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Ultraviolet radiation treatment for ecotoxicity removal of chemical additives in oil and gas produced water.

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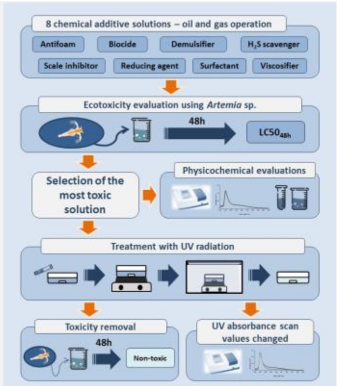

Ultraviolet radiation application on some toxic wastewater may cause photolysis of the components present. Depending on the dose, photolysis can produce a less hazardous effluent in the aquatic environment. In this context, UV radiation application on toxic chemical additives in oil and gas produced water (PW) was proposed to remove acute toxicity to *Artemia* sp. Eight chemical additives solutions were tested: antifoam, biocide, demulsifier, H_2S scavenger, reducing agent, scale inhibitor, surfactant, and viscosifier. Biocide solution was the most toxic to *Artemia* sp ($LC50_{48h}$ = 60.22 (57.42 – 63.14) mg/L). UV treatment was applied to the biocide solution for 30 minutes, which caused a modification in biocide molecules, changing the scan absorbance curve aspect mainly in increasing the peak observed at 210 nm. This treatment completely removed the biocide toxicity for *Artemia* sp., which may be an alternative simple treatment to remove or reduce toxicity.

Introduction

Environmental damage is currently one of the most relevant concerns in the world. It is vital to avoid and mitigate such damages for the future of humanity. In this context, produced water (PW) is the primary wastewater generated in oil and gas exploration. The composition of this effluent is complex, and it contains numerous potential hazard components that may create severe problems in a marine environment [1; 2].

One of the most significant components in PW is the chemical additives, which are compounds added in different steps of oil and gas production, and they are critical to avoid process issues or to mitigate these issues. The concentration of each additive can be significant or low, depending on the use and the process by which it will be applied [1; 2; 3].

Chemical additives are potentially dangerous for the aquatic environment, and still, there is a lack of information about the toxicity of this group of chemicals [4]. These additives include biocides, corrosion inhibitors, antifoam, H_2S scavengers, demulsifiers, reducing agents, and viscosities. [5].

To reduce these compounds' toxicity, applying advanced wastewater treatment, such as AOP(Advanced Oxidative Processes) with UV, is fundamental. The UV radiation can initiate the photolysis process, which may degrade the toxic chemicals.[6; 7].

Ecotoxicity assays can be helpful tools to describe the potential risks of chemicals to the environment, and they can quantify how toxic one chemical could be. Besides, these assays are essential to amplify the knowledge about PW's toxicity and the PW's compounds individually [8].

The main objectives of this study are the evaluation of the toxicity of eight different oil and gas chemical additives solutions (antifoam, biocide, demulsifier, H_2S scavenger, reducing agent, scale inhibitor, surfactant, viscosifier) using synthetic seawater as a diluent and *Artemia* sp. as test-organism. Then, the most toxic chemical additive identified was treated with UV radiation to reduce or remove the acute toxicity for *Artemia* sp.

Material and Methods

All reagents used were high-purity analytical grade. Deionized water was used to prepare the synthetic seawater diluent of all additive solutions [9]. The concentration of the solutions prepared was described by Bento (2020) [4].

The ecotoxicological assays were performed with the addition of *Artemia* sp. in the nauplii II stage on recipients with the test solutions; the recipients were placed in an incubator (SL-224-Solar®) at 25 ºC for 48 hours. The whole experiment followed the Brazilian norm ABNT NBR 16530:2016 [9]. After the experiment, the number of dead organisms was analyzed, and then, the $LC50_{48h}$ value with a 95% confidence interval was calculated using the statistical method Trimmed Spearman Karber (TSK).

The treatment was performed by adding the sample to a glass container, and it was stirred for 30 minutes under UV radiation. The system used two 15W UV-C lamps, and a magnetic stirrer was used to agitate the sample. Another test was performed using the same methodology but did not apply UV radiation; that experiment was used as a treatment blank.

