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Use of clays in the treatment of radioactive aqueous waste generated at the CDTN

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Abstract: Radioactive waste is generated in various activities carried out by industry, whether focused on agriculture, energy, health, or research development. CNEN defines it as all materials with radionuclides above clearance levels, generated by human action, whose use is inappropriate or not foreseen. Proper management is essential to ensure the population's safety, workers occupationally exposed to radiation, and the environment. The research by institutes that develop nuclear technologies generates solid and liquid radioactive waste. To reduce their volume, solid waste is compacted or immobilized in a cement matrix, and liquid waste is treated in such a way as to concentrate the radionuclides present and separate them from the liquid part to release this liquid part in the environment, according to the acceptance criteria of CNEN standard. There are several ways to treat liquid waste, such as precipitation, sorption, ion exchange, membrane filtration, and evaporation. In this work, the precipitation followed by sorption in commercial clays of some liquid radioactive waste generated through research carried out at the Nuclear Technology Development Center was evaluated to reduce the radionuclides content in the aqueous part and concentrate the radionuclides in the clays used.

Keywords: Radioactive aqueous waste, treatment, precipitation, and sorption

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Uso de argilas no tratamento de rejeitos radioativos aquosos gerados no CDTN

Resumo: Os rejeitos radioativos são gerados em diversas atividades executadas pela indústria, sejam ela voltada para a agricultura, energia, saúde e desenvolvimento de pesquisas. Rejeitos radioativos são definidos pela CNEN como todos os materiais com a presença de radionuclídeos acima dos níveis de dispensa, sendo gerados pela ação humana, cujo seu uso seja impróprio ou não previsto. Estes devem ser gerenciados de modo correto como a finalidade de garantir a segurança da população, dos indivíduos ocupacionalmente expostos e do meio ambiente. As pesquisas realizadas pelos institutos que desenvolve tecnologias nucleares geram uma variedade de rejeitos, dentre eles, rejeitos radioativos sólidos e líquidos. Visando a redução de volume, os rejeitos sólidos são compactados ou imobilização em matriz de cimento e os rejeitos líquidos são tratados de forma a concentrar os radionuclídeos presentes e separá-los da parte líquida, de forma que essa última possa ser liberada, de acordo com os critérios das normas da CNEN. Os tratamentos dos rejeitos líquidos podem ser precipitação, sorção, troca iônica, filtração por membranas e evaporação. Neste trabalho, foi avaliado a precipitação seguida da sorção, em argilas comerciais, de alguns rejeitos radioativos líquidos gerados por meio de pesquisas realizadas no Centro de Desenvolvimento da Tecnologia Nuclear, com a finalidade de reduzir a quantidade de radionuclídeos presente na parte aquosa e concentrar os radionuclídeos nas argilas utilizadas.

Palavras-chave: Rejeito radioativos aquosos, tratamento, precipitação e sorção.

1. INTRODUCTION

In nuclear technology research, various types of liquid and solid radioactive waste are generated, which must be specifically managed to protect the environment, workers exposed to occupational hazards, and the general public. Establishing a management process is necessary to ensure that all steps in generating this waste are carried out safely. Radioactive waste management involves the following stages: segregation, treatment, packaging, storage, and disposal. Each stage must comply with CNEN standards.

The Nuclear Technology Development Center (CDTN) conducts research outside the nuclear and related areas; this research may involve using radionuclides, thus generating radioactive waste. The solid waste generated at the CDTN consists of contaminated materials, such as gloves, paper, fabrics, rags, glassware, plastic bottles, scrap, debris, and mineral samples. The liquid waste consists of aqueous and organic solutions from equipment and bench-washing processes.

The waste generated at the CDTN is segregated according to its chemical, physical, and radiological characteristics. For treatment purposes, the waste is grouped according to its similarity. Thus, it is selected into groups and sent for tests to verify its workability and to define the best alternatives for reducing the initial activity, volume, and material consumption.

This study aims to define an appropriate process for treating radioactive waste generated at the CDTN through bench tests. The objective is to reduce radioactive activity and effluent volume by concentrating radionuclides in commercial clays through design, classification, and filtration techniques, in according to the acceptance criteria established by standard CNEN NN 08.01 [1].

