

RADIOLYTIC DEGRADATION OF HUMIC ACID: AN ALTERNATIVE TO COMPLEMENT THE CHEMICAL TEST OF WATER RESOURCES

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ABSTRACT

The process of the radiolytic degradation is a new method of mineralization by advanced oxidation of the water that can be applied for the removal of humic compounds in all water systems. However, the deep mineralization of dissolved humic acid requires very high absorbed doses (tens of kilograys) because of the aromatic nature of the main units of humic acid and the well-known chemical and biochemical stability of its molecules. The effects degradation and absorbed dose of humic acid present in an aqueous solution were investigated on a laboratory scale upon gamma-irradiation from a Co-60 and electron beam source, to assessment the efficiency of decreasing of humic acid presence. We are studying the absorbed doses required to remove 50% and 90% of initial humic acid concentrations in distilled water solutions. Current results show a significant improvement the effectiveness of radiolytic degradation. Gamma-irradiation and electron beams are being used out in distilled water solutions. We are checking decolorization of naturally occurring in degraded at low absorbed doses in distilled water solutions (dilute humic acid solutions) and in occurring precipitation. Additionally, chemical analysis of the total organic carbon (TOC) which is one of the products degradation by irradiation and UV-visible spectroscopic changes were also evaluated by the parameters relating to the concomitant removal of the total organic carbon as well as by the ratios using absorption values at discrete wavelengths.

Key words: humic acid, water treatment, ionized radiation

1. Introduction

Numerous methods can be employed for removal of various classes of organic pollutants. Progress in the field of chemical water treatment resulted in several oxidative degradation procedures based on the generation of highly reactive intermediates that initiate a sequence of reactions to resulting in the destruction and removal of organic matter. They are generally referred as advanced oxidation processes (AOP), which include UV photolysis, photo-catalysis (hydrogen peroxide and ozone), Fenton reagent and radiolysis of water. ^[1] The radiolytic degradation of environment pollutants was employed in recent years for treatment of natural waters and wastes from different origins and it was also used for drinking water treatment. ^[2, 3]

Important characteristics of the organic matter include their ability to: form water-soluble and water insoluble complexes with metal ions and hydrous oxides; interact with clay minerals and bind particles together; sorb and desorb both naturally-occurring and anthropogenically introduced organic compounds; absorb and release plant nutrients and hold water in the soil environment. ^[4]

Humic substances mainly humic acids represent a major fraction of natural organic matter in ground and surface waters that are known to be a complex class of biogenic polyanionic weak electrolytes with varying molecular sizes. ^[5] Humic acids are organic substances and may be water resources (the main biochemical degradation products of plants and animals). Therefore, they are widespread in nature and form the colloidal fraction of soils. ^[6] They are characterized by microbiological stability, high molecular mass and a complex class of biogenic polyanionic weak electrolytes with varying molecular sizes and at macromolecules contain conjugated olefinic, aromatic, phenolic–semiquinone–quinone structures of a wide spectrum with functional groups (–CO, –COOH, –OH, –NH–, –NH₂, –N) and chromophores that are capable of absorbing electromagnetic radiation up to about $\lambda = 1.5 \mu\text{m}$. ^[5] The assessment of concentrations and equilibrium constants of carboxylic and phenolic groups is, therefore, a key step in the characterization of acidity, ion exchange capacity, and charge development properties of humic substance (HS) systems. ^[7]

As a rule, humic compounds are responsible for the color and turbidity of waters. In nature humic acids occur as a wide range of structurally similar but not identical molecules, which contain various functional groups, including amino acid, polysaccharide and benzenoid fragments. ^[8, 6] The structural and conformational characterization of humic acids is extremely challenging because of their highly heterogeneous nature in relation to their photophysical, photochemical and photobiological roles in natural waters. ^[7] Studies previously, it was found that degradation with the formation of CO₂ and H₂O (mineralization) is the most prominent process in the radiolytic conversion of humic acids in aqueous solutions.

