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Treatment of Contaminated Soil with NORM of Oilfields by Chemical Extraction Method

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Abstract

Contamination of soil with naturally occurring radioactive material (NORM) is a common problem in oilfields leading to costly remediation and disposal programs, where ^{226}Ra and ^{228}Ra are the most important radionuclides. This study focuses on treatment of the contaminated soil with NORM to reduce the activity concentration within the allowable limits, that reflect to minimize the risk to workers, the public, and the environment. The study investigated the chemical treatment of two soil samples by a leaching batch test using single and sequential methods with diluted organic and inorganic acids (HNO_3, HCl, $C_6H_8O_7$, $C_2H_4O_2$, EDTA, and H_2SO_4). The initial activity concentrations of the two soil samples were measured for ^{226}Ra and ^{228}Ra using a gamma spectroscopy with a high-purity germanium (HPGe) detector, where they were; 59674.7 ± 2731.2 and 7058.2 ± 451.07Bq.kg^{-1} respectively for the first sample, whereas 7666.6 ± 615.4 and 826.4 ±143.4 Bq.kg^{-1} for the second. The sequential extraction is done in three successive steps (pH moderation, inion exchanging, and leaching with the final solvent). It found that single leaching appeared poor results of radium isotopes extraction from the soil samples with diluted acids, whereas the sequential extraction was the best, where the most effective solvent was 2M acetic acid ($C_2H_4O_2$) with a liquid-to-solid ratio L:S of 5 mL.g^{-1} at a temperature of 40˚C for the first sample, where, 78.4% and 80.6% of ^{226}Ra and ^{228}Ra were removed from the soil and converted to the aqueous phase, whereas 87.9% and 89.8% were removed using 2M HNO_3 for the second sample at the same conditions.

Keywords: Chemical leaching, EDTA, HPGe detector, NORM, ^{226}Ra and ^{228}Ra.

Introduction

Oil and gas extraction produces naturally occurring radioactive material (NORM), and contains radionuclides from the ^{232}Th, ^{238}U series, and ^{40}K. These radionuclides can be concentrated on the surface of equipment and pipes in the form of sludge and scale due to chemical and physical processes from the produced brine water associated with crude oil [1,2]. The produced brines may contain radioactive materials such as ^{226}Ra (1620 years) from the uranium-238 decay chain (4n+2), and ^{228}Ra (5.8 years) from the thorium-232 decay chain (4n) [3,4]. Two types of NORM are typically generated during exploitation processes; if radium is dissolved in the produced brines, and brought to the surface where pressure and temperature changes (decreases) allow it to precipitate as hard insoluble radium/barium sulfate (RaSO4), which deposits on the interior surfaces of pipeline walls and equipment and other installations as scale, the second type is contaminated sludge, which results from the drilling process itself [4-9]. Hence, produced water may be considered the greatest source of radioactive waste production by the oil and gas industry, which is the main source of soil contamination. The ^{226}Ra, ^{228}Ra, and their decays can lead to contamination of soil due to the uncontrolled disposal of the produced water in the surrounding environment of the oilfield [3,10]

Radium has twenty-five radioactive isotopes, it is considered the main environmental hazard in contaminated NORM and technology-enhanced NORM (TENORM) waste [9-12]. Radium is very significant from a radiological protection viewpoint due to its relative presence in nature, long half-life, radiotoxicity, and relatively high physical and biological mobility, furthermore, radium is the radon (^{222}Rn) parent, which is radioactive gaseous [12-14]. The biological behavior of Ra is similar to that of other alkaline earth metals, it is the heaviest alkaline earth metal (group IIA in the periodic table), and it has the same chemical behavior as Ba, Sr, and Ca which belong to the same group of the periodic table, i.e. because of the chemical similarity between radium and calcium, it may be accumulated by plants and animals and transferred to humans through the food chain [15,16]. Since radium element exhibits only one oxidation state (Ra^{++}) therefore it is not easily complex. Hence, most radium compounds are simple ionic which form insoluble salts in water such as sulfate, carbonate, and chromate salts, and soluble salts such as chloride, bromide, nitrate, and hydroxide [4,8,9,12,15]. Radium sulfate is the most insoluble radium compound known yet. The compound is soluble in concentrated sulfuric acid but precipitates upon dilution of the acid. It is converted to radium carbonate by fusion with sodium carbonate resulting in radium carbonates which are soluble in any dilute mineral acid [17-19]

The chemical leaching technique involves extracting a component from a solid that has come into contact with a liquid, it is the one that is most frequently employed to remove materials from ore [20-22]. Therefore, this method is widely used for the treatment of contaminated soil to reduce the radioactivity before final disposal as radioactive waste.

There are two approaches to carrying out the chemical leaching methods; the first one is a single (direct) extraction process (DE) that involves introducing the target solvent directly to contaminated soil and the second is a sequential extraction process (SE) that involves pretreatment in many steps before introducing the target solvent, SE has been frequently utilized to examine how metals are distributed within various phases of soil[21-23,] Leaching sludge, scale, and contaminated soil wastes by high concentrated acid (single extraction DE) can produce better removal for the different radionuclides, yet the use of strong acid with high molarity concentration is not recommended, whereas the sequential chemical treatment of soil despite of time conception but it is recommended, due to allowing minimal contamination with low molarity concentration of solvents that used [17,19].

The treatment methods in this study were carried out by the two approaches mentioned using chemical solutions, with sequential extraction done through three successive steps. (The process involves washing the soil sample with diluting alkali solutions, pretreating with a salty solvent, and leaching with an acid or chelator solution.). The current study objective is to treat the NORM-contaminated soil by leaching processes using low-concentrated solvents at a laboratory scale to reduce the impact of these harmful radionuclides on the oilfield of workers, the public, and the environment. In this study, two actual NORM soil samples from the south Rumaila oilfields in the Basra governorate, Iraq, were utilized with high variance levels in activity concentrations of ^{226}Ra and ^{228}Ra, and the soil profiles of the two samples. The experiments were carried out in two approaches to patch chemical leaching processes: single (direct) and sequential extraction to investigate the response of solvents (almost acids) to extract these radionuclides (radium salts) from different soil samples and transfer them into the aqueous phase.

Materials and Methods

Sample collecting, preparation, and measurement

The soil samples were collected about 3 kg for each sample from an elected location in Al Rumaila southern oilfield in Al Basra governorate /southern Iraq, they were collected from down the degassing stations at different depths (30-120 cm), with the aid of portable radiological survey devices, see Fig. 1.

