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OIL SLUDGE TREATMENT BY ELECTRON BEAM IRRADIATION

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ABSTRACT

Radiation-induced advanced oxidation processes have been proposed for the treatment of various types of wastes. However, electron beam technologies for the removal of recalcitrant compounds in petroleum wastes are still poorly understood. This work aims at evaluating the effects on the degradation of organic matter from oil sludge by electron beam irradiation. The radiometric analysis was also performed to identify radionuclides and measure dose rates. An electron beam accelerator, model Dynamitron II, with variable current up to 25 mA was employed and the irradiation dose values ranged from 20 to 250 kGy. Solutions were prepared with an initial H_2O_2 concentration of 1.34 mol L^{-1}. Samples without H_2O_2 addition, but with water were also evaluated. Control tests with dry and pulverized sludge were submitted to irradiation. The effects on the removal of total organic carbon and the sludge degradation are discussed.

1. INTRODUCTION

Oil and gas extraction activities produce an oil sludge that is a waste classified as Technologically Enhanced Naturally Occurring Radioactive Materials (TENORM), because it contains radioactive daughters from the thorium and uranium decay chains. The oil sludge is composed of extracted sediments, water and oil that accumulates in tanks, pipes and other structures in production oil rigs. In addition to containing radionuclides in radiologically significant concentrations, the sludge produced in Brazilian offshore platforms has high concentrations of sulfur [1, 2] that represent a problem for the storage of this waste, a problem related to the formation of the corrosive sulfuric acid that damages the packages, and the formation of hydrogen sulfide that is a very toxic, corrosive, and flammable gas.

The interest in developing methods for the treatment of this type of waste is increasing, since its accumulation in large quantities and with significant levels of activity in the onshore storage facilities is a growing health risk to the workers and to the local population.

Currently, there is no alternative to storage for this oil sludge in the legal and regulatory structure in Brazil [3]. Article Seven of Law No. 10,308 of 2001 prohibits reinjection into abandoned wells [5], as well current regulations allow the disposal in landfills only for waste with concentration of radionuclides below unrestricted clearance levels. The oil sludge with activities below clearance levels are treated by encapsulation with oleophilic bentonite and disposed of in industrial landfills.

One treatment method tested by other countries have proved satisfactory from the point of view of effectiveness, cost and environmental protection [4]. After transport to onshore facilities, treatment aims at reducing waste hazard, such as mixing the sludge with the oleophilic bentonite in powder form to encapsulate the sludge. The encapsulant has the function of forming a permanent physical barrier that avoids the leaching of toxic products to the environment, especially into groundwater [6] when the waste is disposed of in landfills. There is a number of other methods that can be used to improve treatment and removal of organic compounds that are pollutants and toxic agents. However, most do not have the required performance in eliminating or reducing the impact of disposal in the environment or are not cost effective. This makes necessary the search for alternative methods, which can be used separately or in combination, to improve treatment efficiency.

The use of electron beam irradiation (EBI) is an emerging technology for industrial waste treatment. This technology pertains to the set of techniques so-called advanced oxidation processes (AOP). EBI was previously used in the effluent treatment of the petrochemical industry, showing excellent results with almost 90% removal of organic compounds. [7,8,9]. Despite this, it is necessary to understand how the irradiation acts in the reduction of sulfur compounds [7].

Considering parameters such as costs, yield, duration of the process and impacts to the environment, AOPs have presented good results and are shown as an attractive alternative in the waste treatment. They have been widely studied and are aimed at optimizing processes and reducing costs. However, these processes may result in the phase change of the radionuclides from the solid matrix to the liquid phase. Therefore, the immobilization of the waste is needed, as an additional treatment, since it cannot be discarded as common waste to prevent environmental contamination and to avoid negative impacts.

