Treatment of phosphogypsum waste produced from phosphate ore processing

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HIGHLIGHTS

▶ Purification of phosphogypsum waste by separating the contaminated radionuclides.
▶ Separation process depends on leaching of wastes using suitable organic extractants.
▶ Costs treatment of PG depending on the type and quality of the used reagents.

ARTICLE INFO

ABSTRACT

Phosphogypsum (PG), primary byproduct from phosphoric acid production, is accumulated in large stockpiles and occupies vast areas of land. Phosphogypsum is a technologically enhanced naturally occurring radioactive material (TE-NORM) that contains radionuclides from ^{238}U and ^{232}Th decay series which are of most radio-toxicity. The reduction in concentration of radionuclides content from PG was based on leaching of ^{226}Ra, ^{210}Pb, ^{238}U and ^{40}K using tri-butyl phosphate (TBP) and tri-octyl phosphine oxide (TOPO) in kerosene. The factors which affect the leaching process such as contact time, concentration of the solvent and temperature were optimized. Based on the experimental results, about 92.1, 88.9, 83.4, 94.6% of ^{226}Ra, ^{210}Pb, ^{238}U and ^{40}K respectively were successfully removed from the PG. The reduction in the concentration of radionuclides was accompanied by reduction in the concentration of rare earth elements ($\sum REE$) equals to 80.1%. Using the desired organic extractant under optimum conditions for treatment of the PG waste leads to obtain a decontaminated product that can be safely used in many industrial applications.

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1. Introduction

Phosphogypsum (PG) is a hazardous waste associated with the phosphoric acid production using the wet process [1]. PG is considered a relatively high level natural uranium series radionuclide material, which provokes a negative environmental impact and many restrictions on the use of the PG waste (only 15% of the PG generated is recycled in agriculture, in gypsum board and cement industries). The USEPA has classified PG as Technologically Enhanced Naturally Occurring Radioactive Material (TE-NORM) [2]. Legislations and standard regulations have established maximum limits for PG radionuclides concentration and exposure. The potential problem of PG is the emanation of ^{222}Rn from the alpha-decay of ^{226}Ra. The radon has an intense radiation capacity and a short half-life of 3.8 days [3].

A method for the extraction of radium into a mixture of 2-thenoyltrifluoroacetone (HTTA) and tributyl phosphate (TBP) or trioctylphosphine oxide (TOPO) in n-hexane or cyclohexane with regard to the pH, TBP and TOPO concentrations was studied. The formation of mixed complexes of $Ra(TTA)_2(TBP)_2$ and $Ra(TTA)_2(TOPO)_2$ occurs and the overall extraction constants of both complexes were calculated. The results show that the substitution of n-hexane by cyclohexane has practically no effect on the extraction of radium and the more electronegative TOPO is much more effective than TBP. Further, n-hexane or cyclohexane is more suitable solvents than CCl_4 [4,5]. The extraction of radium and barium into a mixture of 1-phenyl-3-methyl-4-benzoylpyrazol-5-one (HPy) and TOPO in n-hexane or cyclohexane as a function of pH and TOPO concentration was investigated. It was found that the synergistic enhancement of the extraction is due to the formation of mixed complexes of $M(Py)_2(TOPO)_3$. From the calculation of the overall extraction constants of both complexes, the extraction of barium is higher than that of radium and the theoretical separation factor of (Ba/Ra) is equal to 4.6 and 8.5 for n-hexane and cyclohexane, respectively [6].

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El-Didamony et al. [7] studied the reduction in concentration of the radionuclides from PG. The removal process is based on leaching of radionuclides using suitable organic extractants. The factors affect the leaching process such as type of leaching materials, contact time, concentration of the desired solvent, liquid to solid ratio, and temperature were studied. Based on the experimental results, about 71.1%, 76.4%, 62.4%, and 75.7% of ^{226}Ra, ^{210}Pb, ^{238}U and ^{40}K respectively were successfully removed from the PG. The reduction in the concentration of radionuclides was accompanied by reduction in the concentration of total rare earth elements ($\sum$REE) equals to 69.8%. Using the desired organic extractant under optimum conditions for treatment of the phosphogypsum waste leads to obtain a decontaminated product that can be safely used in many industrial applications.

The present work aims to purify the PG, a by-product from the wet process phosphoric acid, and to minimize the environmental pollution during storage, transportation and usage. The main goal is to decrease its radionuclides such as ^{226}Ra, ^{210}Pb, ^{238}U, and ^{40}K to the acceptable level using the synergism of TBP-TOPO in kerosene. The extracted radionuclides can be easily recovered from the solvent and used in many useful processes. So, the stripping investigations were carried out to choose the best conditions that can successfully strip these materials from the organic extractants. Moreover, the optimization of stripping process was performed. The decontaminated product can be safely used in many industrial applications to prepare low cost products.