The soil samples were dried at 80℃ for 8 hours (BINDER oven), sieved by electric sieve shaker 8411 with a maximum rotation speed of 1400 rpm, 30 mish (600 µm pore size) sieve was chosen, and homogenized, then tested by repeating the measurements for ten random samples (32 ml volume) from the main sample. After ensuring the homogeneity of samples, they moved to special standard plastic containers with 32 ml volume. The sample was sealed and stored for 3-4 weeks before the measurement to establish an equilibrium of the decay daughter radionuclides with their parents and measured by gamma spectrometer for one hour for each sample [7-12], as illustrated in Fig. 2.

A gamma spectrometry system (ORTEC company) with Gamma Vision-32 software version-6 was used in this study for the analysis of gamma-ray spectra and determination of the activity concentration of radionuclides, which has 65% relative efficiency and resolution (FWHM) 1.95 keV based on measurements of the (1.332) MeV gamma-ray photo peak of 60Co. This system consists of a coaxial high-purity germanium detector (HPGe) model No. GEM 65P4-95 with a high voltage positive bias (2000V). A 32mL standard multi-gamma radioactive source was used for energy and efficiency calibration type (CPSS2/ certification No.050219-1746026, with reference date 1/5/2019, which contains 11 radioisotopes with different gamma rays energies to cover all radionuclides in NORM samples. Gamma Vision software performs a report that includes information such as radionuclide concentration, dead time, isotope gamma-energies, minimum detection activity (MDA), and compound relative uncertainty for each radionuclide. Quality control procedures were applied using the certified reference material SAEC-448 (radium-226 in soil from an oilfield) which, was provided by the Atomic Energy Commission of Syria.

The activity concentration (A) of radionuclides in the samples was calculated using the following equation: [10]:

$$A = \frac{N}{t \times \gamma \times \mathcal{E} \times M} \quad \dots\dots\dots\dots\dots 1$$

where: N is the net area of the photo peak in gamma spectrum, t is the counting time (s), γ is the emitting probability of gamma-ray (%), $\mathcal{E}$ is the detection efficiency (%) and M (kg) is the sample mass.

The measurements of activity concentration conduct by two methods; direct and indirect, indirect measurement conducts using the progeny radionuclides to determine the activity concentration of parent due to they have no gamma emitters or emit soft energy gamma-ray which confuse and overlap with background, backscatter, and x-ray which lead to not exactly determine of the identified peak. The determination of ^{226}Ra in environmental samples has long been based on the detection of emissions of the radon gas progeny (^{222}Rn) nuclides in secular equilibrium, i.e. ^{214}Pb and ^{214}Bi (solid elements) after an ingrowth period of at least 20 days[10]. The direct measurement method of ^{226}Ra can be used at 186.2 keV energy photo-peak, while ^{235}U activity can determine at 185.72 keV, which overlaps with the 186.2 of ^{226}Ra keV energy line ^{235}U is usually present at a much lower concentration than ^{226}Ra in environmental samples due to its abundance ratio in nature especially in oil and gas extraction fields, while ^{228}Ra determine at 911.2 keV energy photo-peak that belong to ^{228}Ac radionuclide which its the first daughter [24-27].

X-rays fluorescence techneque was used to determine the concentrations of elements of sample, this system manufactured by Spectro Xepos Company, with a detector silicone-lithium, it is connected to the computer via XLab-pro program. The X-ray tube energy has a resolution of 45eV in 5.9 keV of iron (Fe-55) isotope. The analysis works out using the comparative method with standard sources. The targets are highly oriented pyrolytic graphite (HOPG), alumina (Al_2O_3), and Molybdenum.

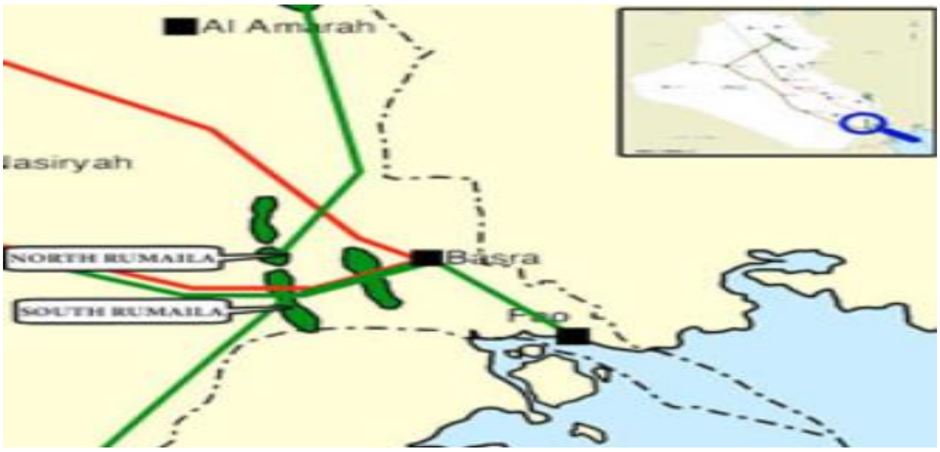


Figure 1. The Al Rumaila oil fields in Basra

Soil samples characterization

1- Soil texture

The grain size analysis (clay, silt, and sand contents) of studied soil samples was determined by the Pipette analysis method. The organic carbon content (Corg) was determined using Carver, R. E. 1971 “Procedures in Sedimentary Petrology”. See Table 1.

2- Oil content

Oil content was carried out by extracting methods where 5 g from NORM soil sample was added to 30 mLCCl_4 solution, the extracted solution filtered by Whatman filter paper, then measured by HORIBA oil content device model: OCMA-350-E. by EPA test method 418.1 " total recoverable petroleum hydrocarbons", see Table 1.

3- pH, TDS, EC, and salinity

The pH determination of samples was performed using the potentiometric method by a commercial glass electrode HQ411d pH/mV HACH company Benchtop meter, which was calibrated before and after each experiment using a series of buffer solutions (pH 4,7, and 10), where pH is the potential of hydrogen or hydronium ion. Salty, total dissolved solid TDS, and electrical conductivity EC were determined according to extracting methods, where the extraction solution was measured directly by inoLab meter Cond 7110 devices, as shown in Fig. 2, the results of pH, TDS, EC, and salinity (part per thousnt ppt) for TS-1 and TS-2 present in Table 1.