The great important to know what happens in the interaction between natural organic matter (OM) and water resources (surface or underground). There are study of the hydrologic process by trace metals and OM interaction. However, the understanding of physical-chemical processes associated with chelation reactions still remains a challenge fundamentally due to the dynamic nature and complexity of OM systems. ^[7] Modeling such interactions requires, among other parameters, accurate determination of acid-base properties (concentrations and equilibrium constants). A major fraction of dissolved OM in water resources is in fact formed by humic substances (HS), which are characterized by the presence of several functional groups with labile protons such as carboxylic acids, phenols and amines. These

moieties are able to bind protons and metal cations that not only affect the geochemistry of natural systems, but also regulate the buffer capacity of waters, soils and sediments, and metal speciation and transport. [7]

The presence of natural organic matter (NOM) in both surface and ground water supplies has received much public attention in recent years because toxic disinfection by-products (DBPs), like trihalomethane were speculated to be carcinogenic and mutagenic, can result from chlorination procedures in the water treatment processes [9]

The UV/H₂O₂ process has been proven effective in treating waters containing a number of aliphatic and aromatic compounds and the process is an example of a homogeneous AOP. Generally, the effectiveness of homogeneous light-driven oxidation processes is associated with very reactive species, such as hydroxyl radicals, which are generated in the reaction mixture by the direct photolysis of H₂O₂ under UV irradiation: $H_2O_2 + h\nu = 2OH$. [9]

The effectiveness of this process was understood due to the formation of hydroxyl radicals (HO), which show an extraordinarily oxidizing power in the reaction mixture and can thus mineralize a myriad of organic contaminants. Hence, the emphasis of this study was placed on the assessment of different additives, including H₂O₂ in conjunction with radiolytic degradation (electron beam and gamma cell) process for the removal of NOM in water. [9]

The present work investigates the effect of absorbed doses on the degradation of humic acid in the aqueous solution with the presence or without additive and control of total organic carbon (TOC) and UV-vis to assess the effectiveness of the radiolysis process.

2. Materials and Methods

2.1. Chemicals and reagents

Humic acid (20% dry ash), technical substance type, was obtained from Sigma Aldrich® used to simulate the organic matter in natural waters. Samples solutions were prepared in distilled water further purified in chemistry laboratory.

Solutions were prepared with humic acids from 5 to 100 ppm concentration using distilled water. Each one of concentration solutions, which were in triplicate, was also added 3 different additives separately in 1%: nitric acid (HNO₃), sulfuric acid (H₂SO₄) and hydrogen peroxide (H₂O₂).

Solutions were packaged in glass vials of 50 mL for irradiation by Co-60 gamma-rays and rectangular glass tray used with 100 mL of solutions for electrons beams (the two forms the radiolytic degradation).

2.2. Irradiation source

A Co-60 gamma-rays source was used for all concentration irradiation studies. A Gamma Cell 220 from MDS Nordion, Canada was calibrated using aqueous ferrous sulfate solution (ASTM Standard Practice E1026, 1997). The dose rate was $1.53 \text{ kGy}\cdot\text{h}^{-1}$ and transit dose was estimated to be 1.33 Gy. Irradiation was conducted at room temperature, 25°C .

Other samples with equal concentration were irradiated by electron beam acceleration. The mutual irradiation grafting was performed using a Job 188 Dynamitron® Electron Beam Accelerator with 1.5MeV energy, the beam current was 25mA, the beam power was 37.5kW and the scan was 50–120 cm. The irradiation conditions comprised a transit dose of 0.1-40kGy and a dose rate of 2.23 and $22.4 \text{ kGy}\cdot\text{s}^{-1}$.