2. Experimental

2.1. Materials and apparatus

Samples of PG (of density equals 2.29 g/cm^3) were provided from the Sebaiya rock, Red Sea Coast, Egypt, by (the wet process phosphoric acid plant) Abu-Zaabal Company for Fertilizers and Chemicals. Tributyl phosphate (TBP) and trioctyl phosphine oxide (TOPO) were provided by Loba Chemie PVT. LTD as well as kerosene was provided by El-Nasr Chemicals Company, Egypt. Metertech UV/VIS SP8001 Spectrophotometer, China, was used for measuring the concentrations of major oxides, fluorine, uranium, thorium and total rare earth elements [8,9].

The γ-ray spectrometer was used for radiometric determination of radionuclides. The different radionuclides in PG samples were identified and quantified using HPGe detector (2201-Oxford, USA, the detector was shielded by lead shield) with relative efficiency of 30% and resolution (FWHM) of 1.95 keV at 1.332 MeV for ^{60}Co. The counting time is 7200 s (2 h). The uncertainty of the measurements was about ± 7% for all radionuclides. The acquisition spectra were processed by 8 k MCA and Genie 2000 software (MCA with 8192-channel is connected with IBM personal computer) [7,10]. Energy calibration was performed using several certified sealed point sources of known γ-energy lines, namely, ^{22}Na, ^{60}Co, ^{133}Ba and ^{137}Cs (Amersham, England). The efficiency as a function of the γ-energy (in keV) for the HPGe detector was determined using reference materials (IAEA 312, 313 and 314) with known activity concentrations provided by the Analytical Quality Control Services (AQCS), International Atomic Energy Agency (IAEA), Vienna, Austria [11–13].

An accurate 50 g of PG was stored in plastic container for radiometric measurements. Activity concentrations of ^{226}Ra, ^{238}U, ^{210}Pb and ^{40}K in the PG were determined from the measured net count rate (c/s) of 186.2 keV (yield per decay of 3.3%), 352 keV (37.1%), 46.2 keV (4%), and 1461 keV (10.7%) respectively.

Table 1
Chemical analysis of phosphogypsum sample.

Components	Concentration	Components	Concentration
Constituents (wt%)			
CaO	30.2	Na$_2$O	0.14
SO$_3$	41.1	K$_2$O	0.08
SiO$_2$	2.27	TiO$_2$	0.4
P$_2$O$_5$	1.56	F	1.39
Fe$_2$O$_3$	1.74	L.O.I.	20.8
Trace concentrations (ppm)			
U	14	$\sum$TE	1307
Th	10	$\sum$REE	395
Radioactive materials (Bq/kg)			
^{226}Ra	482 ± 13.2	^{238}U	164 ± 12.5
^{210}Pb	418 ± 11.7	^{40}K	72 ± 4.9

2.2. Analysis of the phosphogypsum

Morphologically, phosphogypsum is yellowish brown color and relatively soft grains [14–16]. Chemically, the PG consists mainly of SO$_3$, CaO with low contents of SiO$_2$, Fe$_2$O$_3$, and P$_2$O$_5$ as well as traces of Na$_2$O, K$_2$O, TiO$_2$, F and 20.8% ignition loss (L.O.I.). It has also traces from U and Th (measured by Arsenazo III method) as well as some trace elements (TE) such as Cr, Co, Cu, Cd, Zn, Zr, Pb, Rb, Ba, Sn, and Sr (measured using XRF) in addition to radionuclides such as ^{226}Ra, ^{210}Pb, ^{238}U and ^{40}K. The chemical analysis of PG is seen in Table 1.

2.3. Spectroscopic characterization of PG

Chemically, the PG consists primarily of calcium sulfate dihydrate (CaSO$_4$·2H$_2$O) with small amounts of silica, quartz, and unreacted phosphate rock, such composition is in good consistence with its chemical major constituents as reported by El-Gamal [15]. The X-ray diffraction pattern of PG sample is presented in Fig. 1. The spectrum showed main three strong peaks at diffraction angles of 14.7 (d = 6.02 Å), 25.7 (d = 3.5 Å), and 29.8 (d = 3 Å), which are characterized to gypsum CaSO$_4$·2H$_2$O as the phase composition of the PG wastes. The other elements were founded in small amounts which can not be detected by XRD technique, such as silica, phosphate and metallic impurities, e.g. Na, Al, Fe and Sr.