Table 1. The soil samples characterization

Test		TS-1	TS-2
Soil texture	Sand %	35	45
	Silt %	60	50
	Clay %	5	5
	Organic Materials %	8.37	3.35
	Density g/cm^3	1.332	1.65
Oil contents	oil mg/L	1710	270
Acidity, total dissolved solid, salinty, and electrical conductivity	Ph	9.86	8.4
	TDS mg/L	9640	12143
	Sal ppt	11.5	13.6
	EC mS/cm	19.28	25.3

4- Chemical characterization

The X-Ray Fluorescent (XRF)

Table 2 presents the concentration of the major elements of TS-1 and TS-2 soil samples using X-ray fluorescence technique, where about 8-9 g of each soil sample was crashed and compressed as pellet form with diameter of 5.2 cm and measured for 10 min, as presented in Fig. 2.

Table 2. The concentration of the main elements of TS-1 and TS-2 soil samples before and after treatment directly with 2M HNO_3 by XRF- system with an average absolute error 0.003%

Element symbol	**TS-1**		**TS-2**	
	Concentration before treatment %	**Concentration after treatment %**	**Concentration before treatment %**	**Concentration after treatment %**
Si-14	1.358	**1.585**	2.637	**3.555**
S-16	1.04	**1.187**	0.250	0.072*
Cl-17	0.175	0.032*	0.660	0.063*
Ca-20	3.931	0.598*	3.662	0.814*
Mn-25	0.089	0.064*	0.054	0.033*
Fe-26	10.33	8.14*	4.431	3.680*
Ni-28	0.0073	0.0047*	0.0041	0.0033*
Cu-29	0.0073	0.0032*	0.002	0.0008*
Zn-30	2.564	0.439*	0.055	0.010*
Sr-38	0.337	**0.385**	0.07	0.054*
Ba-56	0.574	**1.368**	0.132	0.090*
Ta-73	0.035	0.019*	0.015	0.011*
Pb-82	0.050	0.016*	0.0034	0.0014*
Sum	20.4976	4.525	11.9755	3.555
sample losses	19.7%		13.6%	

* decreasing of element concentration, and bold number increasing of element concentration

5- Radiological characterization

Table 3 presents the activity concentration of the radionuclides for TS-1 and TS-2 of 35 g soil samples. The gamma spectrometry system was used to determine the activity concentrations of the NORM soil samples at one hour of measuring time, as shown in Fig. 2.

Table 3. The concentration of radionuclides of TS-1 and TS-2 NORM soil samples Bq.kg^{-1}

	TS-1		TS-2	
Nuclide	**Activity Bq/kg**	**± Unc.**	**Activity Bq/kg**	**± Unc.**
^{40}K	1551.4	620.5	528.3	118.5
^{212}Pb	8736.6	149.4	1012.3	47.282
^{214}Pb	54866.67	543.8	7142.9	177.43
^{212}Bi	12556.4	1246.5	1187.2	392.55
^{214}Bi	51213.5	744.6	6557.1	239.91
^{226}Ra	59674.7	2731.2	7666.6	615.4
^{228}Ac	7058.2	451.07	826.36	143.4
^{208}Tl	19686.4	619.6	2560.5	298.16

Chemical leaching of radium from contaminated soil

1- Direct extraction procedure

The batch tests were chosen in this study, where the extraction solutions agents used in this study were inorganic and organic acids, deionized water, synthetic and natural chelating agents, and salty solutions (HNO3, HCl, $C_6H_8O_7$, $C_2H_4O_2$, EDTA, Na_2EDTA, H_2SO_4, NaOH, H_2O, Na_2CO_3, $CaCl_2$ and $NaNO_3$) with different molarity concentrations. Each solution (250 mL) was added to the soil sample (50g) in glass beakers (500 mL) under study, and the contents were shaken for 2 h at a constant temperature of 40-50°C with a relative error ±10% for acids and deionized water and 60-70 °C for salty solutions in a hot plate magnetic stirrer (model L-81, and VWR model 984VW7CHSEUA), the mixing ratio of 5:1 (liquid to solid ratio) and 200 rpm stirrer. After shaking, the solution was separated from the solid by filtration using medium filter speed Whatman 40 filter papers (150 mm diameter medium crystalline, 8 µ pore size, and ashless 0.0075), the solid residue was dried at 80℃ 4 h and transferred to a suitable container for counting using an appropriate geometric shape as a calibration standard source to measure by gamma-ray spectrometer after leaching to determine the remaining activity (A), as shown in Fig. 2.

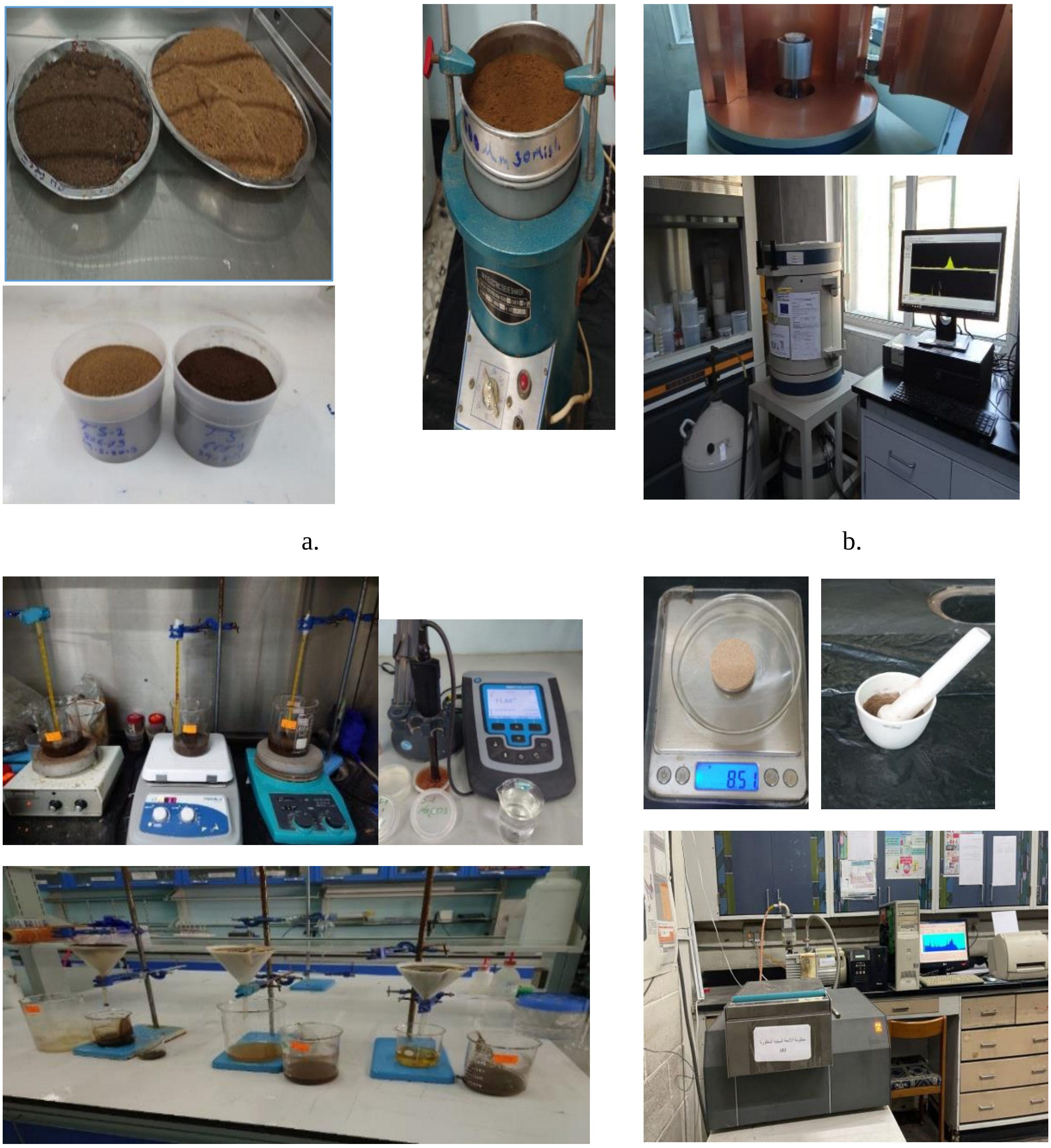
The activity removal percentage (R %) of ^{226}Ra and ^{228}Ra in the chemical leaching process was calculated using the relation below[19,28,29]:

$$R\% = [(A_0 - A)/A_0] \times 100 \ \ldots\ldots\ldots \ 2$$

where; A_0 is the initial activity concentration of the soil sample.

2- Sequential extraction procedure

Three processes were carried out to improve the radium extraction with final solvents as a pretreatment, the first, was washing the soil samples with deionized water twice to remove not-so-important salts (access salts) and elements that can dissolve in water, (40-50°C, 3h, L: S=5, and 200rpm). The second process was converting the reaction conditions from neutral to basic media by washing soil samples with dilute sodium hydroxide solution and 0.07M NaOH (25-30°C, 1h, L:S=3, and 200 rpm), then the third step was washing the soil with sodium carbonate solution (2M Na_2CO_3) to convert the sulfate structure of radium into carbonate structure (70-80°C, 4h, L: S=4, and 200rpm), which easily chemically interacts and dissolves in dilute acids (weak and strong) [15,19,23,28,30], the mixture was then cooled to room temperature, and filtered, then washed with different acids and chelating agents (2M HNO3, 2M HCl, 2M $C_6H_8O_7$, 1M $C_2H_4O_2$, 0.2M Na_2EDTA, and 2M H2SO4) under the optimum conditions (40°C, 2h, L: S=5, and 200rpm).



a. b.

c. d.

Figure 2. a. samples preparation b. gamma-ray spectroscopy c. the chemical washing and pH meter d. XRF-system and sample preperation

Results and Discussion

Direct extraction leaching efficiency

The results of efficiency removable for ^{226}Ra and ^{228}Ra % of leaching from the NORM soil are given in Table 4 and shown in Fig. 3, there are poor results of efficiency percent of radium removing R% into the most used solvents for the first soil sample (TS-1), whereas they were better for the second soil sample (TS-2) by using the same solvents and conditions, as presented in Table 5 and shown in Fig. 4. Where the 2M H_2SO_4, D.W+2M HNO_3 acids and 2M Na_2CO_3 salty solution show the highest efficiency removable of ^{226}Ra for TS-1 sample, they were; 15.8%, 12.1%, and 10.9% respectively, while, the highest efficiency removable of ^{226}Ra for TS-2 sample in direct leaching using 2M Na_2CO_3, 2M

$CaCl_2$ salty solutions, and 2M H_2SO_4 acids were 45.2%, 39.7%, and 36.6%, respectively.

The difference in R% between the two soil samples may be due to the difference in activity concentration (AC), where the AC of TS-1 is greater than TS-2 about eight times, oil content (TS-1 is greater about eight times than TS-2), organic materials (more than twice), and soil texture, as presented in Table 1. The relatively high presence of the organic components in the two samples and the high presence of hydrocarbons in the first sample that made the chemical reaction of acid with the target element have a low probability. Table 2 presents the concentration of major elements of TS-1 and TS-2 soil samples before and after treatment directly with 2M HNO_3 by XRF- system, the results in this table refer to positive R% extracting of some element (Cl, Ca, Mn, Fe, Ni, Cu, Zn, Ta, and Pb) after washing directly with the nitric acid in the TS-1 soil sample. While positive R% extraction of the TS-2 soil sample for the most elements (Cl, Ca, Mn, Fe, Ni, Cu, Zn, Ta, Pb Ba, and Sr). The weight loss as seen in Tables 2, 4, and 5 after washing with the solvents, where the weight loss of TS-1 is greater than TS-2 by washing with the most used solvents, that makes R% of TS-2 better than TS-1. The weight loss might be the main cause of poor removal efficiency R(%) of radium isotopes because the soil loses some of the common elements during the chemical leaching with solvents where these elements compete and contribute with Ra in chemical reactions, such as Ca, Mn, Fe, Ni, Cu, Zn, Ta, Pb, Ba, and Sr. Most of them have the most similar physicochemical characteristics to radium (group-2 in the periodical table), especially barium (Ba^{2+}) ions, so they were dissolved with the acid solution under the same optimal conditions, as presented in Table 2, where the chemical reaction occurred with these elements and most of the reaction results are very soluble components in water [30], for example; the reaction with nitric acid produces nitrate salts, such as $Fe(NO_3)_2$, $Ni(NO_3)_2$, $Cu(NO_3)_2$, $Pb(NO_3)_2$, and $Ta(NO_3)_2$. The presence of co-element ions in the contaminated soil crowded out with radium ions, that reduced the removal efficiency of Ra.