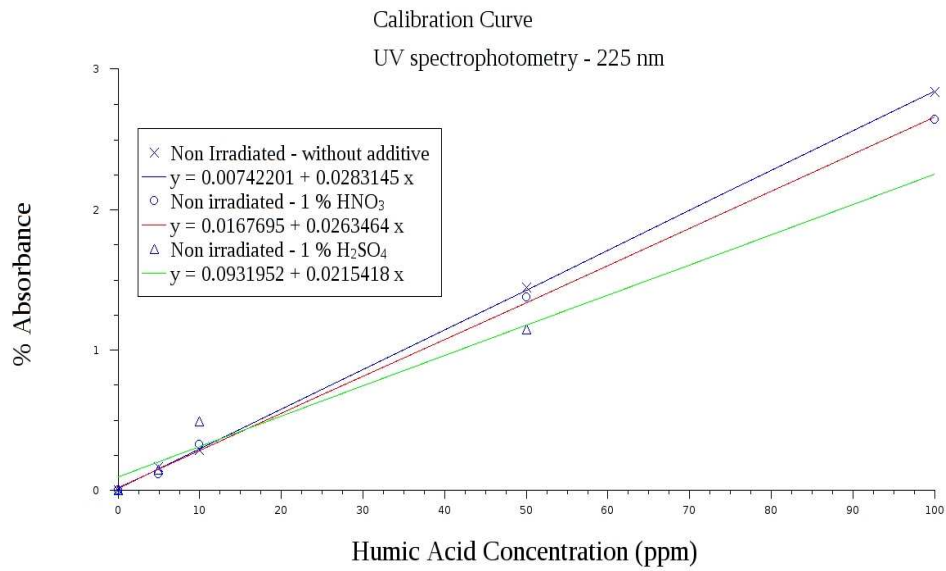
2.3. Instrumental analysis

The oxidation of humic acid as a model compound of natural organic matter by UV absorbance at 225 nm (UV_{225}) in source water, used Amersham 2100 Ultrospec UV/Visible spectrophotometer was utilized and the synchronous scan spectra were acquired in the excitation wavelength of 225 nm within equipment range of 190–900 nm. Total organic carbon and inorganic carbonic TOC measurements of the samples were performed on a Shimadzu TOC 5000A total organic carbon analyzer through combustion/non-dispersive infrared gas analysis method.

3. Results and Discussion

Figure 1b shows concentration results of gamma irradiated humic acid solutions obtained from UV absorbance calibration using non-irradiated humic acid solutions with and without additives (figure 1a). The general effect of gamma radiation is to decrease the humic acid concentration when none additive is used or when 1 % of hydrogen peroxide is added; in this last case, a decreasing of 30 % of the initial concentration is observed when absorbed dose is 10 kGy. When 1 % of sulfuric acid is used as reactional additive, it is observed at 5 kGy a decrease on concentration, near 46 % of initial condition, but at 10 kGy it is observed an increase of concentration (near 63 % of its initial concentration). This behavior can be related to the distinct chemical mechanisms for humic acid degradation when different additives are used. Senesi and co-workers studied humic acid solutions in several pH values and it was observed high solute particle aggregation at irradiated neutral and acid samples, however they suggest these conditions are not well enough to perform humic substances degradation.^[10] Also at figure 1b, a general behavior observed in all samples: the irradiation process applied at samples with 50 ppm of humic acid has higher degradation than that with 100 ppm of this solute and in this case, the obvious dependence of concentration on the kinetic of degradation is shown.

a)



b)

