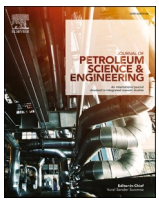
Journal of Petroleum Science and Engineering 211 (2022) 110168

Contents lists available at ScienceDirect

Journal of Petroleum Science and Engineering

journal homepage: www.elsevier.com/locate/petrol



Enhanced removal of radium from radioactive oil sludge using microwave irradiation and non-ionic surfactant

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A R T I C L E I N F O

Keywords:
Radioactive waste
NORM
Radionuclides
Oil sludge
Surfactant
Microwave

A B S T R A C T

Surfactant-based technologies have been studied for the treatment of radioactive waste containing isotopes of radium. Nevertheless, the use of combined processes to remove radium from radioactive oil sludge is scarce in the literature. The objective of this work was to investigate the potential of a non-ionic surfactant to remove radium from raw oil sludge (ROS) and pre-treated, microwave-irradiated oil sludge (POS). Characterization of ROS and POS was made using the following methods: Thermal Gravimetric Analysis, X-ray diffraction, Scanning Electron Microscopy coupled with Energy-Dispersive X-ray Spectroscopy, and gamma spectrometry. The effects of surfactant concentration (0.5–7.5%), temperature (25-60 °C), and contact time (30 and 60 min) were investigated. For ROS, little or no influence on the decontamination process was found for variations in the selected process parameters. For POS, the lowest surfactant concentration (2.5%) was the most efficient, removing about 94% of ^{226}Ra and ^{228}Ra. Neither contact time nor temperature affected removal. For ROS, removal percentages were 50–60% for ^{226}Ra and 35–45% for ^{228}Ra. The results indicated that the surfactant acted more efficiently in the decontamination of POS.

1. Introduction

Currently, off-shore platforms in Brazil produce about three million barrels of crude oil per day. The extraction of oil is accompanied by the extraction of considerable amounts of produced water and sediments containing radioactive elements from the decay chains of thorium and uranium in high enough concentrations to make this oil sludge to be classified as radioactive waste. These sediments are deposited on the bottom of separation tanks and other process equipment, forming an oil sludge that is a mixture of the hydrocarbon and water emulsion and the solid material, and that needs to be removed frequently (de Araujo et al., 2020).

In Brazilian regulations, this radioactive waste is classified as “Class 2.2” (CNEN, 2014), and according to Federal Law 10,308, it cannot be disposed of in the sea or on the seabed, nor on the oceanic islands. Furthermore, there is currently no disposal method approved by the nuclear regulatory authority. The only management option for radioactive waste generated on offshore platforms is storage onshore, in licensed storage facilities (Smith et al., 1998).

The main contributors to the radioactivity of this waste are the radioisotopes of the progeny of ^{226}Ra and ^{228}Ra, which concentrate on oil sludge, precipitated as strontium and barium sulfates or complex salts, due to the similar chemical properties of strontium, barium, and radium (IAEA, 2014; Okyay et al., 2019). As a result of the generation of a significant volume of this waste, there is an interest in finding treatment methods to reduce the volume, as a way to reduce storage costs and, also, mitigate occupational and environmental risks associate with the inflammability and toxicity of the hydrocarbons and the radioactivity.

Several methods are described in the literature with potential application in the treatment of oil sludge, including incineration (Gong et al., 2018, 2021), advanced oxidation processes (de Araujo et al., 2020; Tessaro et al., 2021), simple stabilization, and solidification (Li et al., 2015), microwave irradiation (Sivagami et al., 2021; Yu et al., 2020), and removal of radioactive substances with surfactants (Attallah et al., 2019; M. F. Attallah et al., 2015; Chen et al., 2019; Hilal et al., 2014).

In recent years, microwave irradiation has gained wide popularity as an effective thermal method for treating sludge. This is mainly due to its rapid and selective heating, energy efficiency, the ability to increase yield and product quality, and decrease the formation and emission of

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https://doi.org/10.1016/j.petrol.2022.110168
Received 3 December 2021; Received in revised form 22 December 2021; Accepted 12 January 2022
Available online 15 January 2022