The IR spectra of the PG sample have been measured as potassium bromide (KBr) disc, Fig. 2. The spectra show that there are many vibrational absorption bands, characterized mainly to inorganic sulfur compounds [17]. In this concern, the strong absorption band at ~1125 cm^{-1} is characterized to stretching vibrations of S=O related to sulfate group as calcium sulfate in PG waste sample. This band was confirmed by the appearance of another band at 1012 cm^{-1}. Also, there is a strong absorption band at ~3613 cm^{-1},
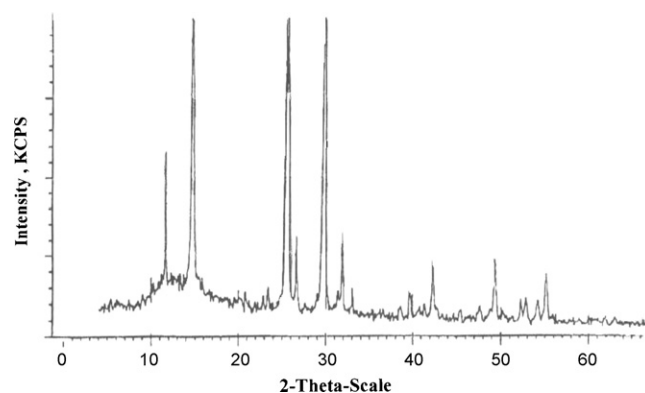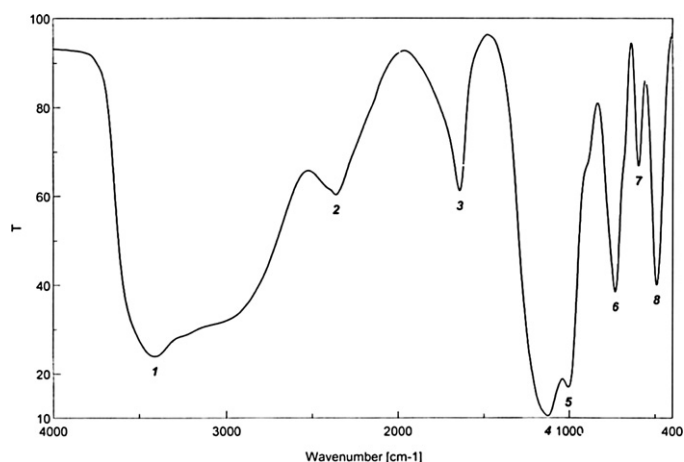

Fig. 1. Spectrum of the X-ray diffraction of PG.

Fig. 2. IR Spectra of phosphogypsum produced from the Sebaiya ore.

Fig. 3. Effect of agitation me on leaching of PG by TBP–TOPO in kerosene.

which is attributed to stretching vibrations of Si—OH group, and is confirmed by another band at $\sim$795 cm^{-1}. The absorption bands at $\sim$3562, and 1620 cm^{-1} are related to OH group of water (as moisture) content in PG. The absorption bands at 2377, 2315, 2222 and 2140 cm^{-1} are attributed to P—OH stretching of the phosphoric acid residue in PG wastes. The vibrations at 662, 600 and 466 cm^{-1} are due to M–O band which is related to the presence of metal-oxides content in PG [18,19].

2.4. Analytical procedure

The principle for leaching process is that the active agents present in a solid matter are extracted and dissolved in a liquid (usually, but not always a solvent), either in nature or through an industrial process. In general, leaching is the process in which inorganic, organic contaminants or radionuclides are released from the solid phase into the water phase under the influence of mineral dissolution [20–23]. The removal of radionuclides from PG by leaching is essentially important in many industries. The amount of the removed radioactive materials depends on conditions of the process.

After dryness and grinding of PG, the bulk sample was carefully sieved to <63 μm (because the radionuclides were concentrated in this size [7]). In 250 ml beakers, a known amount of PG (100 g) was taken, with the addition of known volume of diluent at room temperature and mixed for a known time. Other processes were performed by using suitable organic extractants in the desired diluent at the same standard conditions. The factors affect the desired leaching materials (such as contact time, concentration of solvent, liquid: solid ratio, as well as temperature) were optimized. For the analysis of the radionuclides, an accurate weight of 50 g of the sample was initially counted (C_o) before leaching. After leaching process, the solution was separated by centrifugation. The produced solid residue was dried and radiometrically counted (C_f) again for ^{226}Ra, ^{210}Pb, ^{238}U and ^{40}K.

The removal efficiency (E) of radionuclides and $\sum$REE can be calculated as follow:

$$\text{Removal efficiency} \, (E)\% = \left[\frac{C_o - C_f}{C_o} \right] \times 100$$

where C_o is the initial radionuclides count (or $\sum$REE concentration) of the received PG waste and C_f is the final radionuclides count (or $\sum$REE concentration) of the treated PG. The removal efficiency (E) was expressed as leaching percent (%) of waste materials.
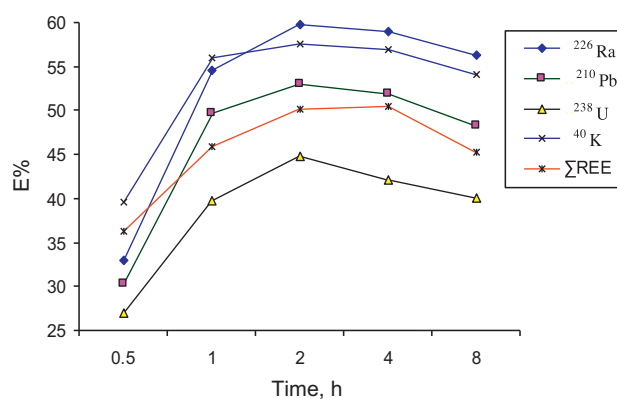
3. Results and discussion

3.1. Synergistic leaching of PG with TBP–TOPO in kerosene

Tributyl phosphate (TBP) is a major extractant and modifier with many applications in hydrometallurgy. The addition of TBP to TOPO can improve the removal efficiency and the mass transfer of leaching process. The factors affect the synergism of TBP–TOPO such as contact time, concentration of solvent, molar ratio and temperature were optimized as the following:

3.1.1. Effect of agitation time

The effect of agitation time on the leaching of PG using TBP–TOPO in kerosene was investigated from 0.5 h up to 8 h at room temperature by the addition of 100 ml of (0.1 M) TBP–TOPO in kerosene to 100 g of solid PG. The results were illustrated by Fig. 3.