1.1. Waste Management

Waste management is defined by CNEN NN 6.09 as a set of administrative techniques and activities involving stages from the generation to the disposal of radioactive waste [2]. The stages of radioactive waste management include pre-treatment, treatment, packaging, storage, transportation, and disposal [3].

> Pre-treatment involves the collection, characterization, and segregation stages. During segregation, the waste is separated according to its chemical, physical, biological, and radiological characteristics; this stage is carried out at the generating site due to knowledge of the waste generated. The treatment of radioactive waste seeks to reduce its volume, change its composition, and remove radionuclides. Treatments involving ion exchange, evaporation, chemical precipitation, sorption, and membrane filtration are applied for liquid waste. After treatment, the waste is conditioned in such a way as to remain chemically and physically stable for the necessary period so that it can be transported and handled safely [4].

The storage of radioactive waste can be carried out at any management stage, where the waste is kept isolated from other materials, environmental protection is ensured, and the following stages are facilitated [3]. Regarding the transportation of radioactive waste for external transfers, the facility must conform to the CNEN NN 5.01 standard, which establishes the safety and radiological protection requirements for transportation [5].

Disposal is the final stage of waste management, carried out after storing these materials, and includes options such as geological formation, near-surface, and intermediate storage. The choice of method depends on the type of waste, the choice of location, and socio-political acceptance [6].

1.2. Treatment: Precipitation and Sorption

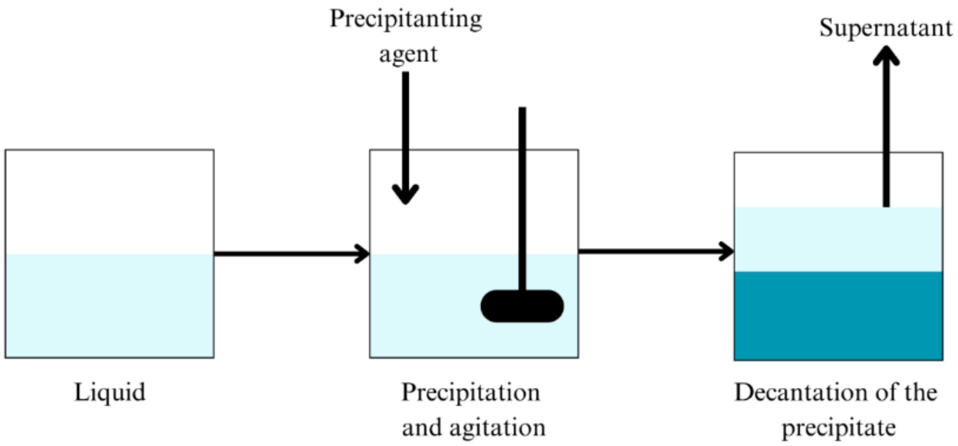
Precipitation is a chemical process used to remove substances dissolved in liquids. In this method, a reagent reacts with the contaminants, forming solid particles (precipitates), which can be separated by filtration or decantation[7].

Two phases are formed during the precipitation: the supernatant or the clarified liquid and the precipitated solid. This process can be applied to treating hazardous waste in the aqueous phase, which can be converted to insoluble [8].

For this to occur, the pH of the solution must be adjusted, which influences the ions' solubility. The use of metal hydroxides also favors the formation of a precipitate [7].

The precipitation occurs through nucleation, in which is observed the mutual aggregation of ions and molecules. The formation of crystals that reach sizes that can be filtered, settle at the bottom of the container, and give rise to a solid phase. The particles formed can be small, with a diameter between 0.001 and 0.1 μm. The precipitate remains in suspension, resulting in a colloidal appearance [9]; in Figure 1, it is possible to observe the precipitation process.

Figure 1: Precipitation process



Source: Bortoletto et al. (2007)

Sorption occurs by transferring one or more constituents, named sorbates, from a fluid phase to a solid phase, named sorbent. This process can occur between the liquid-liquid, gas-liquid, gas-solid, and solid-liquid interfaces [10].

Sorption is a physical-chemical process that involves the phenomena of absorption and adsorption. In adsorption, the solute adheres to the surface of the adsorbent material, while in absorption, the solute diffuses within the absorbent material, which must have a porous matrix. [11].

