

Separation and Purification Residual Salt from Glycerine Pitch from Waste of Refined Glycerine Production

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Abstract. The glycerol refining process produces 5%wt/ton waste in the form of glycerine pitch (GP) and has the potential to pollute the environment if not properly handled and expensive handling costs. In this study, GP was characterized by its chemical composition and spectroscopic analysis using FTIR and UV-Vis. The sodium chloride content of 15-30% contained in GP was separated and purified by solid-liquid extraction. Solvent selection (methanol, ethanol and acetone), solvent ratio (1:3, 1:5 and 1:10) and extraction time (10, 15 and 30 min) were evaluated using one factor at the time (OFAT) method. The methanol was found to be the optimum solvent and the best ratio at 1:5 produced sodium chloride purity around 81%. However, the effect of extraction time was declared not significant with a p-value above 0.05. The TOC result of residual salt was 44 ppm and residual methanol content was not detected after heating. The integrated process of separation and purification of residual salt from GP is easy to apply and zerowaste potential in organic waste after extraction can be achieve by combustion in boiler with a calorific value obtained of 3000-3200 cal/g.

Key-words : Glycerine pitch, OFAT, Residual salt, Solid-liquid extraction.

1 Introduction

The increased consumption of biodiesel based on palm oil was predicted since the implementation of B35 policy established in February 2023 [1]. Biodiesel is produced from Refined Bleached Deodorized Palm Oil/Palm Stearin (RBDPO/RBDPS) through a transesterification process with methanol solvent and sodium methylate catalyst. A by-product of the biodiesel production process produces crude glycerol with a composition of 10 %wt biodiesel and contains 20 % impurities inside [2]. By using the Distillation method, raw glycerin can be refined into pure glycerin (Refined Glycerine-RG) with a purity of 99.5-99.7% (pharmaceutical grade) hence increasing the economic value for the industry. The glycerin refining process produces waste called glycerine pitch (GP) which is produced from the bottom of the distillation column [3]. Based on Indonesia's glycerol

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production of 883 thousand tons in 2019, the RG production process contributes 5 %wt GP of approximately 44 thousand tons per year [4-5].

Glycerine Pitch (GP) is a waste derived from the oleochemical industry, such as fatty acid and biodiesel production. Its composition includes a mixture of impurities such as glycerol, fatty acids, inorganic salts and material organic non glycerol (MONG), therefore it limited commercial value. GP is alkaline ($\text{pH} > 10$) with a physical form of dark brown gel with high viscosity at room temperature [6]. GP is categorized as hazardous and toxic material (B3) which requires handling before disposal. The industry normally chooses to pay commercial contractors to process GP, resulting in a cost of US\$ 400/ton starting from processing and transportation. However, if manufacturers can maximize their processing and utilization, GP can be a useful by-product in addition to minimizing production costs for waste handling [7].

The study of the potential utilization of GP is currently a popular topic among glycerine processing companies. Such as research conducted by utilizing GP as a mixture for making roofing materials and utilizing the salt potential of GP as mineral salt and others. GP with glycerol content $\leq 30\%$ has a salt content of 15-30% and the rest is MONG. Utilization of salt for the food and fertilizer industry from GP as mineral salt requires a purification process. From previous research, the solid-liquid extraction process with polar solvents was selected with consideration of high affinity and economic value [8]. The designed process must be also integrated well to make the GP, that initially is a waste, can be minimized or completely eliminated.

In this study, the separation and purification of residual salt from GP waste by-products of glycerol refining production will be discussed. In addition to create a new innovation in the utilization of glycerol refining waste, it also supports government programs to implement the principle of zero waste in every industry.

2 Materials and methods

2.1 Materials and tools

The GP was collected from Kutai Refinery Nusantara Co., Ltd. East Kalimantan, Indonesia. All chemical, i.e., methanol, ethanol and acetone were purchased from Merck with analytical grade. The tools used in this research are simple distillation set, Erlenmeyer, beaker glass, measuring flask, magnetic stirrer, thermometer, oven, desiccator, Whatman 1 filter paper, Moisture Analyser AND-MIX 50, genesis 150 spectrophotometer, Gas Chromatography Headspace Thermo Scientific Trace 1610, Perkin-Elmer spectrum two with universal ATR and hot plate.