It is clear that, the removal efficiency of ^{226}Ra, ^{210}Pb, ^{238}U and ^{40}K increases with the time up to 2 h then decreases gradually to reach the minimum values at 8 h. The removal efficiency of total rare earth elements ($\sum$REE) also increases with 2 h then slightly increases up to time of 4 h and then decreases at 8 h. At the agitation for 2 h the E% for ^{226}Ra, ^{210}Pb, ^{238}U, ^{40}K and $\sum$REE equals 59.8, 53.1, 44.8, 57.7 and 50.3% respectively. For leaching of radionuclides from PG using TBP–TOPO in kerosene, the agitation time for 2 h was considered as a sufficient contact time to reach the maximum values of the removal efficiency [7]. The main reason for this phenomena that the extracted solid matter must be prepared in the way that the extracted substance can be solved (by the solvent) in short time; this was achieved by grinding the PG to a fine particle size. After grinding, the capillary ways in PG become short so that only a short distance has to be overcome by diffusion and a direct contact of solvent and extracted substance becomes possible in an appreciable time [8,9]. In this investigation the agitation time for 2 h was considered as a sufficient contact time to reach the maximum values of the removal efficiency. Whereas after 2 h the efficiency % of leaching decreases gradually to reach the minimum values at 8 h. This is attributed to available solvent in the mixture is low which leads to the efficiency % of leaching is drastically decrease. Whereas after sufficient contact time for leaching of PG, the particles of PG were saturated with solvent and exceed to the fine size.

3.1.2. Effect of TBP–TOPO concentration

Different concentrations of TBP–TOPO in kerosene ranged from 0.05 M to 1 M were used. At room temperature the samples were agitated for 2 h by the addition of equal ratio of solvent to PG. The relation between the E% and the different concentrations of solvents was shown in Fig. 4.

The results from leaching of radionuclides and $\sum$REE from PG using different solutions of TBP–TOPO in kerosene indicate that,
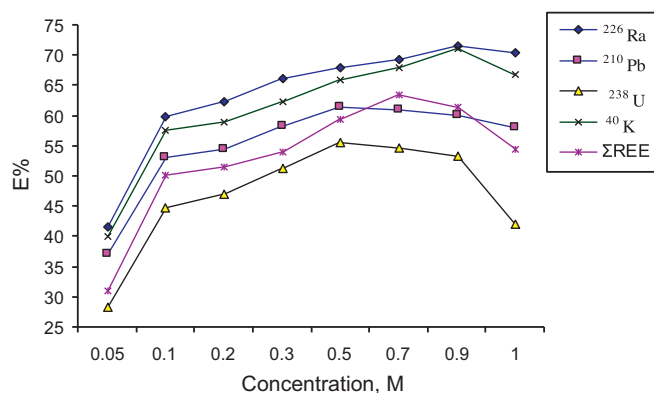
Fig. 4. Effect of concentration of TBP–TOPO in kerosene on leaching of PG.

the leachability percent increases with concentration from 0.5 M up to 0.9 M then, the removal efficiency keeps constant. For the $E\%$ of ^{226}Ra and ^{40}K the maximum values occur at concentration 0.9 M which equal 71.1 and 71.1%, while the maximum leachability of ^{210}Pb and ^{238}U reaches 61.5 and 55.6% at 0.5 M respectively. The $E\%$ of ΣREE increases slowly using dilute solutions of TBP–TOPO till 0.3 M followed by a rapid increase with concentration to reach the highest value at 0.7 M which removes about 63.5% of ΣREE in the PG.

Based on the above data, the best removal efficiency concentrates between 0.5 M and 0.9 M of TBP–TOPO in kerosene result in difference in the values of leachability for radionuclides and ΣREE. To choose the optimum concentration for sufficient leaching of these species, the effect of TBP to TOPO mole ratio was investigated.

3.1.3. Effect of mole ratio TBP–TOPO

The effect of mole ratio of TBP–TOPO in kerosene for leaching of PG samples was studied. A series of experiments was performed at room temperature for 2 h to leach 100 g of PG samples with 100 ml of TBP–TOPO in kerosene. The concentrations of 0.5 M up to 0.9 M for both TBP and TOPO were used in exchangeable way to determine the optimum concentration for maximum efficiency for removal of radioactive materials and ΣREE from PG. The relation between leachability percent and different molar ratios of TBP–TOPO in kerosene is diagrammatically plotted in Fig. 5.