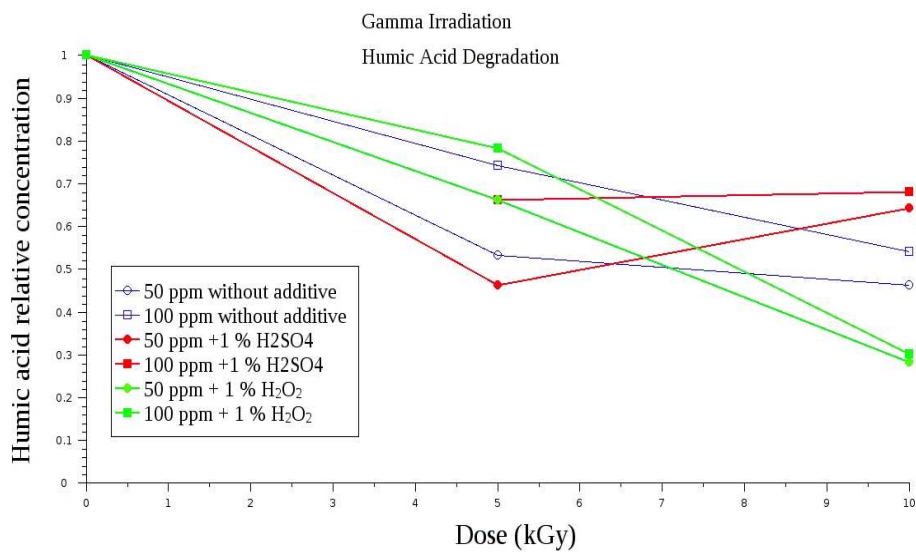
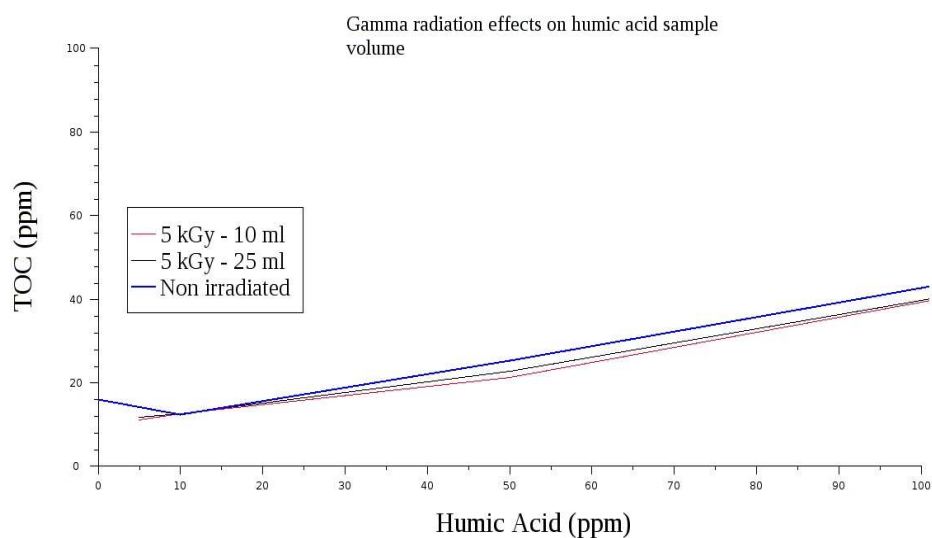


Figure 1: a) Calibration curve of UV spectrophotometry of non irradiated samples and b) humic acid relative concentration calculated from a) vs. Gamma absorbed dose.

The effects of gamma irradiation on total organic carbon (TOC) of humic acid solutions are shown in figure 2. It was observed low discrepancies when irradiation is performed in tubes with different volumes (figure 2a), that is in accordance with this kind of irradiation process: once gamma rays have high penetration, the performance of gamma irradiation process has not any restriction and/or any dependence in terms of material quantity and/or geometry.

Figure 2b shows gamma irradiation effects on TOC responses of 50 ppm humic acid solutions with and without additives. It is observed a decreasing on TOC values with the absorbed dose increasing when humic acid solutions are used without additive and when 1% of hydrogen peroxide is the additive used; in this last case, TOC decrease about 4 times of initial concentration at 10 kGy. However, 1% of sulfuric acid used as reactional additive promotes an increase on TOC concentration mainly at low absorbed dose.

a)



b)