2.2 Determination of chemical composition

Determination of pH, GP (4.00 ± 0.1 g) was diluted in 40 mL of neutral distilled water. The pH of the solution was measured with a digital pH meter (Eutech pH 700) at room temperature. To determine the moisture content of the sample, a Moisture Analyser (MA) AND MX-50 was used. The glycerol determination procedure was carried out by accurately weighing 0.075 ± 0.005 g GP into a 250 ml Erlenmeyer. Next add 45 ml of

distilled water to it. Prepare a blank by adding 45 ml of distilled water. Then add 25 ml of sodium metaperiodate solution to the sample and blank, allow to stand for 15 minutes in a place out of light. Add 5.0 ml of 50% w/v ethylene glycol solution and leave again for 20 minutes in a dark area. Then titrate the sample with 0.1 N sodium hydroxide (NaOH) standard solution with 2-3 drops of PP indicator. Then record the volume of NaOH. The glycerol content was calculated using Eq (1) [8]:

$$(\%) \text{ Glycerol} = \frac{(V_s - V_b) \times N \times 9.209}{W_s} \quad (1)$$

Where V_s = volume (mL) of sample titration, V_b = volume (mL) of blank titration, M = NaOH concentration, W_s = sample weight (g) and 9,209 milli-equivalent glycerol x 100 adjusted in percent.

Ash content was determined by weighing 5 grams of the sample into a porcelain cup and calcining it in a furnace for 7 hours at 600°C. After that, the cup was placed in a desiccator and weighed. The ash content was calculated using Eq (2):

$$(\%) \text{ Ash} = \frac{(M1 - M0) \times 100}{W_s} \quad (2)$$

Where $M1$ = mass of porcelain cup after calcination, $M2$ = mass of empty porcelain cup and W_s = weight of sample (g).

Salt content analysis was carried out by weighing 0.1 gram of glycerine pitch that had been homogenized with an analytical balance into a 250 ml Erlenmeyer, then diluted with 30 ml of distilled water. Next add 5 drops of 5% potassium chromate indicator. The solution is titrated with 0.01 M silver nitrate standard solution until the yellow colour turns brick red. The salt content was calculated using Eq (3):

$$(\text{g}) \text{ NaCl } (\%) = \frac{(V_s - V_b) \times 5.85 \times M}{W_s} \quad (3)$$

Where V_s = volume (mL) of sample titration, V_b = volume (mL) of blank titration, M = concentration of AgNO_3 (silver nitrate) and W_s = sample weight (g).

MONG was measured by subtracting the sum of glycerol, ash, and water content based on a standard method (ISO 2464-1973) [9].

2.3 Isolation of residual salt from GP

Residual salt was isolated from GP by solid-liquid extraction. The extraction was carried out by dissolving 10 grams of glycerine pitch into 50 ml of solvent (methanol, ethanol and acetone). Then stirring was carried out using a magnetic stirrer at 300 rpm with a stirring time of 15 minutes. After the mixture was separated into two phases, the organic and inorganic salt phases were separated using Whatman 1 filter paper with 90 mm diameter and 11 micron pore size using a vacuum pump. Subsequently, physical analysis was carried out on the liquid phase such as colour (indicating the solubility of organic components) with a Genesys 150 thermo scientific spectrophotometer at a wavelength of

400-500 nm [8]. Analysis was carried out on the solid phase in the form of physical colour of salt, recovery and purity.

2.4 Screening using OFAT method

The effects of solvent selection (methanol, ethanol and acetone), GP: solvent ratio (1:3, 1:5 and 1:10) and extraction time (10, 15 and 30 min) on the extraction process of residual salts from GP were investigated using the one factor at a time (OFAT) method. Table 1 shows the experimental design used in this study.