In the second washing with the same acid, the weight loss ratio is less than the first washing, as presented in Tables 4 and 5, that proves the R% of radium isotopes in the second washing is higher than the first, where the solvents react with the target element (radium components) better than in the first washing because most of the co-elements were dissolved in the first washing which gave the acid a chance to react with radium ions to produce radium nitrate which is very soluble in water, that causes improving in R% for radium.

Some salty solutions that were used appeared to be more effective than most acids in direct extraction leaching, where Ra leached with sodium carbonate, calcium chloride, and sodium nitrate solutions for TS-1 and TS-2 soil samples. Carbonate appeared to be more effective than nitrates and chlorides.

Table 4. The removal efficiency % of ^{226}Ra and ^{228}Ra for TS-1 soil sample after treatment with different solvents by direct extraction leaching

Solution	AC of ^{226}Ra ±4.1% ($Bq.kg^{-1}$)	R% of ^{226}Ra	AC of ($Bq.kg^{-1}$) ^{228}Ra ±5.2%	R% of ^{228}Ra	Soil lost%
D.W/2*	56690.3	5.6	7052.4	3.8	2.7
0.05 NaOH	59093.7	0.9	6777.8	1.4	2.0
$NaNO_3$	54526	8.6	6607.4	6.38	2.3
$CaCl_2$	54095.3	9.3	6702.7	7.04	3.1
2M Na_2CO_3	53183.5	10.9	6961.2	9.41	3.5
2M Ac	54820.1	8.1	6413.5	9.1	3.7
2MH2SO$_4$	48428.2	15.8	5586.9	12.1	12.2
EDTA	53842.6	9.8	6580.2	7.8	5.4
2M HCL	59537.7	0.23	6830.3	0.32	17.4
D.W+2M HNO_3	52453.5	12.1	6415.9	9.1	18.3
2M HNO_3	57414.5	3.8	6861.5	2.8	19.9
2M HNO_3+H_2O_2	56033.9	6.1	6486.5	8.1	19.8
2MHNO_3+3M HNO_3	56715.0	5.0	6771.7	4.1	31.23

***** D.W/2; deionized water double washing and Ac: acetic acid

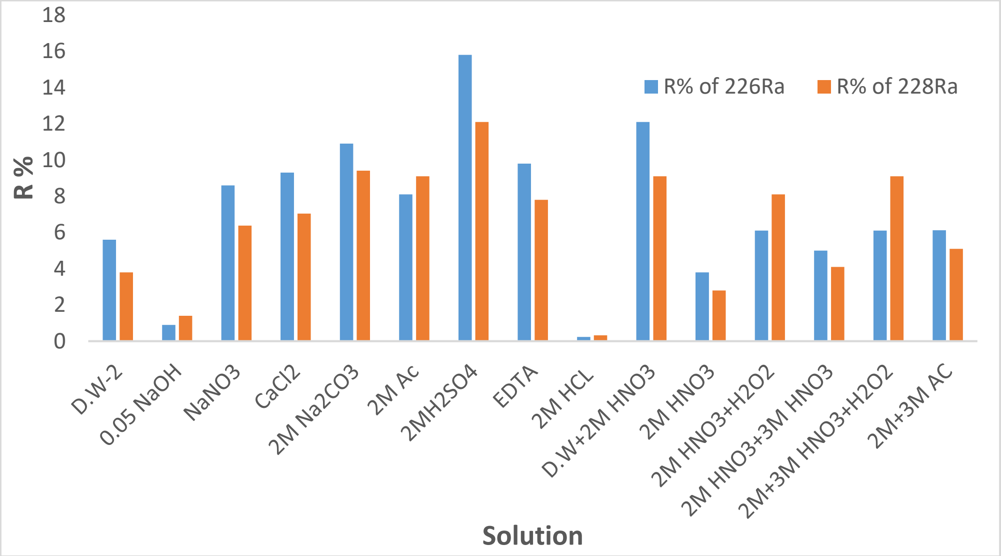


Figure 3. The removal efficiency % of ^{226}Ra and ^{228}Ra for TS-1 soil sample by direct extraction leaching

Table 5. The removal efficiency % of ^{226}Ra and ^{228}Ra for TS-2 soil sample after treatment with different solvents by direct extraction leaching

TS-2	AC of ^{226}Ra ±10.6% (Bq.kg^{-1})	R% of ^{226}Ra	AC of ^{28}Ra ±16.3% (Bq.kg^{-1})	R% of ^{228}Ra	Soil lost%
D.W/1	6898.5	10.4	752.024	9.1	1.1
D.W/2	7510.4	2.3	814.9	1.495	2.1
2M $CaCl_2$	4621.1	39.7	480.5	42.7	2.8
2M Na_2CO_3	4199.2	45.2	486.8713	41.1	3.2
2M $NaNO_3$	6643.3	13.3	704.8	15.7	2.4
2M HCl	5480.8	0.28	634.2	0.23	11.2
2M H_2SO_4	4859.9	36.6	576.6	0.3	9.6
2M Ac	5289.8	31.2	595.8	0.28	8.5
2M HNO_3+D.W	6849.8	10.6	730.8	12.5	14.2
2M HNO_3+H_2O_2	5612.2	26.8	768.7	7.4	13.6
2M HNO_3	6758.9	11.8	628.8	23.9	14.5
2M+3M HNO_3	3219.72	58.1	413.2	50.2	18.4

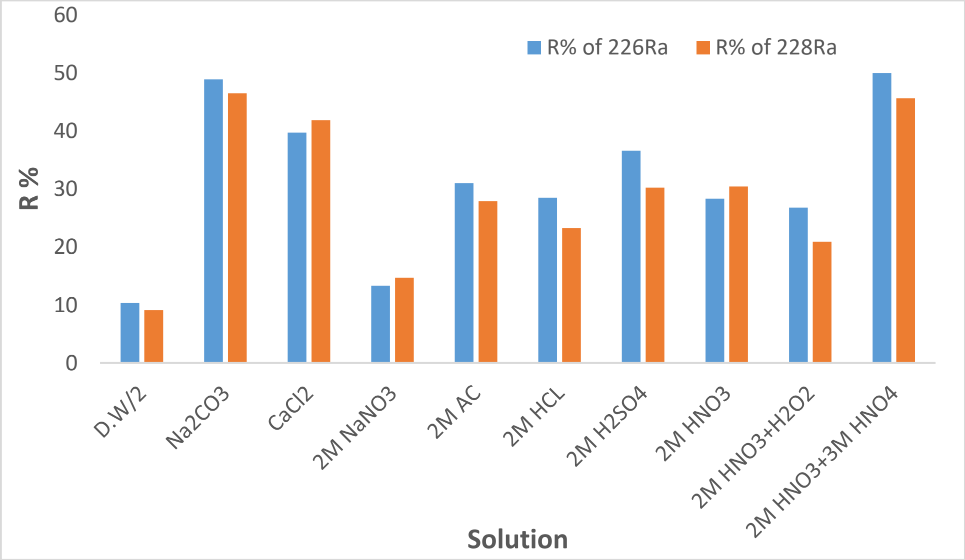


Figure 4. The removal efficiency % of ^{226}Ra and ^{228}Ra for TS-2 soil sample by direct extraction leaching