The high concentration of organic compounds can directly affect the sludge immobilization quality, making it difficult to assure safety in relation to the integrity of the drums and immobilization matrices by the action of these compounds over time. To adapt the EBI method for the treatment of oil sludge, the characterization of the waste and identification of the hydrocarbons and radionuclides are necessary for verify that the maximum degradation is achieved. In this context, EBI application can ensure safe long-term storage of the radioactive sludge by degrading most of the organics.

2. METHODS

2.1. Preparation and Characterization of the Samples

Oil sludge was received in three (3) plastic 200 L drums from a petroleum platform of the Campos Oil Field. Samples from the three drums were homogenized individually before collecting representative aliquots from each one for the irradiation assays. Sample S1 presented supernatant liquid, while samples S2 and S3, have no free liquid, but had noticeable moisture. A fourth composite sample named SC was created (Fig. 1) by mixing equal amounts from samples S1 to S3. It is expected that this sample will be the most representative for the treatment in the industrial scale.

Figure 1: Petroleum sludge (SC sample).

2.2. Electron-Beam Irradiation (EBI)

EBI breaks water molecules by radiolysis, generating various oxidizing species, including $HO^{\bullet}$, $H^{\bullet}$, and solvated electrons (e_{-aq}). EBI can also transform H_2O_2 into $HO^{\bullet}$ and H_2O, generating great amounts of hydroxyl radicals by coupling both H_2O_2 photolysis as well as water radiolysis. When these radicals interact with organic molecules, they oxidize the matter followed by dissociation and degradation into CO_2 and H_2O (3)

The Electron Beam Accelerator, Radiation Dynamics Inc., emits electrons of 1.5 MeV with a current range from 1 mA to 25 mA. The electron beam scans an area of 60 cm length per 4 cm width at a frequency of 100 Hz. The samples were prepared with 3.3 mm thickness and 6.0 mm to raw and dry samples, respectively. Table 1 shows the experimental conditions. Unirradiated samples were used as baseline composition for analysis.

Table 1: Experimental conditions of electron beam irradiation of oil sludge

Sample Identification	Experimental Condition	Volume added of water or H_2O_2	Irradiation dose (kGy)
A	Raw sludge	-	200
B	H_2O_2 (1.34 mol L^{-1}) added	10 mL	100
C	H_2O_2 (1.34 mol L^{-1}) added	10 mL	200
D	Tap water added	10 mL	-
E	Dry sample	-	250
F	Raw sludge	-	-

2.3. Total Organic Carbon (TOC)

TOC parameter was evaluated to measure the mineralization of the organic compounds. Dry, raw and other samples were analyzed using a Shimadzu TOC-L equipment, coupled to an autosampler (ASI-L) and a solid combustion chamber (TOC-5000A). TOC was measured indirectly by the difference between total organic (TC) and inorganic carbon (IC).

2.4. Scanning Electron Microscopy (SEM)

Samples were dried in oven at 80°C and compacted in the form of disc tablets. The equipment used was the HITACHI TM3000 MEV. Acceleration voltages of 5 and 15 kV; tungsten source; magnification of 15 to 30,000× and resolution of 30 nm.

2.5. Determination of Radionuclides

Cadmium zinc telluride (CZT) semiconductor detector, Kromek Raymon10, was used for gamma analysis and dose rate measurement. Energy resolution and energy interval were setup between 2.0-2.5% full width at half maximum (FWHM) and from 60 keV to 3 MeV, respectively. The counting time was 72,000 seconds.

3. RESULTS AND DISCUSSION

3.1. Total Organic Carbon (TOC)

TOC contents were measured for both solid and liquid phases. The values are listed in Table 2.