The results indicate that, the effect of TBP–TOPO mole ratio on the $E\%$ of radionuclides and ΣREE can be divided into three parts of equal, high and low TBP–TOPO mole ratio. For equal concentration of TBP and TOPO (0.5–0.5, 0.7–0.7 and 0.9–0.9 M), the $E\%$ for
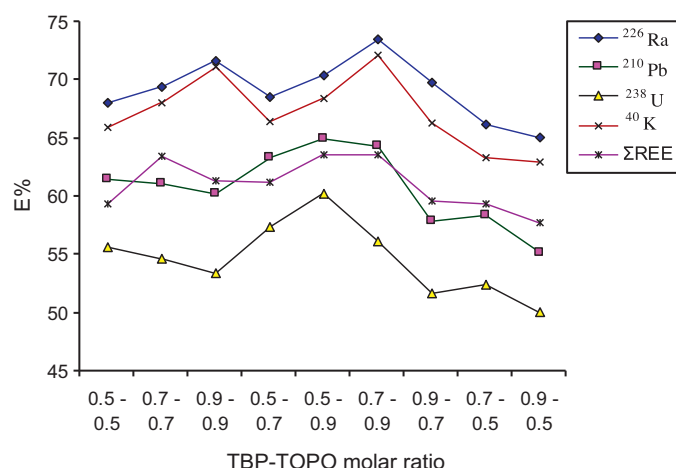

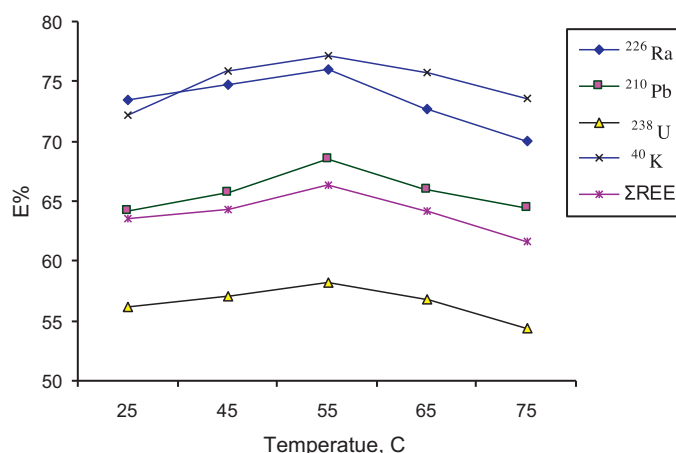Fig. 5. Effect of TBP–TOPO molar ratio in kerosene on leaching of PG.

Fig. 6. Effect of temperature on leaching of the PG by TBP–TOPO in kerosene.

^{226}Ra, ^{210}Pb, ^{238}U, ^{40}K and ΣREE increases with the concentration of both solvent and reaches the values of 71.6, 60.2, 53.4, 71.1 and 61.4% respectively. The increase in the concentration of TBP than that of TOPO (0.9–0.7, 0.7–0.5 and 0.9–0.5 M) was accompanied by decrease in the $E\%$ and reaches the minimum values at 0.9–0.5 M. On the other hand, by increasing the concentration of TOPO than that of TBP (0.5–0.7, 0.5–0.9 and 0.7–0.9 M), the $E\%$ for ^{226}Ra, ^{210}Pb, ^{238}U, ^{40}K and ΣREE reaches the maximum values of 73.5, 64.3, 56.2, 72.2 and 63.6% respectively at 0.7–0.9 M.

3.1.4. Effect of reaction temperature

The effect of reaction temperature on the leaching process was studied. About 100 g of PG (particle size <63 μm) were agitated with 100 ml of TBP–TOPO in kerosene (0.7–0.9 M) for 2 h at temperature ranged from 25 °C to 75 °C. The relation between temperature and leachability of radioactive materials and ΣREE from PG is plotted in Fig. 6.

The results indicate that a remarkable increase in the removal efficiency of radionuclides and ΣREE occurs at 55 °C. At higher temperatures, the $E\%$ decreases as the concentration and viscosity of TBP–TOPO in kerosene were increased. Thus, 55 °C is the applicable temperature required to give the maximum removal efficiency of ^{226}Ra, ^{210}Pb, ^{238}U, ^{40}K and ΣREE from PG samples which equals 76.1, 68.6, 58.3, 77.2 and 66.4% respectively. Based on the above results, the high temperature has no effect on the leachability of radionuclides and ΣREE as the solvent was concentrated [7,21–23].

3.1.5. Choice of the optimum conditions

Based on the above results, the optimum conditions required for the leaching of radioactive materials and ΣREE from homogenous PG (<63 μm), using TBP–TOPO in kerosene, were summarized as follow:

    01 – Agitation time equals 2 h.
    02 – Concentration of TBP–TOPO: 0.7–0.9 M
    03 – Liquid: solid ratio equals (1:1) (volume of solvent per weight of PG).
    04 – Reaction temperature of 55 °C.

3.2. Successive leaching processes

The leaching of radionuclides and ΣREE from the PG, of homogenous particle size (<63 μm) treated by TBP–TOPO in kerosene, was carried out under the previously optimum experimental conditions. The results are graphically represented in Fig. 7.