Sequential extraction leaching

Tables 6 and 7 present that 22.6±% and 19.1± % from the initial activity of ^{226}Ra and ^{226}Ra respectively were removed in the third step of the TS-1 soil sample, whereas 47.7% and 44.5% were removed from the TS-2 soil sample after washing them separately by sodium carbonate solution. Finally, different diluted organic and inorganic acids and one organic salty solution Na_2EDTA (chelating agent) were used as the last chemical leaching sequence for treating the TS-1 soil sample. The illustrated results in Fig. 5 show both acetic acid and Na_2EDTA solutions ensure high-efficiency removable percentage (R%) of ^{226}Ra and ^{226}Ra, where 78.4% and 80.6% respectively, were removed from initial activity using acetic acid, and, 68.4% and 71.5% removed respectively using Na_2EDTA for TS-1 soil sample. Table 7 appears a high response to TS-2 soil sample by washing with nitric and acetic acids as a last step, where 87.7 % and 91.1% of ^{226}Ra and ^{228}Ra respectively, were removed from the initial activity using nitric acid.

Table 6. Activity Concentrations AC of TS-1 soil sample after treatment (Bq.kg^{-1}) with different solvents and total removal efficiency % of sequential extraction leaching

AC after washing by 2M Na_2CO_3 ± Unc.%		**Removal efficiency %**		**AC of soil sample after treatment with different solvents and total removal efficiency %**							
^{226}Ra±4 %	^{228}Ra± 5%	R% ^{226}Ra	**R% ^{228}Ra**	**Solution**	**^{226}Ra ± 3.6%**	**^{228}Ra± 5.1%**	**R% ^{226}Ra**	**R% ^{228}Ra**	**Rtot % ^{226}Ra**	**Rtot % ^{228}Ra**	**Soil pH**
46196.6	5713.7	22.6	19.1	**2M HNO3**	29800	3231.6	27.5	35.1	**50.1**	54.2	3.84
				1M Ci*	37800	4513.9	14.1	17	**36.6**	36.1	4.53
				2M H_2SO_4	38553.36	4799.44	**12.8**	13.5	**35.4**	32.6	4.1
				2M HCl	25278.7	3625.6	35.2	29.2	**57.6**	48.6	5.2
				2M Ac	12876.3	1301.5	55.8	61.5	**78.4**	80.6	7.2
				0.1M Na_2EDTA	28760.8	3387.8	29.2	32.7	**51.8**	51.8	10.15
				0.2M Na_2EDTA	18815.7	2006.2	45.8	52.4	**68.4**	71.5	11.85

Ci: citric acid

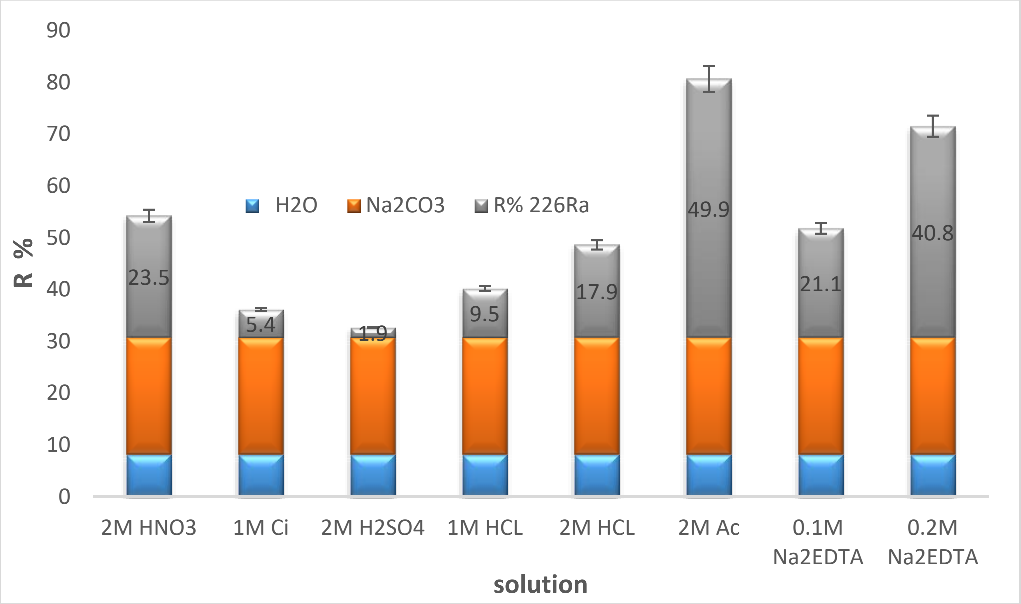


Figure 5. The removal efficiency % of ^{226}Ra and ^{228}Ra for TS-2 soil sample by sequential extraction leaching

Table 7. Activity concentrations of TS-2 soil sample after treatment (Bq.kg^{-1}) with solvents and total removal efficiency % of sequential extraction leaching

AC(Bq.kg^{-1}) of soil sample after treatment with 2M Na_2CO_3 and R%				**AC of soil sample after treatment (Bq.kg^{-1}) with different solvents**							
^{226}Ra±9 %	**^{228}Ra± 14%**	**R% ^{226}Ra**	**R% ^{228}Ra**	**Solution**	**^{226}Ra ± 34%**	**^{228}Ra ± 32%**	**R% ^{226}Ra**	**R% ^{228}Ra**	**R_{tot} % ^{226}Ra**	**Rtot % ^{228}Ra**	**Soil pH**
4010.5	459.7	47.7	44.5	2M HNO_3	940.3	83.6	40.2	45.4	87.9	89.8	3.5
				HCl	931.14	97.22	40.2	43.7	87.9	88.2	5.2
				1M Ac	1135.2	113.4	37.5	41.8	85.2	86.3	7.8
				0.1EDTA	1441.4	145.8	33.5	37.9	81.2	82.4	11.3

Conclusion

The single chemical leaching experiments with different acidic, alkaline, and salty solutions showed low extraction results for removing radium from the soil samples, which indicates radium in contaminated soil may be in the form of insoluble salt, such as sulfate ($RaSO_4$), where it is the least soluble of all known sulfate salts and has extremely very low solubility in water and aqueous solutions, this indicates that the NORM soil under this study requires chemical preparation before leaching with acids using some selective extraction solutions. Therefore, there is no significance to washing soil under this investigation directly with solvents and diluted acids while using strong acids is not recommended. Although the sequential extraction process is time-consuming, it can be a useful tool and better than single extraction for evaluating the chemical fractionating and mobility of radium with low molarity concentrations of acids (strong and weak) that finally allow minimal contamination of soil.