All the physicochemical parameters were determined according to the methodology described by the Standard Methods for the Examination of Water and Wastewater: pH (method 4500-B, Sensoglass®); TOC (Total Organic Carbon, method 5310 B, TOC-L Shimadzu®); UV Absorbance scan from 200 to 290 nm (method 5910-B, UV-1800-Shimadzu®) [10].

Results and Discussion

Toxicity was observed in three chemical additives solutions: biocide, demulsifier, and H_2S scavenger. Calculating $LC50_{48h}$ for the biocide solution was possible using the TSK method. However, demulsifier and H_2S

scavenger solutions $LC50_{48h}$ were considered above the highest concentration tested (Table 1). All the other solutions were non-toxic for the acute 48-hour assay with *Artemia* sp. in the concentrations tested. Then, as biocide was the only chemical additive that presented $LC50_{48h}$ below its concentration observed in PW, it was selected as the most toxic additive solution tested in this work. This biocide has three components: 2,2-dibromo-3-nitrilopropionamide (DBNPA, the principal biocide component), diethylene glycol, and ethylene glycol [4].

Table 1. 48-hour *Artemia* sp. assay results for 8 chemical additive solutions observed in oil and gas PW.

Additive solutions (chemical concentration)	**$^{a}LC50_{48h}$, mg/L (^{b}CI of 95%)**
Antifoam (40 mg/L)	Non-toxic
Biocide (200 mg/L)	60.22 (57.42 – 63.14)
Demulsifier (45 mg/L)	>45
H_2S scavenger (200 mg/L)	>200
Reducing agent (20 mg/L)	Non-toxic
Scale inhibitor (5 mg/L)	Non-toxic
Surfactant (300 mg/L)	Non-toxic
Viscosifier (1000 mg/L)	Non-toxic

[a]Median lethal concentration for the 48-hour test, [b]Confidence interval.

The scanning ultraviolet absorption data changed after 30 min, as shown in Figure 1. Significant changes were observed between 260 nm and 220 nm with an absorbance reduction and an absorbance peak increasing at 210 nm (from 0.466 cm^{-1} to 0.535 cm^{-1}) caused by DBNPA modification.

Blanchard et al. (1987) observed that DBNPA is sensitive to UV radiation in an aqueous medium [4;11]. This modification may convert the nitrile group into the amide group, which was represented by the absorbance increase on 210 nm caused by the non-bonding orbital electron (n) transition to an antibonding orbital π (π*) in carboxylic compounds [12].

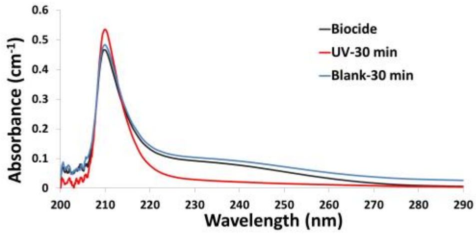

Figure 1 – Absorbance scan from 200 to 290 nm to biocide, 30 min UV treatment, and blank (without UV for 30 min).

A slight reduction in TOC was observed after treatment. Finally, this treatment removed toxicity for *Artemia* sp., probably caused by the nitrile group conversion (Table 2), as it was pointed out by Blanchard et al. (1987).

Table 2.

Samples	**$LC50_{48h}$, mg/L (CI^{b} of 95%)**	**pH**	**TOC, mg/L (CI^{b} of 95%)**
Biocide (200 mg/L)	60.22 (57.42 – 63.14)	7.90	87.98 (82.56 – 93.40)
30 minutes without UV (blank)	63.70 (60.44 – 67.12)	7.86	84.40 (82.19 – 86.62)
30 minutes of UV applied	Non-toxic	7.69	76.39 (74.99 – 77.78)

[b] Confidence interval

Conclusions

UV radiation treatment for 30 minutes was sufficient to cause DBNPA photolysis, completely removing the biocide toxicity for *Artemia* sp. That knowledge may be necessary to reduce or remove wastewater toxicity using a simple technique.

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