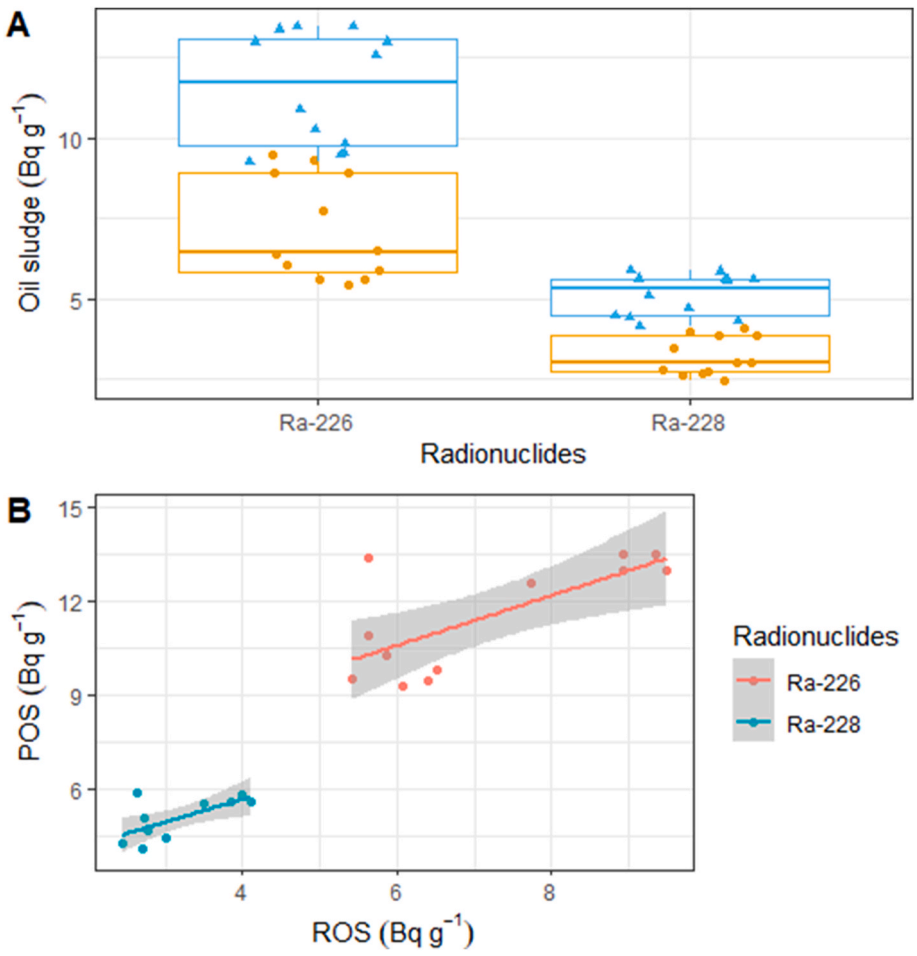

Fig. 1. Activity concentration of the three main radionuclides found in oil sludges: ^{226}Ra and ^{228}Ra. (A) Box-plot of () ROS versus () POS. (B) Relation between ROS and POS considering the equation $y = \alpha + \beta x$, where y is [POS] and x is [ROS]).

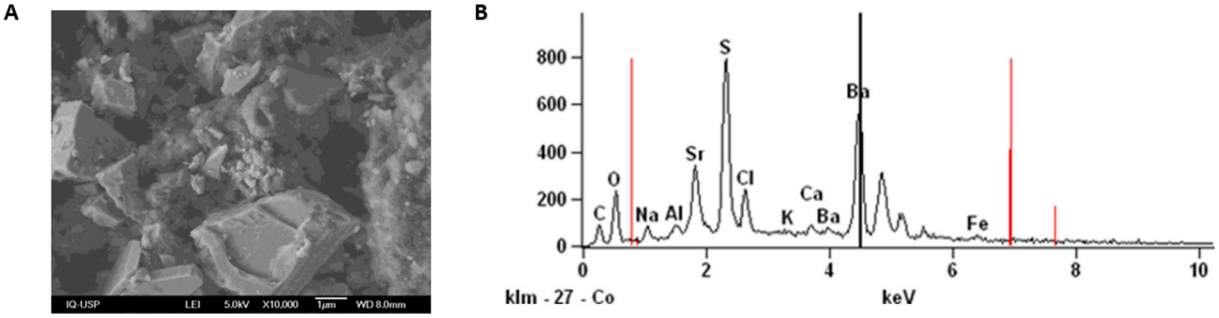

Fig. 2. ROS (a) micrograph (magnification of × 10,000); (b) EDS.

dangerous by-products.

Microwaves are electromagnetic radiation in the frequency range between 300 MHz and 300 GHz, however, domestic or industrial ovens generally operate at 2.45 GHz frequency. Microwave heating can have several advantages in the treatment of different types of waste, such as a significant reduction in volume, rapid heating, and the possibility of reaching high temperatures. Other features of microwave irradiation include selective heating of some waste components, flexibility for application without direct contact with the radioactive waste and with less risk for the operator, low cost and easy maintenance, and lower energy consumption compared to other alternatives (Gomez et al., 2019; Kostas et al., 2017).

Microwave energy provides a highly efficient heating process by directly penetrating the material through molecular interaction with the electromagnetic field. This heating effect breaks up the water/oil emulsion and decreases the viscosity, accelerating the settlement of water droplets in the emulsion (Tan et al., 2007). The rapid temperature rise can also lead to the breakdown of the chemical bonds of heavy hydrocarbons, turning them into lighter compounds. Microwaves can also move through materials with low dielectric loss and with little energy absorption.

The use of surfactants is also an effective method for treating sludge (Ramirez et al., 2021). Surfactants are amphipathic substances that can decrease the surface tension or influence the contact surface between two liquids (Hantal et al., 2019). The reason is that they form self-assembled molecular clusters named micelles, which are formed in

Table 1
EDS analysis of ROS.

Element	Composition (%)
C	41.0
O	45.4
Na	3.5
Al	0.3
Sr	0.4
K	0.5
S	2.6
Cl	1.9
Ca	0.2
Fe	2.1
Ba	2.1
Total	100.0

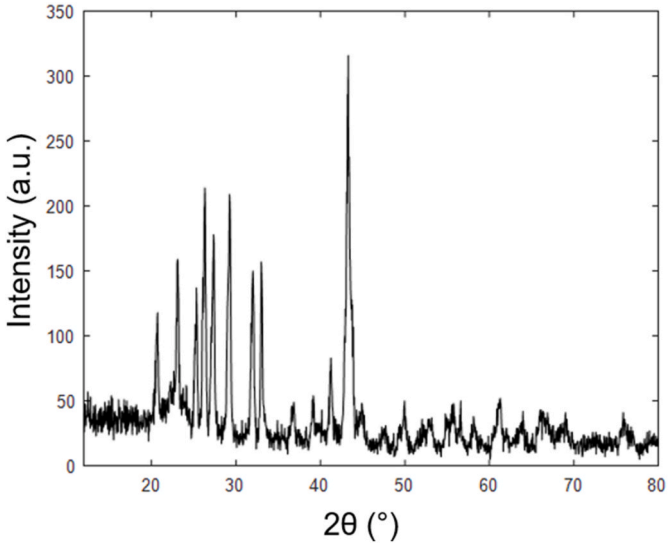

Fig. 3. Diffractogram of ROS.