From the results, the removal efficiency for ^{226}Ra, ^{210}Pb, ^{238}U, ^{40}K and ΣREE increases after second step of leaching process and
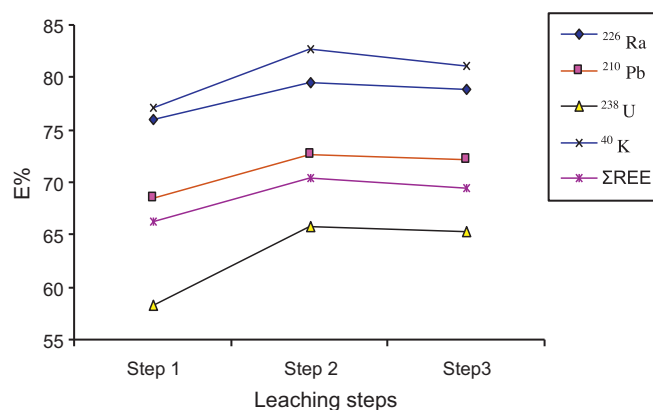
Fig. 7. Effect of successive leaching of PG by TBP–TOPO in kerosene.

becomes 79.6, 72.7, 65.9, 82.7 and 70.4% respectively. On the other hand, the third step leaching has no effect on the leachability of radionuclides and ΣREE from PG samples[7].

3.3. Sequential chemical treatment

Radium species in the phosphogypsum are in the form of insoluble $RaSO_4$, soluble salts of $RaCl_2$, $RaCO_3$ and $Ra(NO_3)_2$ in addition to some traces of radium bounded to the surface of PG. The sequential leaching of radioactive materials in PG was based on the decomposition of insoluble agents those could not be extracted by organic extractant. Phosphogypsum of homogeneous particle sizes (<63 μm) was washed with 100 ml of very hot (0.5 M) Na_2CO_3 solution for 1 h at 25 °C followed by leaching with (0.7–0.9 M) of TBP–TOPO in kerosene under optimum conditions. The results show that the removal efficiency becomes 92.1, 88.9, 83.4, 94.6, 80.1% for ^{226}Ra, ^{210}Pb, ^{238}U, ^{40}K and ΣREE in PG respectively.

3.4. Analysis of the products

After the separation of leaching products by centrifugation, the obtained decontaminated PG contains ^{226}Ra, ^{210}Pb, ^{238}U and ^{40}K of 38.1 ± 4.2, 46.4 ± 3.1, 27.2 ± 1.4 and 3.9 ± 1.1 Bq/kg with 101.7 ppm ΣREE which corresponding to remove about 92.1, 88.9, 83.4, 94.6 and 80.1% of theses materials respectively Table 2. This was indicated by analysis of the obtained organic solution which contains about 440 ± 9.7 Bq/l, 364 ± 5.2 Bq/l, 122 ± 1.7 Bq/l, 60.1 ± 3.1 Bq/l and 433.5 ppm of ^{226}Ra, ^{210}Pb, ^{238}U ^{40}K and ΣREE respectively.

The results for the removal efficiency of radioactive materials are higher than those obtained by El-Afifi et al. [24] for leaching of ^{226}Ra and ^{210}Pb from PG using (2.5 M) HNO_3 acid solution. The removal efficiency of ^{226}Ra and ^{210}Pb after two successive leaching steps was 51.3% and 45% respectively. Also these values are higher than those reported by El-Gamal [15] for the removal of ^{226}Ra from PG by leaching with ammonium carbonate. The data in this work are considered as good results in comparison with those reported by Pulhani et al. [25] for leaching of ^{226}Ra and ^{238}U from vertisol

Table 2
Radiometrical analysis of radionuclides (Bq/kg) and ΣREE (ppm) in the PG treated by TBP–TOPO in kerosene.

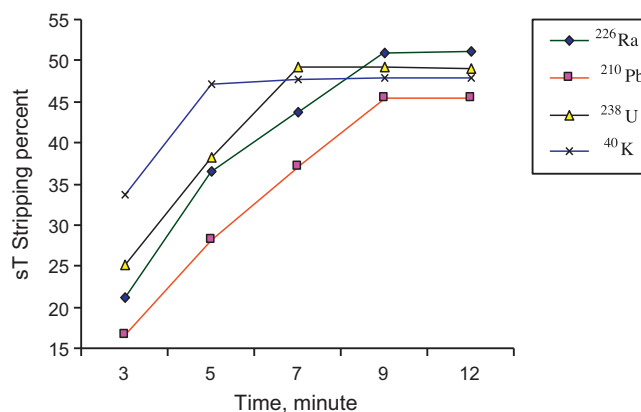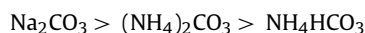| Materials	Concentration		E (%)
	Before	After	
^{226}Ra	482 ± 6.2	38.1 ± 4.2	92.1
^{210}Pb	418 ± 12.7	46.4 ± 3.1	88.9
^{238}U	164 ± 8.5	27.2 ± 1.4	83.4
^{40}K	72.3 ± 1.9	3.9 ± 1.1	94.6
ΣREE	556.1	101.7	80.1

Fig. 8. Effect of time on the stripping of radionuclides from organic extractants.

soil by ground water in which the probability of leaching was 77% and 40% for ^{226}Ra and ^{238}U respectively. In the work of Haridasan et al. [26] for leaching of ^{226}Ra from PG waste, the actual E% of ^{226}Ra through ten successive leaching steps was found to be 24 and 18% using distilled water and rainwater, respectively. Azouazi et al. [27] carried out an extensive study on the leaching of PG with different aqueous solutions. The leaching percentages were 24.5–29.1% and 23.8–26.4% for ^{226}Ra and ^{210}Pb respectively.