2. MATERIALS AND METHODS

2.1. Radioactive Waste

The liquid radioactive waste studied in this work was generated from research activities carried out at the CDTN. This waste came mainly from washing benches and equipment used in radionuclides experiments. During these processes, acidic aqueous solutions containing sulfate and phosphate were generated, which could contain uranium, thorium, radium, and ions. The volumes of aqueous waste were grouped for treatment in a volume of 181 L of waste stored in a 200 L drum. Based on the nature of the activities carried out at the CDTN, the main radionuclides expected in the waste included uranium (U-238), radium (Ra-226 and Ra-228), and thorium (Th-232 and its decay products). In addition, lead-210 (Pb-210), a decay product of radium, was also present, contributing to the sample's total activity. Because of the presence of these radionuclides, extinction characterization was performed using elemental analysis and spectrometry techniques.

Thus, the analytical technique of ICP-IOE was performed to determine the elements and compounds present in the sample. Gamma spectrometry techniques in HPGe were also conducted to identify and quantify the gamma-emitting radionuclides. The delayed neutron activation technique was used to determine the U-238 present in the sample. In addition to the methods to identify and quantify the elements present in the sample, the liquid evaporation/proportional counter technique was applied to determine the total activity of the residue. These techniques were chosen based on the need to quantify the radionuclides present in the residue and assess their compliance with the limits established by the CNEN NN 08.01 standard.

2.2. Design of the Experiment

To evaluate the efficiency of the treatment, a 2^2 factorial design was carried out, in which two factors were analyzed: the type of clay used (kaolinite or bentonite) and the amount applied (1 g or 5 g). The experiments were performed in duplicate to ensure the reproducibility of the results. Two commercial clays, bentonite and kaolinite, were defined, and the amount varied between 1g and 5g. The design was carried out in replicates, totaling eight treatments. In Table 4, observing the experiment design defined in coded parameters was possible. Code -1 refers to clay, and code 1, bentonite, refers to 5g bentonite. Regarding the quantity of clay, code -1 refers to the amount of 1g, and code 1 refers to the quantity of 5g.

Table 1: Treatment Design 1

Clay Type	Amount of clay	Treatment characteristics
-1	-1	Kaolinite 1g
1	-1	Bentonite 1g
-1	1	Kaolinite 5g
1	1	Bentonite 5g
-1	-1	Kaolinite 1g
1	-1	Bentonite 1g
-1	1	Kaolinite 5g
1	1	Bentonite 5g

Source: prepared by the author

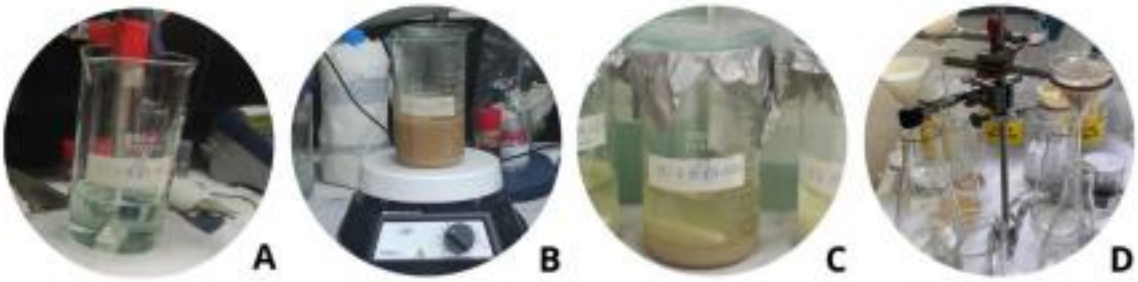
2.3. Treatment 1

In the first stage of treatment, the preparation process was carried out using NaOH as a precipitating agent in a solution of 10 mol per liter. Thus, using this metal hydroxide, the pH of the waste was adjusted; initially, the pH of the untreated waste was -0.30. Therefore, the waste was placed in a beaker as proposed, and, with the aid of a burette, small amounts of NaOH were added to the waste, and the pH was measured again until it reached a scale of 6, as shown in Figure 2, in stage A. The pH scale used in the offers was defined according to Vogel (1981), which states that incidents occurred from pH 6 for NaOH solutions.