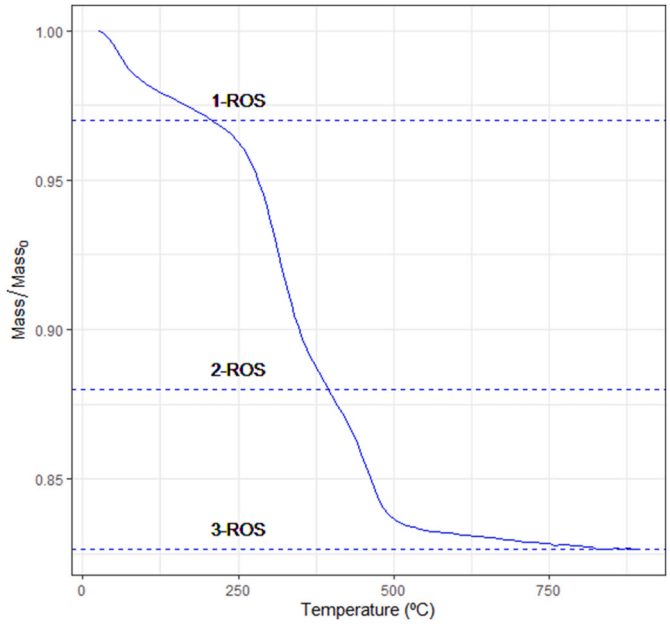

Fig. 4. Spectra obtained through thermogravimetric analysis of the ROS. Each dashed line corresponds to a temperature range. For more information, refer to Table 2.

water or oil phases (Nakama, 2017). Another feature is that they can adsorb to the interface between a solution and a different phase, such as gases and solids. It occurs as a result of the presence of two distinct regions in the surfactant molecule, allowing it to have great adsorptive power at the air-water or oil-water interfaces, as well as on the surface of solids (Free, 2008).

This work investigates the use of surfactant in two types of oil sludge waste, the raw oil sludge (ROS) and the pre-treated oil sludge (POS) by microwave irradiation. Considering that the use of surfactant in the treatment of Brazilian radioactive oil sludge has never been investigated, especially pre-treated with microwave irradiation, we now consider a detailed characterization and analysis approach based on the removal of radium isotopes from this waste. For the characterizations, the following techniques were used: Thermal Gravimetric Analysis (TGA), X-ray diffraction (XRD), Scanning Electron Microscopy coupled with Energy-Dispersive X-ray spectrometer (SEM/EDS), and gamma spectrometry. The results of this work may assist in the choice of more cost-effective and safe routes for the management of NORM waste from oil production platforms.

2. Materials and methods

The experimental part was divided into six stages. Step 1: Collection of samples from drums containing waste; Step 2: Sample preparation; Step 3: Decontamination tests; Step 4: Characterization analyses; Step 5: Radiometric analysis; Step 6: Treatment and analysis of results. Step 3 was subdivided into (i) use of surfactant to decontaminate POS; (ii) use of hot and cold water to decontaminate ROS; (iii) use of surfactant to decontaminate ROS.

All solutions were prepared with deionized water or ultrapure water (MilliporeMilli-Q®). In the decontamination experiments with surfactants, solutions prepared with Triton X100 P.A. (Synth) were used. The oil sludge samples utilized in this investigation were obtained from storage tank bottoms of floating production, storage, and offloading (FPSO) units in the Campos Basin Oil Field and were received in five 200 L drums.

Two sets of samples were used in this work, the raw waste material and one that had been previously irradiated with microwaves in another research work.

2.1. ROS samples

To carry out decontamination tests, samples from the five drums were collected, mixed, and homogenized according to Brazilian standards (ABNT, 2004). A single representative sample was obtained and is here named ROS sample. The raw sample was kept in a closed polyethylene bottle and refrigerated to preserve its physicochemical characteristics.

2.2. Microwave pretreated samples

ROS samples were irradiated with microwaves in a previous research work of our group (Vicente et al., 2017), and are here called POS. Both ROS and POS are from the same collections and can be directly compared for subsequent treatment with the surfactant. In this previous work, portions of ROS were transferred to an Erlenmeyer glass flask. The flask was then placed inside the microwave oven and coupled to a vapor condenser. At the condenser outlet, another Erlenmeyer was connected to collect the distillate and, in addition, one glass containing water was used for washing the off-gases. During processing, the vapor and condensate temperatures and the vacuum level were monitored. The microwave oven was operated at 900 W. After drying, the samples were weighed, transferred to hermetic 1 L flasks for gamma-ray counting, and kept at rest for 38 days so that the ^{222}Rn would come into equilibrium with the ^{226}Ra.

Among the process parameters used in previous work (Vicente et al.,

Table 2
TGA and DSC data of the ROS samples from 25 to 900 °C.

TGA						
Temp. range (°C)	**Mass loss (%)**	**Temp. range (°C)**	**Mass loss (%)**	**Temp. range (°C)**	**Mass loss (%)**	**Residue mass (%)**
25–190	2.77	190–405	9.70	405–900	5.00	82.53
DSC						
Endothermic peaks	**Step**	**Endothermic peaks**	**Step**	**Endothermic peaks**	**Step**	
75	Evaporation	375	Decomposition	460	Decomposition	

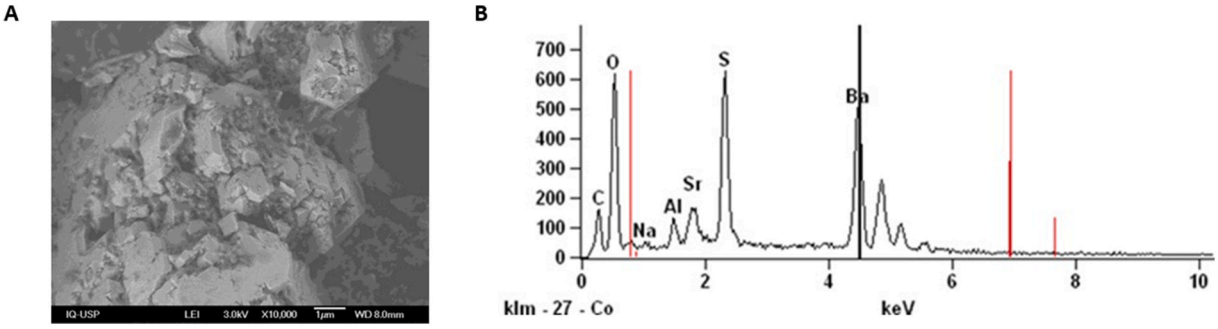

Fig. 5. POS (a) micrograph (magnification of × 10,000); (b) EDS.

Table 3
EDS analysis of irradiated sludge.