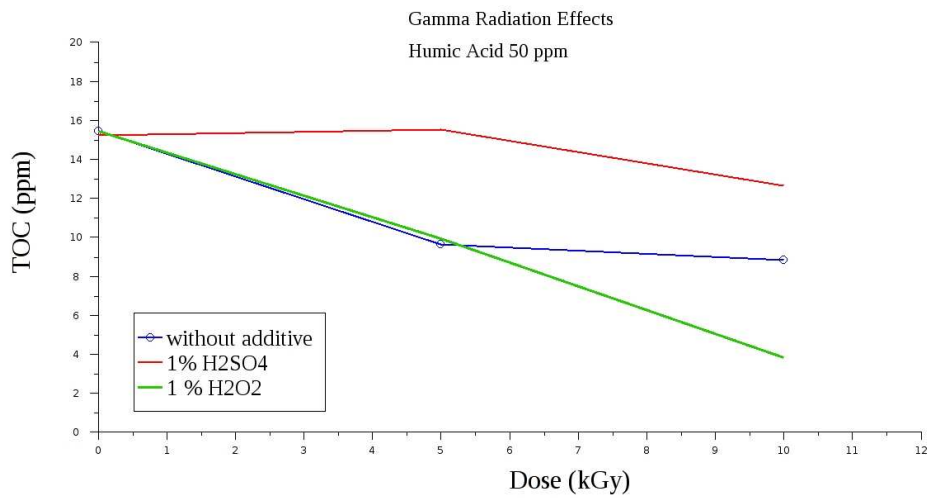


Figure 2: a) Effect of gamma irradiation on total organic carbon (TOC) of humic acid sample volume and b) Gamma irradiation process applied on humic acid samples without additive, with 1% of sulfuric acid and with 1% of hydrogen peroxide and its effects on TOC in function of absorbed dose.

Figure 3 shows TOC concentration of humic acid irradiated with additives compared to TOC results from non irradiated humic acid solutions; this graphic confirms high TOC values at low humic acid concentration values in solutions with sulfuric acid as additive and at low absorbed dose values.

This behavior can be related to that observed by Bludenko and co-workers, where they suggest the formation of low molecular mass carboxylic acid by radiolytic recombination mechanism. If it is true, this resulting product may responsible by TOC increase.^[6] Still in this figure, the decrease of TOC concentration on humic acid samples with hydrogen peroxide compared to non-irradiated samples is confirmed in all concentration range of humic acid and the lowest values are observed at high dose value (10 kGy).

Gamma Radiation Effects

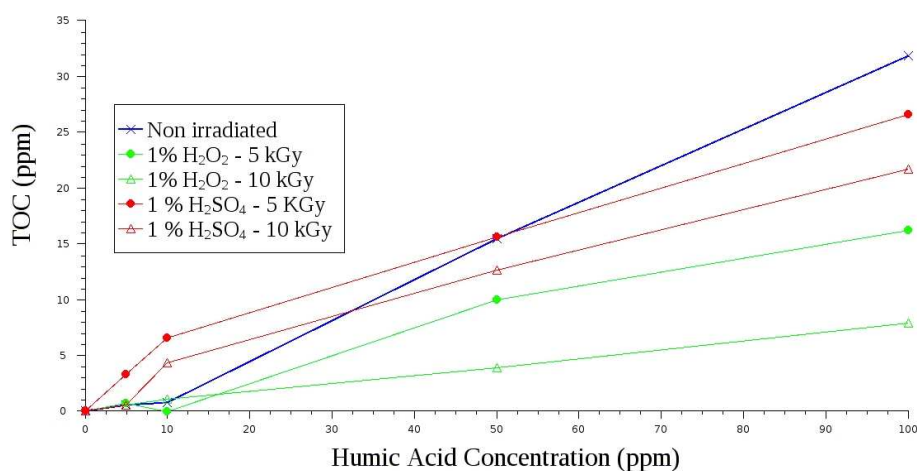


Figure 3: Gamma effects on TOC of humic acid solutions with 1% of sulfuric acid and with 1% of hydrogen peroxide at 5 kGy and 10 kGy.

The inorganic carbon (IC) was also determined and these results are shown in figure 4. It can be observed high levels of IC at irradiated samples with hydrogen peroxide as additive in all humic acid concentration range compared to non-irradiated samples. Here, the degradation mechanism is related to effects of hydrogen peroxide radiolysis; this kind of additive seems to be more effective on humic acid degradation. The aggressivity of the oxide/peroxide radicals can allow the destruction of aromatic rings that are present in humic acid composition. The hydroxyl induced mineralization on humic acid solutions was verified by Goldstone and co-workers; in this study the authors evaluate the effect of gamma irradiation on humic acid solutions and they suggest humic compounds mineralization must occur under high hydroxyl concentration. ^[11]