After adjusting the pH scale, commercial clay was added to the waste as planned in the experimental design. The clays used were kaolinite and bentonite, and the quantities varied between 1 g and 5 g, as planned. Thus, the waste with added clay was left to improve for 1 hour and 30 minutes to perform the classification identified in step B of Figure 2.

After the improvement period, the waste was left to decant for 24 hours and filtered. Samples were taken for alpha and beta analysis to quantify the total activity of the treated waste, the determination of Ra-226 and Ra-228 by gamma spectrometry in HPGe, and the decantation and filtration steps are shown in Figure 2 in steps C and D.

Figure 2: Stages of the Treatment 1



Source: prepared by the author

2.4. Treatment 2: Retreatment

After the results obtained in the alpha-beta and uranium analysis in treatment 1, it was proposed to perform retreatment, following the same steps shown in Figure 2. However, the pH was adjusted from 6 to 6.6. Retreatment was performed due to the high values for the total specific activity and uranium activity that in some samples of treatment 01 were above that predicted by the CNEN NN 08.01 standard. It was shown in Table 6 the planning levels (1 and -1) in Table 3, treatment 1, and treatments equivalent to treatment 2. This information was used to perform statistical analysis.

Table 2: Planning and treatments performed

Clay Type	Amount of clay	Treatment code 1	Treatment code 2
-1	-1	1P	11P
1	-1	2P	13P
-1	1	3P	10P
1	1	4P	14P
-1	-1	5P	16P
1	-1	6P	9P
-1	1	7P	12P
1	1	8P	15P

Source: prepared by the author

3. RESULTS AND DISCUSSIONS

3.1. Waste characterization

For characterization of the waste, it was proposed that some analytical techniques, such as ICP-OES, be used to determine the compounds present in the sample and quantify the concentration of these compounds. The results obtained are shown in Table 03.

Table 3: Characterization by ICP-OES technique

Elements	**Name**	**mg.L^{-1}**
Fe	Iron	650 ± 20
P	Match	51700 ± 1551
SO_4	Sulfate	27500 ± 825

Source: prepared by the author

These results highlighted the information on the composition of the waste generated at CDTN, showing the presence of sulfate identified by the concentration of SO4 in the sample and the presence of P, which indicates that the composition of the waste had a high phosphate content.

The radioisotope content and their respective activities were specified for gamma spectrometry analysis in HPGe, which detected and quantified the gamma radiation emitted by radioactive waste. The results obtained were shown in Table 4 for comparison with the exemption levels provided for by standard CNEN NN 08.01.

Following standard CNEN NN 08.01, if the radionuclides were known but the concentrations of one or more were unknown, the concentration limit for the mixture was the limit specified in Annex II of the standard for the radionuclide with the most restrictive concentration limit. Among the non-rejected radionuclides, the most restrictive were Ra-226 and Ra-228, which have a value of 1.1×10^3 $Bq.m^{-3}$ or 1.10 $Bq.L^{-1}$.

Table 4: Characterization by gamma spectrometry analysis

Element	Specific activity ($Bq.L^{-1}$)
Pb-210	< 0.10
Ra-226	24.63 ± 1.55
Ra-228	81.94 ± 2.81

Source: prepared by the author

From the data presented in Table 4, it was observed that Pb-210 was below the detection limit of the device, which was 0.10 $Bq.L^{-1}$, and lower than that established by CNEN NN 08.01 demonstrating that the concentration had to be 1.9×10^2 $Bq.m^{-3}$ or 0.19 $Bq.L^{-1}$. This value strongly indicated that the presence of lead in the sample was relatively low, close to the values of environmental samples.

The uranium concentration in the sample was analyzed through neutron activation by delayed neutrons, and the uranium activity was quantified in the untreated waste. The limits established by the CNEN NN 08.01 standard for natural uranium were 5.6×10^3 $Bq.m^{-3}$ or 0,0056 $Bq.ml^{-1}$.