Element	Composition (%)
C	35.4
O	50.3
Na	–
Al	0.5
Sr	1.4
K	–
S	7.0
Cl	–
Ca	0.2
Fe	–
Ba	5.4
Total	100.0

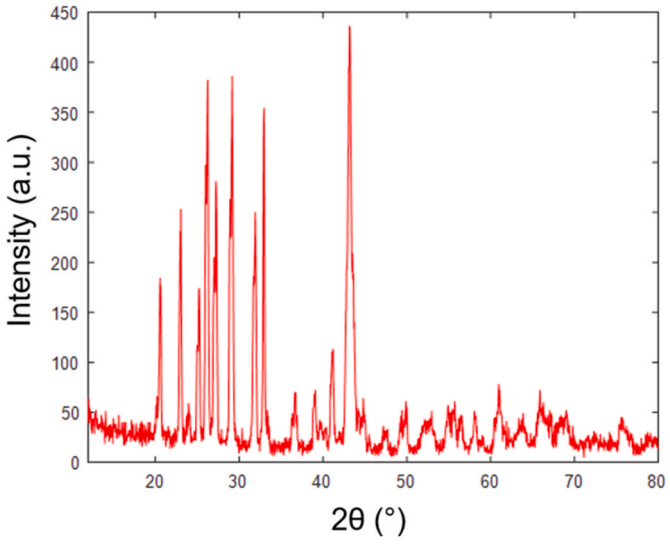

Fig. 6. Diffractogram of POS.

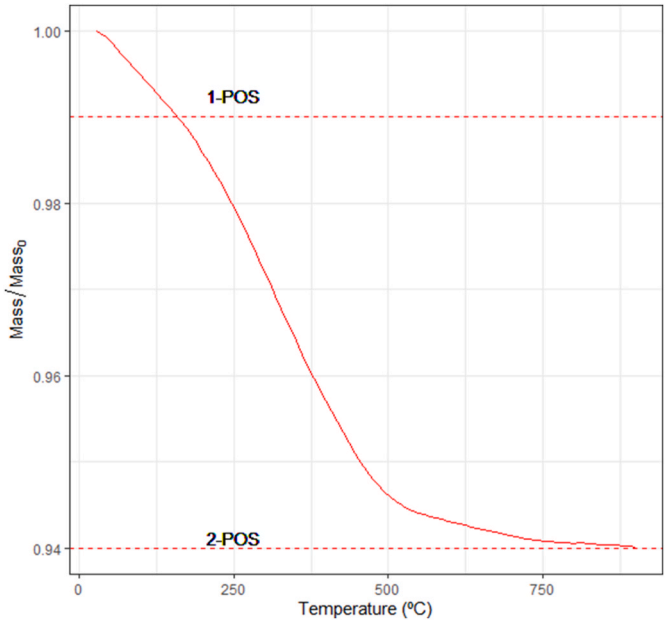

Fig. 7. Spectra obtained through thermogravimetric analysis of the POS. Each dashed line corresponds to a temperature range. For more information, refer to Table 4.

2017), the ones that may be responsible for explaining the relation between the concentrations of radium radioisotopes, before and after the microwave treatment, are reduction of oil sludge mass (M_{OS}) and removal of liquid fraction (RL, %). The reason is that these elements tend to concentrate in the solid portion of the oil sludge throughout treatment. That is, the concentrations of these elements are seen as dependent on their initial concentrations as well as on the removal of water and oil over the treatment time. For that reason, we employed an equation (Eq. (1)) that takes into account the initial concentration of these two elements as well as the differences observed in M_{os} and RL:

$$Y_i = \alpha + \beta_j X_j \quad (1)$$

Table 4
TGA and DSC data of the POS samples from 25 to 900 °C.

TGA						
Temp. range (°C)	**Mass loss (%)**	**Temp. range (°C)**	**Mass loss (%)**	**Temp. range (°C)**	**Mass loss (%)**	**Residue mass (%)**
25–240	2.00	240–410	2.60	410–900	1.50	93.90
DSC						
Endothermic peaks	**Step**	**Endothermic peaks**	**Step**	**Endothermic peaks**	**Step**	
75	Evaporation	275	Decomposition	440	Decomposition	

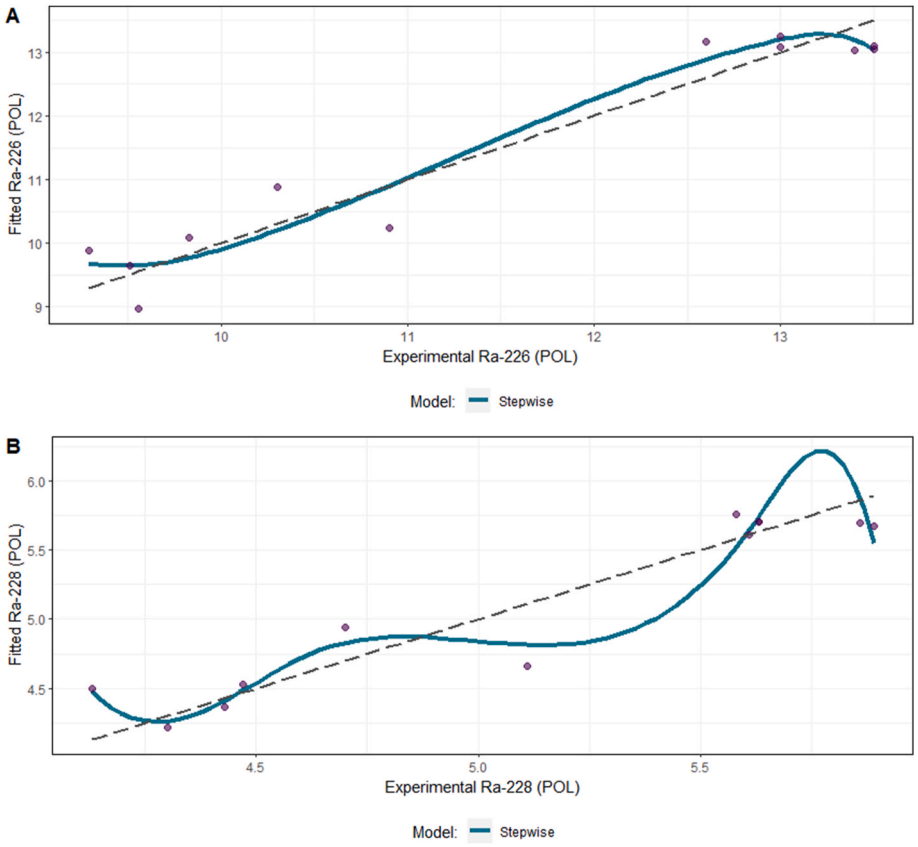

Fig. 8. Experimental versus fitted values for POL. The stepwise method was used to keep in the models only the statistically significant parameters. For the equations, refer to Table 6.

where Y_i is the activity of each radioisotope ($i = {}^{226}$Ra and ^{228}Ra) after microwave treatment, α is the intercept of the straight-line graph, β_j is the line slope for each parameter of interest (M_{os} and RL) and X_j is the experimentally measured value of each parameter of interest (M_{os} and RL).