Table 2: TOC contents for oil sludge before and after electron beam irradiation

Sample		Sample condition	Irradiation dose (kGy)	TOC ($mg\ L^{-1}$)[a]
Liquid-phase	A	Raw sludge	200	265.4
	B	Addition of H_2O_2 (1.34 mol L^{-1})	100	1022
	C	Addition of H_2O_2 (1.34 mol L^{-1})	200	751.4
	D	Addition of water	-	179.2
Solid-phase				**TOC ($mg\ g^{-1}$)[a]**
	A	Raw	200	30.8
	B	Addition of H_2O_2 (1.34 mol L^{-1})	100	33.1
	C	Addition of H_2O_2 (1.34 mol L^{-1})	200	28.7
	D	Addition of water	-	43.2
	E	Dry	250	64.9
	F	Raw	-	47.1

a. Inorganic carbon corresponds to less than 2% of the total carbon

The addition of water to Sample D could have diluted the organics present in the sludge oil phase. Araujo et al. [8] utilized a similar sludge and found that the TOC of the liquid phase is about 4×10^2 mg L^{-1}. Interestingly, for the liquid phase, the use of H_2O_2 with the irradiation doses of 100 and 200 kGy, resulted in the highest TOC values. Sample C indicated lower TOC values for solids and liquids than sample B. This is an indication that the 200 kGy irradiation dose was more adequate than the 100 kGy, removing more than 40% of the TOC content ($[TOC]_{raw}$= 47.1 mg L^{-1}).

3.2. Scanning Electron Microscopy (SEM)

Since sample B showed the most contrasting final TOC content, SEM analysis was performed to evaluate alterations as regards the oil sludge surface (Fig. 2)

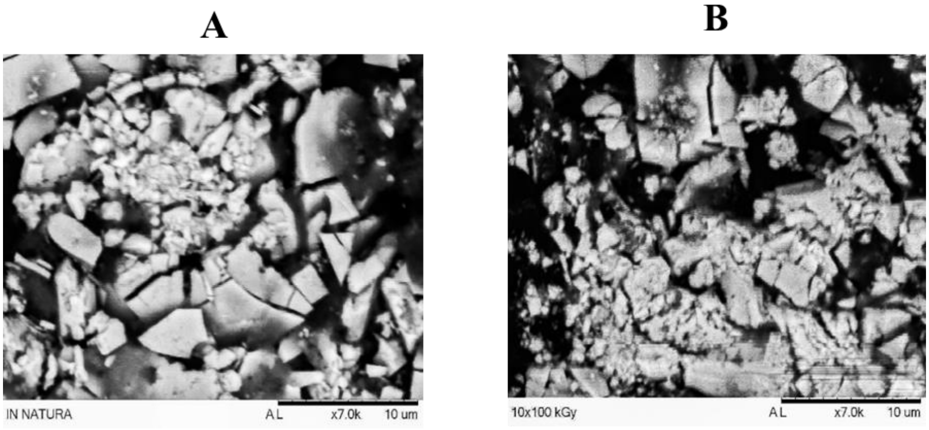

Figure 2: Oil sludge surface. (a) raw form; (b) sample B, added H_2O_2 (1.34 mol L^{-1}) after electron beam irradiation at 100 kGy.

Surface alteration is not directly related to the removal of organic compounds. However, it may be an indication that there was a change in the solid surface caused by the electron beam irradiation process. As indicated by Fig. 2, there may have been a change in the sludge surface indicating breakage of the target material.

3.3. Determination of Radionuclides

The identification of the radionuclides is shown in Fig. 3. The radionuclides present were those expected in this type of waste. The contact dose rate for 100 g was 5 µSv h^{-1} for the raw sludge.