Table 5: Characterization of neutron activation by delayed neutrons

Element	Specific activity ($Bq.ml^{-1}$)
U-238	11.9 ± 0.6

Source: prepared by the author

With the data presented in the table above, it was assessed that the value of the uranium concentration in the untreated waste sample presented a higher uranium concentration than that determined by the standard. However, CNEN NN 08.01 determined that the concentration of the most restrictive radionuclide must be considered. Therefore, the values Ra-226 and Ra-228 were considered. However, due to the values found for uranium, their concentration was evaluated after retreatment.

3.2. Treatment 01

The results presented in Table 6 indicated a significant reduction in radioactivity after treatment, confirming the effectiveness of the precipitation and sorption processes. This suggested that the removal of radionuclides was successful, concentrating them in the solid phase and allowing the separation of the treated effluent. The alpha and beta activity values were added to obtain the specific activity. These values were analyzed using analysis of variance (ANOVA) in Minitab 2018 software to assess whether the type of clay used and the amount influenced the reduction in the specific activity of the waste. These values also contributed to determine the decontamination factor and decontamination efficiency.

Table 6: Total activity result of Treatment 01

Treatment 1	**Treatment characteristics**	**Alpha (Bq.L $^{-1}$)**	**Beta (Bq.L $^{-1}$)**	**Specific activity (Bq.L $^{-1}$)**
0P	Radioactive Waste	$1.27x10^4 \pm 7x10^2$	$5x10^3 \pm 3x10^2$	$1.77x10^4$
1P	Kaolinite 5g	$6x10^2 \pm 1x10^2$	$1.4x10^3 \pm 2x10^2$	$2x10^3$
2P	Bentonite 5g	$1x10^3 \pm 2x10^2$	$1.9x10^3 \pm 2x10^2$	$2.9x10^3$
3P	Kaolinite 1g	$6x10^2 \pm 1x10^2$	$1.4x10^3 \pm 2x10^2$	$2x10^3$
4P	Bentonite 1g	$7x10^2 \pm 1x10^2$	$1.6x10^3 \pm 2x10^2$	$2.3x10^3$
5P	Kaolinite 5g	$6x10^2 \pm 1x10^2$	$1.5x10^3 \pm 2x10^2$	$2.1x10^3$
6P	Bentonite 5g	$4x10^2 \pm 1x10^2$	$1.2x10^3 \pm 2x10^2$	$1.6x10^3$
7P	Kaolinite 1g	$8x10^2 \pm 1x10^2$	$1.5x10^3 \pm 2x10^2$	$2.3x10^3$
8P	Bentonite 1g	$6x10^2 \pm 1x10^2$	$1.4x10^3 \pm 2x10^2$	$2x10^3$

Source: prepared by the author

After obtaining the specific activity results, the uranium concentration after treatment one was determined. In this case, a reduction in the uranium concentration was observed. However, the values for all samples (1P to 8P) were observed to remain above that determined by the CNEN NN 08.01 standard. The concentration of Ra-226 and Ra-228 in the samples (1P to 8P) was also evaluated using gamma spectrometry in HPGe, which demonstrated that all samples were below the detection limit of the device, which is 0.10 Bq.L^{-1}. Thus all samples subjected to treatment 1 were below the limit of the CNEN NN 08.01 standard.

Table 7: Uranium concentration after treatment 01

Amostra	U^{238} (Bq. ml^{-1})
1P	1.04 ± 0.05
2P	2.3 ± 0.1
3P	6.5 ± 0.3
4P	3.5 ± 0.2
5P	7.7± 0.4
6P	3.9 ± 0.2
7P	1.38 ± 0.07
8P	2.1 ± 0.1

Source: prepared by the author

3.3. Retreatment

Retreatment was then performed to assess whether different combined clays influenced the reduction of uranium activity and the decrease in uranium concentration. Thus, retreatment was statistically evaluated using the Student's t-test, and the hypothesis test was performed to determine whether the treatments were statistically different and whether retreatment presented lower results than the first treatment. The samples were removed and sent for liquid evaporation/proportional counter analysis; the specific activity and alpha and beta activities were shown in Table 8.