Table 1. Design of experiment using OFAT method

Variation	Solvents	Sample and solvent ratio (g : mL)	Extraction time (min)
Solvent type	Methanol Ethanol Acetone	1:5	15
Ratio of sample and solvent	Optimum solvent	1:3, 1:5, 1:10	15
Extraction time	Optimum solvent	Optimum solvent ratio	10, 15, 30

2.5 Spectroscopic analysis

The FTIR analysis of GP samples was performed at wavelengths of 4000 - 500 cm⁻¹ to confirm the composition of GP and residual salts. FTIR is based on peak absorption which indicates the characteristics and functional groups of a sample. FTIR analysis was performed using a Spectrum Two FTIR Spectrometer (Perkin Elmer, USA).

2.6 Thermal analysis

Thermogravimetric analysis (TGA) was performed with a Mettler Toledo TG thermal analyser, under nitrogen flow at a heating rate of 10°C/min from 25-600°C. The calorific values of glycerol samples were determined using a bomb calorimeter, Parr 6200 Calorimeter (Illinois, USA) according to ASTM D5868–07. The analysis of the measurement was performed using OriginLab®Origin 8.5.1 software.

3 Result and discussion

3.1 Physicochemical and composition of GP

Physicochemical analysis of GP was conducted to perform initial identification of the sample. In Fig. 1, GP is blackish brown in colour and paste-shaped, which makes density and viscosity analysis on GP impossible. The pH value of GP is obtained as 11.72, this value is in accordance with research conducted by Hazimah et al [6], pH value > 10 indicate high alkaline.



Fig. 1. Sample of glycerine pitch.

Table 2. Chemical composition of GP

Parameter analysis	Glycerine pitch (%)	References [5] (%)
Salt content	21.64 ± 0.07	Monitoring
Glycerol content	18.76 ± 0.08	0-30
Ash content	23.80 ± 0.34	20-60
Moisture content	0.19 ± 0.03	0-2
MONG	57.52 ± 0.11	40-60

The results of GP characterization analysis can be seen in table 2. The GP composition value obtained is in accordance with the specifications issued by the majority of the Oleo-chemical Industry in Indonesia (APOLIN). Some industries only focus on the spec of glycerol content contained in GP which is below 30%. Glycerol content greater than 30% is considered as a loss in product yield and minimizing it makes the cost of steam for evaporation in the distillation process and the capacity of the machine is impacted.

3.2 Optimum solvent, ratio and time selection with OFAT

3.2.1 Selection of optimum solvent

To determine the optimum conditions of the variables solvent type, ratio and extraction time, the OFAT method was used. The OFAT method involves testing one factor at a time instead of several factors simultaneously [10]. This study applied the OFAT method to determine the optimum solvent between methanol, ethanol and acetone. GP and solvent were mixed into a 100 ml beaker with operating conditions at 80°C and 300 rpm of stirring. Subsequently, it was allowed to separate into 2 layers, the organic liquid layer and the solid layer of residual salts. It was separated by filtration method and heated in an oven at 120 °C for 15 minutes. The residual salt was analysed for purity as NaCl and salt recovery. In this study, the response of residual salt purity was used as the primary factor.

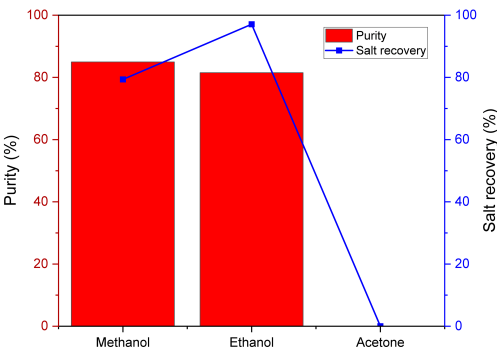


Fig. 2. Solvent comparison vs residual salt purity and recovery.

Fig. 2 shows the comparison of methanol, ethanol and acetone solvents towards the response of residual salt purity. It was obtained that extraction using methanol solvent produced the highest purity of 84.97%, ethanol solvent of 81.52% and acetone solvent could not dissolve GP. Methanol and ethanol solvents with polar characteristics have high affinity and solubility to organic components in GP. While acetone solvent showed no extractive strength. Acetone with a log P value of -0.24 is hydrophilic, remaining soluble in hydrophobic substances such as oil and hydrophilic substances such as glycerol. However, the solubility of glycerol in acetone is limited and formed two layers. The solubility of glycerol to acetone was 5% w/w [11].

