Silva, T. Matos, P. Effects of gamma radiation on wastewater microbiota. *Radiat. Environ. Biophys.* **551** (2015) 125, https://doi.org/10.1007/S00411-015-0617-2.