Table 8: Retreatment activity values

Treatment 2	Treatment characteristics	Alpha (Bq.L $^{-1}$)	Beta (Bq.L $^{-1}$)	Specific activity (Bq.L $^{-1}$)
11P	Kaolinite 5g + Bentonite 1g	$2.3x10^{2} \pm 6x10^{1}$	$1.4x10^{3} \pm 1x10^{2}$	$1.63x10^{3}$
13P	Bentonite 5g + Kaolinite 1g	$4.1x10^{2} \pm 8x10^{1}$	$1.8x10^{3} \pm 1x10^{2}$	$2.21x10^{3}$
10P	Kaolinite 1g + Bentonita 1g	$1.4x10^{2} \pm 6x10^{1}$	$1.5x10^{3} \pm 1x10^{2}$	$1.64x10^{3}$
14P	Bentonite 1g + Kaolinite 1g	$9x10^{1} \pm 5x10^{1}$	$1.8x10^{3} \pm 1x10^{2}$	$1.89x10^{3}$
16P	Kaolinite 5g + Bentonite 1g	$3.8x10^{2} \pm 7x10^{1}$	$1.7x10^{3} \pm 1x10^{2}$	$2.08x10^{3}$
9P	Bentonite 5g + Kaolinite 1g	$3x10^{3} \pm 7x10^{1}$	$1.3x10^{3} \pm 1x10^{2}$	$1.60x10^{3}$
12P	Kaolinite 1g + Bentonita 1g	$1.9x10^{2} \pm 7x10^{1}$	$2.1x10^{3} \pm 1x10^{2}$	$2.29x10^{3}$
15P	Bentonite 1g + Kaolinite 1g	$3.8x10^{2} \pm 7x10^{1}$	$1.6x10^{3} \pm 1x10^{2}$	$1.98x10^{3}$

Source: prepared by the author

Regarding U-238, a decrease in the value of treatment 1 was observed. However, it was noted that these values were still above the value determined by CNEN NN 08.01. The samples were also subjected to gamma spectrometry in HPGe to evaluate the concentration of Ra-226 and Ra-228 (11P to 16P). However, as expected for the samples of treatment one depicted, they remained below the limit established by the standard.

Table 9: Uranium concentration after treatment 01

Amostra	U^{238} (Bq. ml^{-1})
11P	0.56 ± 0.04
13P	0.53 ± 0.04
10P	0.69 ± 0.05
14P	1.19 ± 0.06
16P	0.48 ± 0.03
9P	0.63 ±0.04
12P	0.59 ± 0.04
15P	0.48 ± 0.3

Source: prepared by the author

3.4. ANOVA

The ANOVA was performed using Minitab 18 software, and the analysis was conducted with a 95% confidence level. This served as a parameter to determine the effects of interactions between the factors (quantity and type of clay), influencing the decrease in the specific waste activity after treatment. When experimenting, it was evaluated Table 10, the interaction factors, and the responses obtained.

Table 10: Coded coefficients

Term	Effect	Coef	EP of Coef.	T-value	P-value	VIF
Constant		2150	171	12.54	0.000	
Clay type	100	50	171	0.29	0.785	1.00
Amount of clay	0	0	171	0.00	1.000	1.00
Type of clay*Amount of clay	100	50	171	0.29	0.785	1.00

Source: prepared by the author

In the table of coded coefficients, it was observed that the values attributed to the p-value were greater than 0.05. This indicated that no significant relationship existed between the factors for the responses obtained. This demonstrated that within the range of studies, the amount of clay (1g and 5g) and the type (kaolinite and bentonite) did not exert a significant statistical influence on the reduction of activity. Evaluating the values provided by the coefficient table, retreatment was proposed using the smallest amount of clay but alternating the type of clay compared with Treatment 1. This choice was based on the p-value, which indicated that the factors did not significantly affect activity.

3.5. Student’s t-test

The Student's test was performed using Minitab 18 software to compare the results obtained in both treatments, assessing whether treatment 1 presented a mean specific activity more significant than the mean results of treatment 2. Thus, through the Student's test, the sample means submitted to different samples were compared. Therefore, the test was performed considering two hypotheses: the null hypothesis, which stated that the mean of the treatment was less than or equal to zero, thus not allowing the conclusion that the mean of the data obtained in treatment 1 was greater than the mean of the data of treatment 2, and the alternative hypothesis, which confirmed that it was possible to state that treatment 1 presented a mean of results greater than treatment 2. In Table 11, the parameters used for comparison between treatments were evaluated.