The results expose that acetic acid with a low concentration is an effective solvent for soil treatment that depends on its ability to react with radium salts, acidity, optimum used molarity concentration, cost, and availability. The pH of soil after treatment with Ac- acid was 7.2 (neutral acidity), as presented in Tables 6 and 7, and the generated liquid waste was 5.6, therefore, the dilute organic acid solution can be chosen as the best medium of chemical treatment for radium extraction from NORM oilfield soil.

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Authors' Declaration

- Conflicts of Interest: None.
- We hereby confirm that all the Figures and Tables in the manuscript are ours. Furthermore, any Figures and images, that are not ours, have been included with the necessary permission for re-publication, which is attached to the manuscript.
- No animal studies are present in the manuscript.
- No human studies are present in the manuscript.
- Ethical Clearance: The project was approved by the local ethical committee at University of Baghdad.

Authors' Contribution Statement

Z. H. I. drafting the MS, implementation, and acquisition and analysis of data, A. H. Al. supervision, revision, and proof reading. All authors agreed to the final version of this manuscript.

References

1. Salahel DK, Rashed W. Assessment of norm levels and radiological hazards from petroleum extraction in the onshore oil fields, Egypt. Radiat Prot Dosimetry. 2021; 194(4): 223–332. https://doi.org/10.1093/rpd/ncab099
2. Shihab AK, Al-Mashhadani AH. The Danger Arising From Exposure to Natural Radionuclides as A Result of Working in Majnoon Oil Field in Southern Iraq. AIP Conf Procs. 2022; 2394: 090045. https://doi.org/10.1063/5.0121015
3. Al-Haleem AA, Al-Razaq A. Oilfield Produced Water Management: Treatment, Reuse and Disposal. Baghdad Sci J . 2012; 9(1):124–32.
4. International Atomic Energy Agency IAEA. The Environmental Behaviour of Radium: Technical Reports Series No. 476. Austria-Vienna: The IAEA; 2014. 188-210.
5. International Atomic Energy Agency IAEA. Management of Residues Containing Naturally Occurring Radioactive Material from Uranium Production and Other Activities: No. SSG-60 Specific Safety Guides. Austria-Vienna: The IAEA; 2021. 6–58.
6. Ali MM, Zhao H, Zhongyu L, Maglas NM. Concentrations of TENORMs in the petroleum industry and their environmental and health effects. RSC Adv. 2019; 9(67): 39201-39229. https://doi.org/10.1039/c9ra06086c
7. Attallah MF, Abdelbary HM, Elsofany EA, Mohamed YT, Abo-Aly MM. Radiation safety and environmental impact assessment of sludge TENORM waste produced from petroleum industry in Egypt. Process Saf Environ Prot. 2020; 142: 308–316. https://doi.org/10.1016/j.psep.2020.06.012
8. Hilal MA, Abdelbary HM, Mohamed GG. Physicochemical and radiation hazardous properties of scale TENORM waste: evaluation by different analytical techniques. Radiochemistry. 2018; 60: 444-449.
9. Afifi EM El, Mansy MS, Hilal MA. Radiochemical signature of radium-isotopes and some radiological hazard parameters in TENORM waste associated with petroleum production: A review study. J Environ Radioact. 2023; 256: 1-16. https://doi.org/10.1016/j.jenvrad.2022.107042
10. Ibrahim ZH , Al-Mashhadani AH. Radionuclides Determination and Hazard Indices Assessment of NORM Contaminated Soil for Oil Fields in Southern Iraq. Iraqi J Sci. 2024; 65 (11).
11. Arneodo F, Balata M, Benabderrahmane ML, Bruno

G, Giovanni DA, Fawwaz O. Characterization of Naturally Occurring Radioactive Material (NORM) Generated from the Lower Cretaceous Carbonate Formations in the Arabian Peninsula and Gulf. BHM Berg- und Hüttenmännische Mo. 2020; 165(8): 353–363. https://doi.org/10.1007/s00501-020-01011-z