3.5. Stripping processes

Stripping of the extracted radioactive materials from the organic layer was performed using sodium carbonate. The stripping investigations were carried out to choose the best conditions that can successfully strip these materials from the organic extractants. The effect of shaking time and organic to aqueous phase ratio were studied. Khorfan et al. [28] studied the stripping of uranium from organic extractants in kerosene using different acids and alkalis. The results showed that stripping by alkaline solutions was always higher than any acidic solutions. Stripping by alkaline solutions decreased in the following order:

$$Na_2CO_3 > (NH_4)_2CO_3 > NH_4HCO_3$$

3.5.1. Effect of shaking time

The effect of shaking time on radioactive materials stripping from TBP–TOPO in kerosene was investigated using sodium carbonate (0.5 M) with aqueous: organic phase ratio equal 1.00 at room temperature, while the shaking time was ranged from 3 min to 12 min. The results are diagrammatically represented in Fig. 8. The results indicate that stripping efficiency slightly changes from
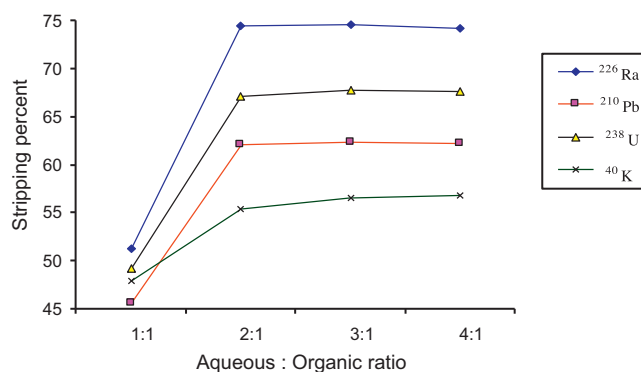

Fig. 9. Effect of aqueous: organic ratio on the stripping of radionuclides from organic extractants.

Phosphogypsum Solid Waste

PG was dried at 110°C for 2 hours, fractionated to < 63 μm then washed with Na_2CO_3 (0.5M) at 25°C for 1 h

Leaching by (0.7-0.9M) TBP-TOPO in kerosene at 25°C for 2 hours, the E% of ^{226}Ra, ^{210}Pb, ^{238}U, ^{40}K & ΣREE equals **92.1, 88.9, 83.4, 94.6, 80.1 %** and **90.7, 84.6, 80.3, 92.1, 89.8 %** from PG-Se & PG-AT respectively.

Organic solution contains ^{226}Ra, ^{210}Pb, ^{238}U and ^{40}K, stripping with Na_2CO_3 by 2:1 aq.: org. phase ratio for 9 minutes, leads to recover 74.5, 62.1, 67.2 and 55.4 % of ^{226}Ra, ^{210}Pb, ^{238}U and ^{40}K respectively.

Decontaminated product contains less concentrations of radioactive materials under the permissible limits can be safely used in many industrial applications to prepare low cost products
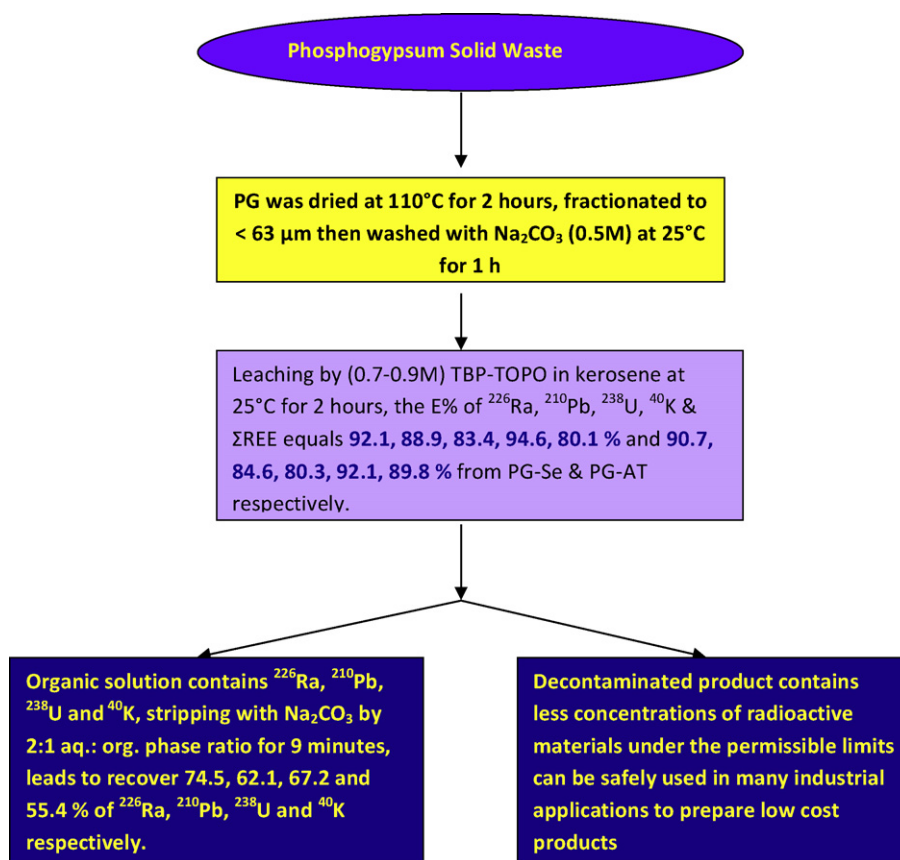
Fig. 10. Flow Sheet of PG Treatment.