2.3. Sludge decontamination tests

Exploratory tests were carried out to check the miscibility of the radioactive waste when put in contact with the surfactant solutions. For POS, the minimum concentration was 2.5%, and for ROS, 0.5%. Thus, concentrations of 2.5, 5 and 7.5% (POS) and 0.5, 1, 2.5 and 5% (ROS) were adopted as study ranges. The contact times were 30 and 60 min. Three temperatures were investigated (25, 45, and 60 °C) only for ROS, because, in the case of POS, the high efficiency of decontamination at room temperature was verified in the experiments themselves.

The water was tested as a decontaminant because the sludge is mainly composed of sand and we wanted to test the hypothesis of the radionuclides being loosely deposited on grain surfaces and possibly washed with water. For this, tests were performed varying the temperature (25 and 60 °C) and the contact time (30 and 60 min).

In all the experiments, 25 g of sludge were transferred to a polyethylene container of 200 mL with a lid, and agitated in an Orbital Shaker Incubator (BIOTHEC, model BT400), according to the time and temperature already described. After stirring, the liquid phase was separated from the solids in a FANEM centrifuge (Excelsa II, model 206 BL). All samples were sealed and stored for at least 30 days to allow for the ingrowth of the radium progeny. The of ^{226}Ra and ^{228}Ra in the liquid samples were then determined using the gamma lines of ^{214}Bi and ^{228}Ac, respectively, on Canberra gamma spectrometers models GX2518 and Falcon 5000, both with high purity germanium (HPGe) detectors. All decontamination tests were performed in duplicate. The removal (%) of Ra^{226} and Ra^{228} was calculated based on the activities before and after treatment, using the expression (2):

$$R\% = \frac{A_i - \overline{A}_{(t)}}{A_i} 100 \quad (2)$$

where R% is the removal percentage of the radium isotopes from sludge,

Table 5
Summary of the equations generated from the microwave treatment of oil sludge petroleum regarding activity concentrations of the radium isotopes –^{226}Ra and^{228}Ra. (Shapiro-Wilk normality test)^{226}Ra: W = 0.89389, *p*-value = 0.1323;^{228}Ra: W = 0.98319, *p*-value = 0.9933.

Material	Coefficients	Estimate	Std. Error	t value	Pr (>|t|)	
^{226}Ra	Intercept	12.67	1.72	7.38	4.34e-05	
	Reduction of mass (g)	0.07	6.7e-03	10.805	1.87e-06	***
	Removal of liquid fraction (%)	−0.20	0.05	−3.86	3.86e-03	**
	R^2	0.93				
^{228}Ra	Intercept	5.05	0.79	6.37	1.3e-04	
	Reduction of mass (g)	0.03	3.01e-03	8.59	1.24e-05	***
	Removal of liquid fraction (%)	−0.06	0.02	−2.51	3.35e-02	*
	R^2	0.89				

Significant codes: 0 '***' 0.001 '**' 0.01 '*' 0.05.

Table 6
The equations related to the microwave treatment of oil sludge for each nuclide. A = Reduction of mass (g); B = Removal of liquid fraction (%). $Y_{i\ (i = 1\ and\ 2)}$ is the concentration of the fitted values of POS for each element. $Y_1 = [^{226}Ra]_{POS}$; $Y_2 = [^{228}Ra]_{POS}$.

Treatment	Element or material	Equation
Microwave	^{226}Ra	$Y_1 = 12.67 + 0.07$ A–0.20 B
	^{228}Ra	$Y_2 = 5.05 + 0.03$ A–0.06 B

A_i is the initial radium activity, $\bar{A}_{(t)}$ is the arithmetic mean of activity measurements performed in duplicate. In addition, for all radiometric tests, the calculated standard deviations did not exceed ±7%.

2.4. Characterization of sludge

Scanning electron microscopy (SEM) analyzes were performed using a FESEM JEOL JSM-7401 F microscope, with field emission gun, acceleration voltage from 30.0 kV to 0.1 kV, 1.0 nm resolution (15 kV) or 1.5 nm (1 kV), and a maximum magnification of 1,000,000. Thermogravimetric analysis (TGA) was used to predict the thermal stability and the decomposition profile of the material. For this, a Mettler Toledo (model 851) was used, with carrier gas injection (synthetic air, flow rate: 80 mL min^{-1}); oven heating from 25 to 900 °C with a heating rate of 20 °C min^{-1}; crucible material: 150 μL platinum with perforated lid; sample mass: 10–20 mg, without the presence of a catalyst. FTIR analyzes were conducted with a Nicolet 4700 spectrometer (40 scans, 4 cm^{-1} resolution, 400-4000 cm^{-1} region). XRD analyzes were carried out with a Bruker D8 Advance equipment equipped with a copper tube with detector: scintillation, 2θ interval from 12 to 80°, with 3 s per step of 0.04°. The DIFFRAC-EVA software (BRUKER) was used for phase identification.

3. Results and discussion

3.1. Comparison of POS and ROS in terms of activity concentration

Samples from twelve drums were collected and analyzed before and after microwave pre-treatment. Fig. 1 shows all the measurements for both ROS and POS before the treatment with surfactant.