Gamma Radiation Effects

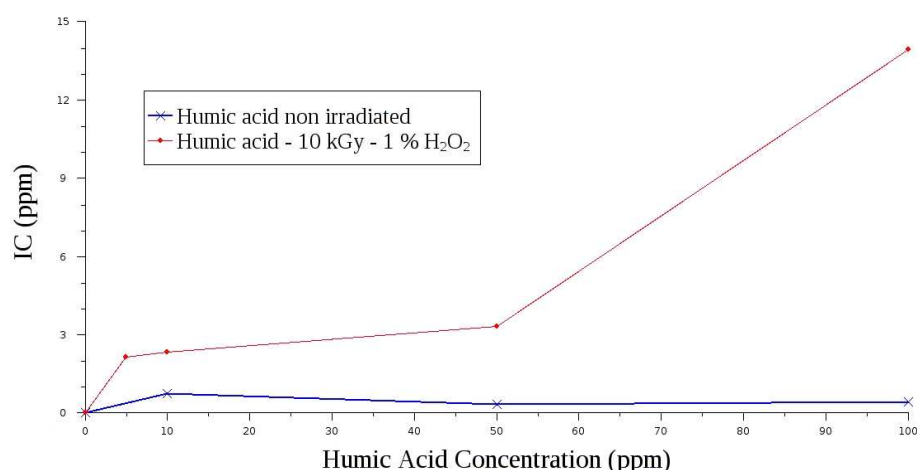


Figure 4: Gamma effects on inorganic carbon concentration at non-irradiated and at 10 kGy of humic acid solutions without additive and with 1% of hydrogen peroxide.

Finally, figure 5 shows the behavior of humic acid solutions exposed to electron beam irradiation at two distinct dose rates. As a general behavior, the lowest dose rate allow low relative concentration values for humic acid with or without additives at low absorbed dose, where relative concentration can reach null values at 5 kGy. The increase of absorbed dose values does not contribute to enhance this behavior; it can observed great relative concentration values of humic acid at 20 kGy and it is independent of dose rate effect. Also in this process, the hydrogen peroxide presence allows the lowest relative concentration values in both dose rates investigated; the exception is at 40 kGy and at the higher dose rate investigated, where the relative concentration of humic acid is near 50% above initial concentration. This last result is abnormal and must be investigated.

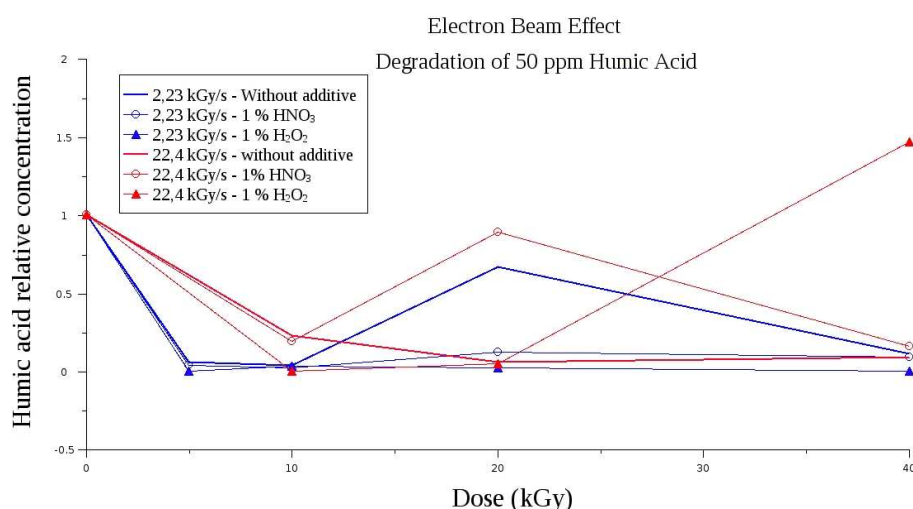


Figure 5: Electron beam effects on humic acid concentration at samples without additive (—), with 1% of nitric acid (○) and with 1% of hydrogen peroxide (▲); two dose rates were investigated: 2,23 kGy/s (blue) and 22,4 kGy/s (red).

4. Summary

The mineralization of humic acid solutions is investigated in his work. The humic acid can be degraded by high energy irradiation methods, but the use of electron beam irradiation can be vantageous since it is faster: at low dose rates and absorbed doses can occur the total humic acid elimination. The use of additives like hydrogen peroxide is the key to enhance the humic acid degradation process and to promote the mineralization of these solutions.

5. References

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