Table 11: Hypothesis Test

Null hypothesis	Mean (Treatment 1) – Mean (Treatment 2) ≤ 0
Alternative hypothesis	Mean (Treatment 1) – Mean (Treatment 2) > 0
α level	0.05

GL	T-value	p-value
7	-2.5657	0.019

Source: prepared by the author

Based on the hypothesis tests, it was concluded that Treatment 1 presented higher values than Treatment 2 since the result value was 0.019, lower than the α value, representing the 95% confidence level. This conclusion was related to the p-value: if it is below 0.05, it was considers that the null hypothesis (H0) should be rejected and the alternative hypothesis accepted.

It was shown in Table 12 the difference in means between treatments, and it was observed that the mean of treatment 2 was -235.00 lower than the results of the first treatment. Regarding the standard deviation, there was observed variability between the results obtained, demonstrating a variation between treatments. Another piece of data that helped in the interpretation of the results was the upper limit of 95% (confidence level), which presented the lower limits of – 61.470 and the upper limit of 0, which suggests that statistically, it was stated that treatment two was lower than treatment 1, with a reliability of 95%. Thus, the data presented by the hypothesis test could be confirmed by the data shown in Table 12.

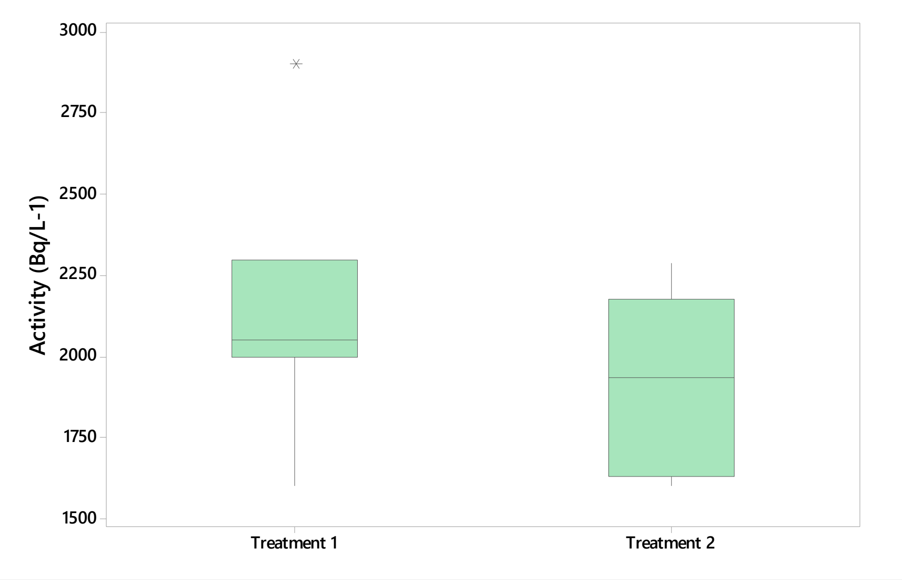
Table 12: Difference: mean (treatment 1) - mean (treatment 2)

Difference	Standard deviation	Lower limit 95%	Upper limit
-235.00	259.06	-61.470	0
The upper limit is less than 0. It is possible to state that the Mean (Treatment 2) < Mean (Treatment 1).			

Source: prepared by the author

To complement the results presented, the graph in Figure 2 was generated, which presented the boxplot of the treatments.

Figure 2: Boxplot of treatments



Source: prepared by the author

In the first treatment, the median was above the median of the second treatment, indicating that the second treatment presented lower activity values. This was confirmed by the variability between quartiles 1 and 3. The graph showed that, in the first treatment, there was a greater variation between these quartiles, suggesting a more significant dispersion of the results. In the second treatment, the variability was lower, indicating that the results were more consistent. Also notable was the presence of outliers in the first treatment, which represented higher values than those presented by the other samples. In addition, the whisker lines of the first treatment were longer, delivering a wider range of results. In contrast, the whisker lines of the second treatment were shorter, indicating a narrower and more controlled range.