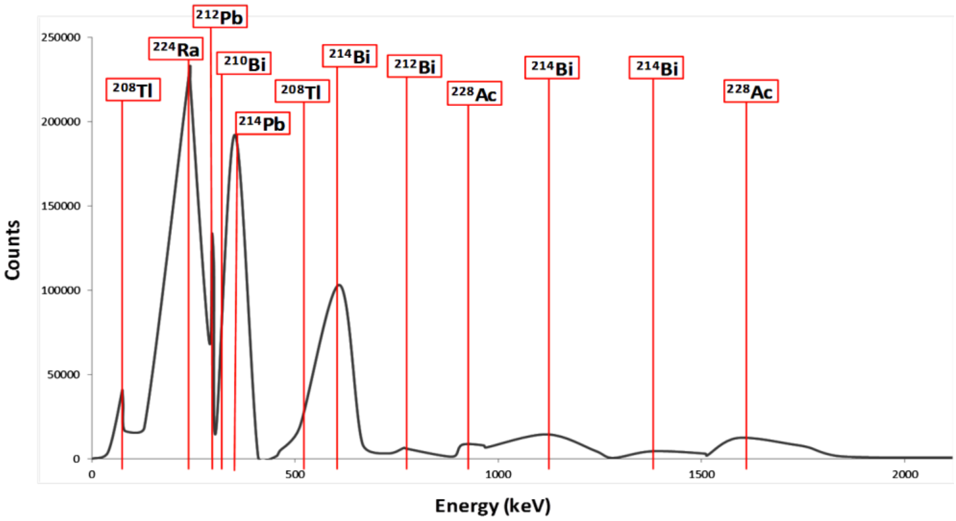

Figure 3: Spectrum acquired with Kromek Raymon10, portable spectrometer in 72,000 s.

The analysis performed with the Raymon10 handheld detector could not yield conclusive values for the activities. Nevertheless, it can be employed for faster monitoring routines.
The identified isotopes, such as ^{208}Tl, ^{212}Pb, ^{212}Bi and ^{228}Ac allow the determination of all radioactive daughters of ^{228}Ra, from the ^{232}Th decay chain, and ^{214}Pb and ^{214}Bi allow the determination of the daughters of ^{226}Ra, from the ^{238}U decay chain [9].

4. CONCLUSIONS

EBI process is very complex in real matrices since there are many chemical reactions occurring simultaneously, such as AOP-based processes (H_2O_2/salt ions). Moreover, the presence of both inorganic (e.g., NO_3^-, HCO_3^-, PO_4^{3-}, etc.) and organic (dissolved organic matter, DOC) constituents may either promote or inhibit the degradation of the target compounds, as a result of the generation and/or scavenging of reactive species, respectively.

Additionally, direct EBI formation of by-products by all the aforementioned processes, undoubtedly affects the kinetics and mechanism of degradation of the sludge. More work is needed, aiming at a complete characterization of the target residue, as well as an in-depth study on the kinetics for this system.

It is worth noting that the efficiency of the process could not be evaluated, as contrasting mineralization rates may have occurred under different experimental conditions and no enough data was obtained to make correlations. Note that if 1 mg g^{-1} of solid material is degraded to the liquid phase, the final TOC content of the liquid could increase by 100 mg L^{-1} since there is about 10 mL of liquid volume for each experimental run.

Sample C indicated lower TOC than sample B values for solids and liquids. This is an indication that the 200 kGy irradiation dose was more adequate than the 100 kGy, removing more than 40% of the TOC content ($[TOC]_{raw}$= 47.1 mg L^{-1}).

The results indicated that the EBI-driven treatment might modify the physical properties of the sludge, as presented in the SEM results. In future, it is intended to apply EBI for the liquid and solid phases separately to systematically verify if there is a change in the removal efficiency of organic compounds. Doses in the lower (50-150 kGy) and the higher ranges (>250 kGy) will be considered in further investigations. A statistical study will be also conducted in order to identify optimum conditions.

The results obtained in the TOC analysis are not conclusive and further experiments should be performed to gain a better understanding of the process. Furthermore, the measurements of the hydrocarbon content, before and after treatment are crucial to assess changes in sludge structure.

Despite the low dose rate of the samples, the isotopes measured and those inferred by the decay chain are in the "medium-upper" group of radiotoxicity, requiring adequate disposal as radioactive waste.

Finally, future work is needed to evaluate the pre-disposal treatment effectiveness to reduce toxicity, the costs and eventually the usefulness for compatibility with immobilization matrices, depending on the results of the characterization and the assessment of the possible alternatives for final disposal.

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