As expected, ^{226}Ra presents higher activity concentration, given its half-life ($t_{1/2}$ = 1600 y) when compared to ^{228}Ra ($t_{1/2}$ = 5.75 y). Radium is within the oil sludge and precipitates with barium, strontium, and calcium salts. Attallah et al. (2015) found the values of 11.96 Bq g^{-1} for ^{226}Ra and 1.75 Bq g^{-1} for ^{228}Ra, which are close to those found in this present work. The higher concentration of POS is expected due to the reduction of the mass of the sample by the drying effect of the microwave treatment, concentrating the radioactivity of the waste. The amounts of water measured in POS and ROS were equal to 5 and 70%, respectively. The apparent densities of POS and ROS were about 0.89 and 0.95 g cm^{-3}, respectively.

There is a significant linear correlation (R = 0.93, R^2 = 0.87) between the values of POS and ROS, indicating linearity of the process as a whole. The equation generated in this scenario is [POS] = 1.00 + 1.41 × [ROS]. Nevertheless, when the elements are considered separately, the correlation ROS vs POS is little explained by only one parameter ([ROS]), with R^2 = 0.52 (R = 0.72) for ^{226}Ra and R^2 = 0.45 (R = 0.67) for ^{228}Ra.

Since the raw samples differ as concerns water and oil content, changes in respect of M_{OS} and *RL* may play major roles, explaining the presence of the "outliers" that were not well fitted by the linear model with only one parameter. Also critical is that each nuclide may act differently under microwave treatment since they come from different sources, or as a daughter (^{228}Ra) of the thorium decay (^{232}Th) or as a daughter (^{226}Ra) of the uranium decay (^{238}U). Moreover, the elements may be unevenly distributed in the multiple phases of the waste – oil, water, or solid – and are in distinct orders of magnitude in terms of mass given they possess different half-lives.

3.2. ROS characterization

Fig. 2 shows the analysis of the microstructure of a ROS sample by SEM at a magnification of 10,000 times and its respective EDS spectra.

Oil sludge is made up of very fragmented and irregular particles, both in size and in morphology, presenting more compacted material, following what was observed by (Guimarães et al., 2016). EDS analysis indicated that metals and non-metals are present in the samples (Table 1).

Aluminum (Al) is present because it is usually found in the soil in ores in the form of alumina (Al_2O_3) (Zhao et al., 1998). EDS analysis indicated the presence of metals: sodium, potassium, aluminum, calcium, iron, and barium; and non-metals: carbon, oxygen, strontium, sulfur, and chlorine.

Mineralogical analysis by XRD revealed the presence of only one mineral (Fig. 3). Only one crystalline phase was observed, and the most pronounced peaks refer to the compound barite-strontium (barium or strontium sulfate), which showed a high concentration. This evidences the presence of incrustation in the sludge, formed by the precipitation of barium and strontium with the injection water rich in sulfate.

TGA analyzes in an oxidizing atmosphere were performed to observe the decomposition profile of the samples and evaluate the mass of residues formed, as well as the variation in the mass loss for a wide range of temperatures. Fig. 4 and Table 2 show the results of TGA and DSC analysis of the ROS samples.

The amount of residue formed (Table 2) is indicative of the presence of inorganic material in the oil sludge composition. ROS sample had its first mass loss between 180 and 405 °C (1 to 2-ROS, Fig. 4), due to the decomposition and volatilization of less complex organic compounds. The second loss of mass occurred between 405 and 900 °C (2 to 3-ROS, Fig. 4), due to the decomposition of heavier organic compounds (Karayildirim et al., 2006). A great mass loss was noticed, with the greatest losses being observed in the higher temperature ranges, which can be attributed to the pyrolysis of hydrocarbons.

3.3. POS characterization

Fig. 5 shows the analysis of the microstructure of the POS sample by SEM at a magnification of 10,000 times and its respective EDS spectra.

Again, fragmented and irregular particles are observed, in addition to the compacted material. EDS analysis for POS highlights the same

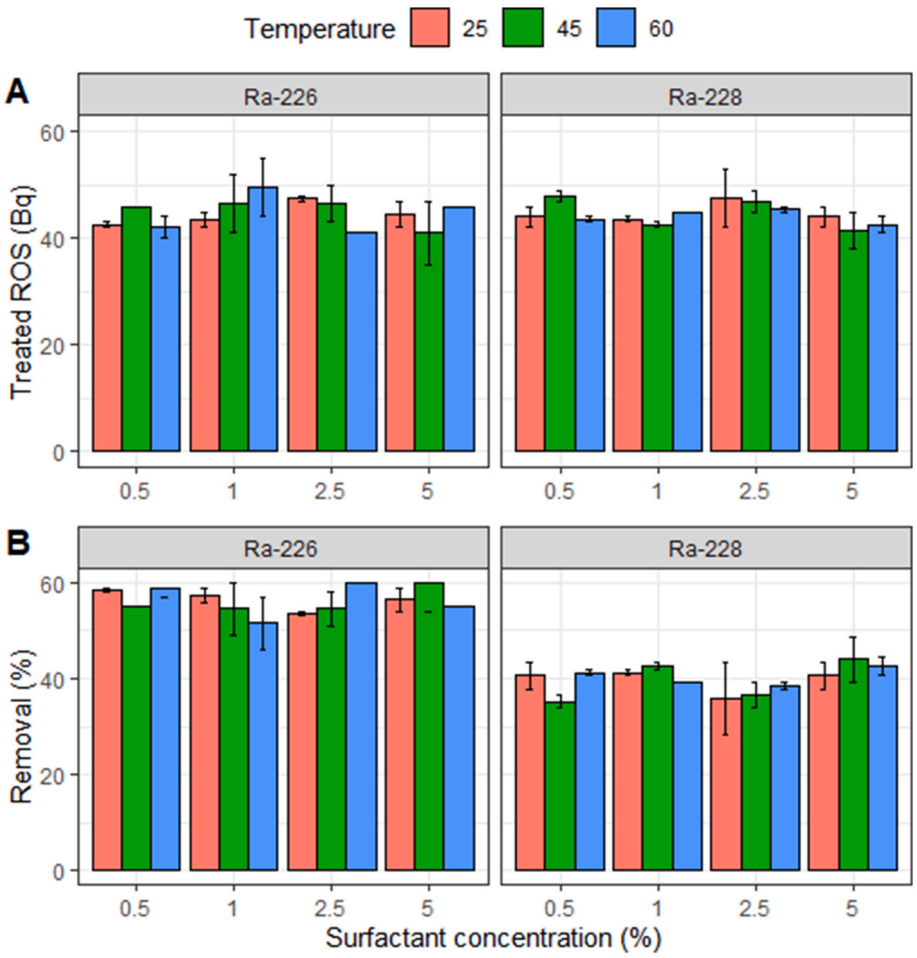

Fig. 9. Removal of radium from ROS by surfactant (a) Final ^{226}Ra and ^{228}Ra activities in the solid sludge; (b) ^{226}Ra and ^{228}Ra removals (%).