3.6. Decontamination efficiency

The decontamination factor was calculated for each sample according to Research 1. It was estimated that the decontamination efficiency of the planned treatment process would be evaluated in percentages. Then, the efficiency of the decontamination factor was calculated using Research 2. The values obtained for the decontamination efficiency for treatments 1 and 2 were presented in Table 13.

Equation 1: Decontamination factor

$$\mathbf{FD} = \frac{\text{Initial contamination concentration}}{\text{Final contamination concentration}}$$

Equation 2: Decontamination efficiency (%)

$$\boldsymbol{\eta} = (1 - \frac{1}{FD}) \cdot 100$$

Table 13: Post-treatment decontamination efficiency

Treatment code 1	% Reduction in activity	Treatment code 2	% Reduction in activity
1P	88.70	11P	90.79
2P	83.62	13P	87.51
3P	88.70	10P	90.73
4P	87.01	14P	89.32
5P	88.14	16P	88.25
6P	90.96	9P	90.96
7P	87.01	12P	87.06
8P	88.70	15P	88.81

Source: prepared by the author

It should be noted that the values advanced for decontamination efficiency related to the specific activity were intermediate between the exemption limits established by CNEN NN 08.01, which were associated with the concentration of radionuclides present and not rejected. It was also necessary to evaluate the quantities of U-238 through neutron activation by delayed neutrons and determine the concentration of Ra-226 and Ra-228 by gamma spectrometry in HPGe. In particular, gamma spectrometry in HPGe quantified the concentration of the most restrictive radionuclides and provided information on compliance with the standard.

4. CONCLUSION

The analysis of variance indicated that the quantity and type of clay used did not significantly influence the reduction of the specific activity of the waste. Statistically, with a 95% confidence level, the variation of these factors did not impact the reduction of activity, allowing the use of the lowest-cost clay in smaller quantities.

However, when evaluating the combination of clays in the second treatment, using the paired t-test, it was found that the combined use of kaolinite and bentonite promoted a more significant reduction in activity than the isolated use of each one. This result was confirmed by the analysis of hypotheses and by comparing the treatment means, also evidenced in the boxplot, which highlighted the difference between the means and the variability of the data obtained. Thus, from a statistical point of view, the second treatment demonstrated greater effectiveness in reducing radioactive activity.

Regarding decontamination efficiency, the values obtained ranged from 83.64% to 90.96% in the first treatment and from 87.06% to 90.79% in the second treatment, indicating an improvement in the radionuclide removal process.

The gamma spectrometry analysis in HPGe revealed that, in the first treatment, the specific activity of Ra-226 and Ra-228 remained below the detection limit (0.10 $Bq.L^{-1}$) in all samples, meeting the requirements established by CNEN NN 08.01. Since they are the most restrictive radionuclides according to the regulations, it can be stated that the study's main objective was achieved.

However, the uranium concentration in the first treatment remained above the limit established by the standard for this radionuclide. The second treatment contributed to the reduction of the uranium concentration, but despite the observed decrease, the values remained above the individual limit specified by CNEN NN 08.01.

Despite this, according to CNEN NN 08.01, when there is a mixture of radionuclides, the effluent discharge may follow the following criteria: Suppose all the radionuclides present in the mixture are identified, but the concentration of one or more of them is unknown. In that case, the concentration limit applicable to the mixture will correspond to the most restrictive radionuclide specified in the standard.

Therefore, even if the uranium remained above the individual permitted limit, the treated effluent may be discharged, as it met the normative specifications for radioactive mixtures.

The results demonstrated that combining kaolinite and bentonite was an effective strategy for treating liquid radioactive waste, reducing the specific activity of radionuclides. Furthermore, the treated effluents met the criteria established by CNEN NN 08.01, allowing their safe release. While the first treatment effectively removed Ra-226 and Ra-228, the second treatment was more efficient in reducing total activity and decreasing uranium concentration, ensuring that the treated effluent met regulatory criteria for release.

WORKS FUTURES

- Use of calcined clays and activated clay.

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CONFLICT OF INTEREST

Hellen Késia Santos de Souza declares receiving a research grant from CNPq. The other authors declare no conflicts of interest.

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