12. Al-Mashhadani AH, Ibrahim ZH. Remediation of Contaminated Soil with Radium -226 and 228 by Various Methods. J Radioanal Nucl Chem. 2024; 57(1D).
13. Hilal MA, Attallah MF, Mansy MS, El Afifi EM. Examination of the parameters affecting of 222Rn emanation for some industrial and environmental samples using gamma-spectroscopy. Appl Radiat Isot. 2022; 186:110272. https://doi.org/10.1016/j.apradiso.2022.110272
14. Rejah BK. Specific activities of natural radionuclides and annual effective dose due to the intake of some types of children powdered milk available in Baghdad markets. Baghdad Sci J. 2017; 14(3): 619–24. http://dx.doi.org/10.21123/bsj.2017.14.3.0619
15. Kirby HW, Murrell L Salutsky W. The Radiochemistry of Radium, Annual Reports Section ‘A’ (Inorganic Chemistry) Nuclear Science Series. National Academy of Sciences: National Research Council Printed in USA; 1964; 76: 247. https://doi.org/10.1039/ic9797600247
16. Attallah MF, Hamed MM, El Afifi EM. Remediation of TENORM scale waste generated from petroleum industry using single and mixed micelles solutions. J Mol Liq. 2019; 294: 111565. https://doi.org/10.1016/j.molliq.2019.111565
17. Awwad NS, Attallah MF, El-Afifi EM, Ibrahium HA, Aly HF. Overview about Different Approaches of Chemical Treatment of NORM and TE-NORM Produced from Oil Exploitation. Advances in Petrochemicals. InTech; 2015. Chap 5: 85-113. http://dx.doi.org/10.5772/61122
18. Garner J, Read D. Optimisation of radium removal from saline produced waters during oil and gas extraction. Minerals. 2020; 10(3): 1–11. https://doi.org/10.3390/min10030278
19. Al Abdullah J, Al-Masri MS, Amin Y, Awad I, Sheaib Z. Chemical fractionation of radium-226 in NORM contaminated soil from oilfields. J Environ Radioact.. 2016; 165: 47–53. https://doi.org/10.1016/j.jenvrad.2016.09.003
20. El Afifi EM, Shahr El-Din AM, Hilal MA. Kinetics and mechanism of radium-isotopes dissolution in TENORM scale waste associated with petroleum production using certain organic carbon source: lactic acid solution. Environ Sci Pollut Res. 2020; 27: 38134–38147. https://doi.org/10.1007/s11356-020-09863-1
21. Yue Y, Dou J, Xue Y, Jin N, Yang K. Chelating Agents in Assisting Phytoremediation of Uranium-Contaminated Soils: A Review. Sustain.2022; 14(10): 1–22. https://doi.org/10.3390/su14106379
22. Attallah MF, Hamed MM, El Afifi EM. Remediation of TENORM scale waste generated from petroleum industry using single and mixed micelles solutions. J Mol Liq. 2019; 294:111565. https://doi.org/10.1016/j.molliq.2019.111565
23. Lim S, Syam NS, Maeng S, Lee SH. Determination of ^{226}Ra in TENORM sample considering radon leakage correction. J Radiat Prot Res. 2021; 46(3): 127–33. https://doi.org/10.14407/jrpr.2021.00087
24. Desouky O, Morsi T, El-Marakby S. Evaluating the Radiological Hazards of Contaminated Soil with Natural Radioactive Materials (NORM) Resulting from Produced Water during Oil & Gas Production. Arab J Nucl Sci Appl. 2021; 54(1):162–72. https://doi.org/10.21608/ajnsa.2020.53169.1422
25. Masok FB, Masiteng PL, Mavunda RD, Maleka PP, Winkler H. Measurement of radioactivity concentration in soil samples around phosphate rock storage facility in Richards Bay, South Africa. J Radiat Res Appl Sci. 2018; 11(1): 29–36. https://doi.org/10.1016/j.jrras.2017.10.006
26. El-Taher A, Massoud ES, Abdel-Rahman MAE. Assessment of Natural Radioactivity Levels and Radiological Hazard Indices in Soil Samples Collected from the Central Region of Saudi Arabia. Radiochemistry. 2022; 64(3): 399–408. https://doi.org/10.1134/S1066362222030183
27. Abdelbary HM, Elsofany EA, Mohamed YT, Abo-Aly MM, Attallah MF. Characterization and radiological impacts assessment of scale TENORM waste produced from oil and natural gas production in Egypt. Environ Sci Pollut Res . 2019; 26: 30836–30846. https://doi.org/10.1007/s11356-019-06183-x
28. El Afifi EM, Attallah MF, Hilal MA, El Reefy SA. Treatment of TENORM waste: Phosphogypsum produced in fertilizer industry. Radiochemistry. 2010; 52(4): 441–445. https://doi.org/10.1134/S106636221004020X
29. Maryadele JO’Neil, Patricia EH, Peter HD, Kristin JR. The Merck Index: An Encyclopedia of Chemicals, Drugs, and Biologicals. 15th edition. Royal Society of Chemistry: Cambridge: U.K.; 2013; 2708 p. ISBN 10: 1849736707 ISBN 13: 9781849736701.
30. Attallah MF, Imam DM. Green approach for radium isotopes removal from TENORM waste using humic substances as environmental friendly. Appl Radiat Isot. 2018; 140: 201–208. https://doi.org/10.1016/j.apradiso.2018.07.019

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معالجة تربة الحقول النفطية الملوثة بالمواد المشعة ذات المنشأ الطبيعي بطريقة الاستخلاص الكيميائي

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الخلاصة

يعد تلوث التربة بالمواد المشعة التي تحدث بشكل طبيعي (NORM) مشكلة شائعة في حقول النفط مما يؤدي إلى برامج مكلفة للمعالجة والتخلص النهائي (الطمر), حيث ان أهم النويدات المشعة في هي ^{226}Ra و ^{228}Ra . تركز هذه الدراسة على معالجة التربة الملوثة ب NORM لتقليل النشاط الاشعاعي ضمن الحدود المسموح بها والذي ينعكس على تقليل مخاطر الإشعاع على العمال والجمهور والبيئة. تناولت الدراسة المعالجة الكيميائية لعينتين من التربة عن طريق اختبار الترشيح باستخدام التنقيات المنفردة والمتتابعة بمذيبات كيميائية مخففة عضوية وغير عضوية (مثل HNO3 و HCl و $C_6H_8O_7$ و $C_2H_4O_2$ و EDTA و H_2SO_4)، حيث تم قياس تراكيز النشاط الأولي لـ ^{226}Ra و ^{228}Ra باستخدام محلل مطيافية كاما بكاشف الجرمانيوم عالي النقاوة (HPGe) ، حيث كانت 59674.7 ± 2731.2 و 7058.2 ± 451.07 Bq.kg^{-1} على التوالي للعينة الأولى، في حين كانت 7666.6 ± 615.4 و 826.36 ± 143.4 Bq.kg^{-1} للعينة الثانية. الاستخلاص المتسلسل انجز في ثلاث خطوات متتالية (تعديل الحامضية وتبادل الأيونات والترشيح بالمذيب النهائي). أن الترشيح المنفرد أعطى نتائج ضعيفة في استخراج نظائر الراديوم من التربة بواسطة المحاليل المخففة, بينما الترشيح المتسلسل كان أفضل ، وجد أن المذيبات الأكثر فعالية هي حمض الأسيتيك ($C_2H_4O_2$) 2M مع نسبة سائل إلى صلب L:S قدرها 5 mL/g عند درجة حرارة 40 °C للعينة الأولى، حيث 78.4% و80.6% من ^{226}Ra و ^{228}Ra تم ازالتها وتحويلها إلى الطور المائي، بينما تمت إزالة 87.9% و91% باستخدام 2M HNO_3 للعينة الثانية وبنفس الظروف.

الكلمات المفتاحية: الترشيح الكيميائي, EDTA ، كاشف HPGe، NORM، ^{226}Ra , ^{228}Ra .