Table 7
Summary of the equations generated from the treatment of ROS and POS by surfactants.

Material	Coefficients	Estimate	Std. Error	t value	Pr (>|t|)	
ROS	Intercept[a]	56.16	0.79	70.71		
	Nuclide^{228}Ra	−16.35	1.12	−14.56	8.93e-13	***
	R^2	0.90				
POS	Intercept[a]	219.23	55.82	3.93		
	Nuclide^{228}Ra	−207.39	47.61	−4.36	1.83e-03	**
	Concentration of surfactant (%)	22.23	7.63	2.91	1.73e-02	[a]
	R^2	0.75				

[a] The intercept includes the influence of [^{226}Ra]. Since the variables related to the radium isotopes are qualitative, they were considered as such and calculated as dummies in this model.

Table 8
The equations related to the treatment of oil sludge by surfactant. D = Effect of changing from^{226}Ra to^{228}Ra; E = concentration of the surfactant (%). $Y_{i\ (i\ =\ 3\ \text{and}\ 4)}$ is the removal of radium for ROS (i = 3) or POS (i = 4).

Treatment	Element or material	Equation
Surfactant	ROS	$Y_3 = 56.16–16.35D$
	POS	$Y_4 = 219.23–207.39D + 22.23\ E$

elements of those seen in ROS, but with different percentage compositions (Table 3).

The amount of carbon decreased and that of strontium and barium increased in the irradiated sample (POS versus ROS), probably due to the breakdown and volatilization of organic compounds in the case of carbon. Also, concentration in the case of strontium and barium is expected to increase because of the drying effect of microwave irradiation.

As observed for ROS, XRD analysis for POS (Fig. 6) also indicated the presence of only one mineral. Furthermore, it also shows only one crystalline phase and the pronounced peaks of the compound barite-strontium (barium or strontium sulfate).

TGA analyzes were also conducted for assessing POS (Fig. 7 and Table 4). TGA data demonstrated that ROS and POS have contrasting thermal profiles. POS sludge has more inorganic material in its composition since it showed low decomposition in an oxidizing atmosphere (up to 900 °C). The sample presented a distinct profile, with only two stages of degradation, namely: dehydration (25–170 °C; 1-POS, Fig. 7) and decomposition (>170 °C; 1 to 2-POS, Fig. 7). Table 4 also shows that POS little varied in terms of mass loss in the three analyzed ranges, around 2%.

Fig. 8 shows the fitting of the models with the significant parameters (Table 5) for each radionuclide concentration under microwave treatment and Table 6 lists the equations generated by the empirical modeling concerning this treatment.

3.4. Decontamination tests

3.4.1. ROS

The decontamination with surfactant was applied to ROS and POS materials. In the case of ROS, the tests were made by varying the

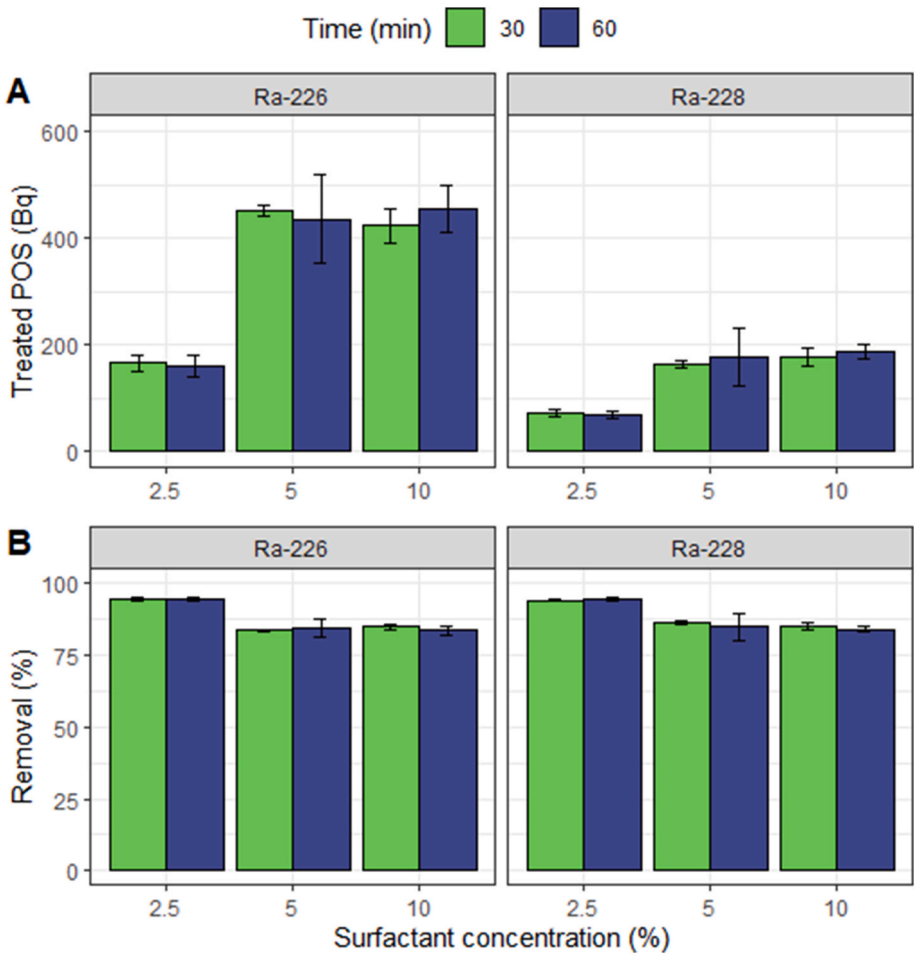

Fig. 10. Removal of radium from POS by surfactant (a) Final ^{226}Ra and ^{228}Ra activities in the solid sludge; (b) ^{226}Ra and ^{228}Ra removals (%).

concentration of the surfactant (0, 0.5, 1, 2.5, and 5%) and the temperature (25, 45, and 60 °C). Fig. 9 shows the activity concentration of ^{226}Ra and ^{228}Ra in the treated solid portion and the removal rates of both radionuclides.