3 min to 9 min and then remains more or less constant at 12 min. This indicates that the process is rapid, i.e. is not a diffusion controlled process. At 9 min the stripping percent equals 51.1, 45.6, 49.3 and 47.9% for ^{226}Ra, ^{210}Pb, ^{238}U and ^{40}K respectively.

3.5.2. Effect of aqueous/organic ratio

The effect of organic: aqueous phase ratio on radionuclides stripping from TBP–TOPO in kerosene has been studied using sodium carbonate (0.5 M) at room temperature. The shaking time was 9 min, while aqueous: organic phase ratio was varied from 1:1 to 4:1. The results are illustrated by Fig. 9.

Upon increasing aqueous: organic ratio, the radionuclides stripping efficiency increased to exhibit a maximum at a ratio equals 2:1 which equal 74.5, 62.1, 67.2 and 55.4% for ^{226}Ra, ^{210}Pb, ^{238}U and ^{40}K respectively. Further increase in aqueous: organic ratio was associated with a very slight increase of the radionuclides stripping percent. Accordingly, aqueous: organic ratio of 2:1 is recommended for stripping with Na_2CO_3 solution.

Radium was formerly used in self-luminous paints for watches, nuclear panels, aircraft switches, clocks, and instrument dials. Radium was once an additive in products like toothpaste, hair creams, and even food items due to its supposed curative powers. Radium (usually in the form of radium chloride) is used in medicine to produce radon gas which in turn is used as a cancer treatment. The isotope of radium is currently under investigation for use in medicine as cancer treatment of bone metastasis. It is well known that the average worldwide activity concentration of U, Th and ^{40}K are 50, 50 and 500 Bq/kg, respectively as established by UNSCEAR, 1993 [29]. Also, the maximum acceptable Ra-eq index in materials must be less than 370 Bq/kg as reported for safe uses in several civil purposes [30].

The flow sheet for the treatment process was illustrated in Fig. 10.

The 1 ton of PG waste requires the following chemicals to be purified:

- 53 kg of Na_2CO_3 → for pretreatment step (also for stripping process)
- 97–174L (TBP–TOPO) → for leaching process
- 1000 L kerosene → as a diluent for the used organic extractant

The total costs for the treatment of PG depending on the type and quality of the used reagents.

4. Conclusions

A successful leaching procedure of phosphogypsum, a by-product from acidulation of the Sebaiya phosphate rock by the wet process phosphoric acid, has been developed in the present work. This was possible through leaching of radionuclides by using TBP–TOPO in kerosene. The corresponding relevant factors were studied and the conclusions can be summarized as follows:

1. The best leachability percent obtained of ^{226}Ra, ^{210}Pb, ^{238}U, ^{40}K and ΣREE from PG was reached 79.6, 72.7, 65.9, 82.7, 70.4% by the synergism of (0.7–0.9 M) TBP–TOPO in kerosene through two successive steps respectively. In case of sequential chemical treatment by hot solution of Na_2CO_3 (0.5 M) followed by TBP–TOPO in kerosene (at optimum conditions), the highest removal efficiency occurs and equals 92.1, 88.9, 83.4, 94.6, 80.1% for ^{226}Ra, ^{210}Pb, ^{238}U, ^{40}K and ΣREE respectively.
2. The obtained decontaminated product contains ^{226}Ra, ^{210}Pb, ^{238}U and ^{40}K of 38.1 ± 4.2, 46.4 ± 3.1, 27.2 ± 1.4 and

3.9 ± 1.1 Bq/kg with 101.7 ppm ΣREE respectively. The decontaminated product can be safely used in many industrial applications to prepare low cost products.

3. The extracted radionuclides can be easily recovered from the solvent and introduced in many useful processes. The best conditions for the stripping of radioactive materials using 0.5 M of Na_2CO_3 were aqueous: organic phase ratio of 2:1 for 9 min which leads to recover 74.5, 62.1, 67.2 and 55.4% of ^{226}Ra, ^{210}Pb, ^{238}U and ^{40}K respectively from the extracted solution. Radium and other radionuclides in the organic phase can be: easily stripped using suitable stripper then introduced in many useful processes.

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