The use of water alone resulted in an undetectable removal of radium. Furthermore, no significant difference in the activities of the solutions was noticed for variations in temperature and concentration of surfactant, although different removal values were observed for the radium isotopes (Fig. 9). Table 7 lists the significant parameters of this process and Table 8 lists the equations generated by the empirical modeling as regards this treatment.

The contrasting removal efficiencies are expected due to the greater amounts of ^{226}Ra ($t_{1/2}$ = 1600 y) than ^{228}Ra ($t_{1/2}$ = 5.75 y) in the oil sludge, facilitating the removal of the element with more mass. As shown in Table 8, for ROS, the efficiency of the surfactant application is lower for ^{228}Ra, indicated by the negative value of the coefficient estimate (−16.35). In all cases, the final activity was between 40 and 50 Bq. Based on the initial activities of ^{226}Ra (102 Bq) and ^{228}Ra (74 Bq), removal percentages were 50–60% for ^{226}Ra and 35–45% for ^{228}Ra (Fig. 9(B)).

3.4.2. POS

The decontamination tests with POS were performed by varying the concentration of the surfactant (0, 2.5, 5, and 10%) and the contact time (30 and 60 min), and the results are present in Fig. 10.

Again, the use of only water did not result in any removal of radium. The best result was achieved by using the lowest surfactant concentration (2.5%), with no significant difference observed between the solutions with 5 and 7.5%. The statistically significant effects of the process were the elements themselves and surfactant concentrations (Table 7). For the empirical models as regards this treatment for POS, refer to Table 8.

The initial ^{226}Ra and ^{228}Ra activities of POS were 2720 and 1159 Bq per sample (25 g), respectively. Based on these values, we concluded that the 2.5% solution was the most efficient in this process, having removed about 94% of both radionuclides. In the case of solutions of 5 and 7.5%, removal of about 84% was observed for both radium isotopes (Fig. 10(B)). Furthermore, the increase in contact time, in the range tested, did not affect the decontamination process with any of the experimental runs.

The results obtained in the experiments with POS and ROS showed that the increase in concentration, contact time, and temperature did not influence the process, a fact not observed by Attallah et al. (2015) and Awwad et al. (2015). The authors worked with cationic and anionic surfactants, with concentrations of 0.25, 0.5, 1, 2, 4, and 8%, and observed an increase in the removal of ^{226}Ra and ^{228}Ra with increasing surfactant concentration, up to 1%. Above this value, there was a decrease. According to the authors, there is an increase in the solubility of radium species in the surfactant micelles, and the change in the concentration of the surfactant may lead to an alteration in its physical properties, such as the formation of micelles and its solubilization effect. They also observed similar behavior with the contact time, having obtained the maximum removal in 60 min and lower values in 120 and 240 min. As for the temperature, the increase from 25 to 60 °C doubled the percentage of removal.

The ^{226}Ra and ^{228}Ra removal percentages achieved in the present work with ROS were similar to those presented by these authors (Attallah et al., 2015; Awwad et al., 2015) at 60 °C. At lower

temperatures, they obtained much lower percentages, in some cases 50%. However, when they applied a mixture of cationic and anionic surfactants, this percentage increased to over 80%.

The much higher removal percentages observed with POS can be explained by the breakdown of the complex hydrocarbons into smaller compounds and CO_2, as indicated by the lower amounts of carbon identified in EDS analysis. Also, the microwave could have demulsified the water-oil emulsion, which would facilitate the passage of metals into the aqueous phase. There were no reports in the literature on the use of surfactants to remove radium or other metals from microwave post-irradiated sludges, which could provide results for comparison. These results show, however, what Hu et al. (2013) stated, that no specific method can be considered as a unique solution for the treatment of sludge since each one has different advantages and limitations. That is, the combination of methods may provide better results.

4. Conclusions

This work aimed to develop a method of decontamination of radioactive waste formed by oil sludge from oil extraction platforms, classified as NORM, specifically aimed at removing radium isotopes with a surfactant.

Microwave pretreatment changed the physicochemical characteristics of the oil sludge, making the surfactant act as a more efficient decontaminating agent. Increasing the surfactant concentration and temperature when treating POS did not improve the radium removal process. The most efficient surfactant concentration was 2.5%. Thereafter, there was a slight decrease in decontamination. The contact time, temperature, and concentration of surfactant did not interfere in the decontamination process of ROS. Water alone was not capable of removing radium from ROS and POS.

The combined use of techniques (microwave and surfactant) offers better results in sludge decontamination. Thus, it can be stated that the decontamination of sludge with a surfactant is a viable, low-cost, and easy-to-apply method and that the use of a pre-treatment technique, such as the microwave, synergistically helped in this process.

This work does not end the study, it is necessary to carry out more evidential tests and use other sludge degradation techniques.

Credit author statement

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This study was financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brasil (CAPES) - Finance Code 001. The authors acknowledge the fellowship awarded by the Brazilian National Nuclear Energy Commission to L.G. de Araujo. The authors thank the Analytical Instrumentation Center of the Institute of Chemistry of the University of São Paulo (USP) for the SEM analyzes. Also, we are thankful to the Laboratory of Polymers and Composites of the Technological Center of the Navy of São Paulo (CTMSP) for the FTIR and TGA analyzes. Finally, we also thank the X-Ray Analysis Laboratory of the Nuclear Fuel Center (CCN), located at IPEN/CNEN-SP for the XRD analyzes.

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