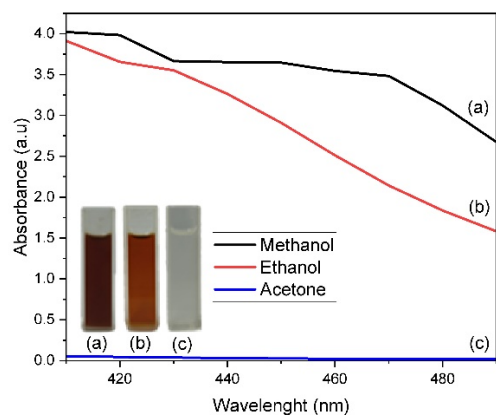


Fig. 3. The results of UV-VIS Spectra on each solvent (a) methanol, (b) ethanol and (c) acetone.

Fig. 3 show the results of UV-VIS absorbance test of the organic liquid phase where extraction using methanol solvent produces a slightly dark colour with an average absorbance of 3.53, ethanol absorbance of 2.82 and acetone 0.03 measured at a wavelength of 400 - 490 nm. Due to the salt being transparent when in solution, the colour present in the liquid phase was tied to the presence of organic matter (impurities) that were extracted from the residual salt. Hence, the higher the absorbance, the better extraction process. Methanol solution performed better than ethanol solvent. This was influenced by the higher polar index of methanol compared with ethanol. Hence, methanol was selected as the solvent in this study.

3.2.2 Selection of optimum solvent

The effect of GP: solvent ratio on extraction with methanol solvent 1:3, 1:5 and 1:10 was evaluated. Table 3 is the result of the purity of the residual salt and the salt recovery as an independent response.

Table 3. Results of comparison of glycerine pitch ratio: methanol with extraction time 15 minutes

Parameter	Ratio GP : methanol		
	1:3	1:5	1:10
Purity	76.87 ± 0.04	84.35 ± 0.29	80.59 ± 0.05
Salt recovery	93.15 ± 0.00	78.80 ± 0.15	50.69 ± 0.00

The purity of residual salt increased and was linearly related to the increase in methanol ratio. On the other hand, the salt recovery was inversely obtained. This trend is explained by two factors caused by an increase in solvent fraction, which are an increase in the extraction performance of the organic phase and an expansion in the amount of residual salt [8]. This assumption is confirmed by the visual aspect observed in the residual salt, see Fig. 4, where at a ratio of 1:5 a white residual salt is produced

compared to the 1:3 and 1:10 ratios which are creamier in colour. This is indicated by the presence of organic impurities remaining in it.

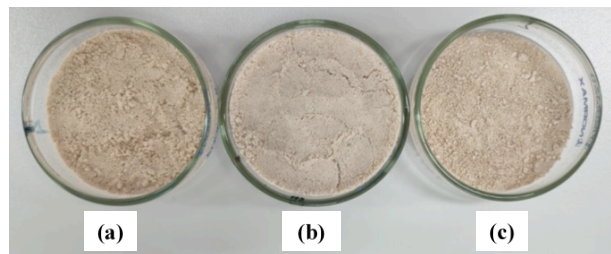


Fig. 4. Visual of residual salt after extraction with solvent ratio (a) 1:3, (b) 1:5 and (c) 1:10

The colour of the residual salt which is close to white indicates a more efficient extraction process. This is supported by the absence of glycerol content observed in the characterization of the residual salt for the 1:5 ratio, see Table 5. Based on this result, the best solvent ratio of 1:5 was selected because it produces cleaner salt and the purity obtained is also the highest compared to the ratios of 1:3 and 1:10.

3.2.3 Selection of optimum extraction time

The effect of the extraction time ratio was carried out with a methanol ratio of 1:5. The results of extraction at various times are shown in Table 4.

Table 4. Results comparison of extraction time to salt content and salt recovery with a ratio of 1:5

Extraction time (min)	Purity (%)	Salt recovery (%)
10	78.07 ± 0.08	71.92 ± 0.05
15	80.60 ± 0.01	71.10 ± 0.17
30	79.06 ± 0.08	72.07 ± 0.08

Salt content and salt recovery at 10, 15 and 30 minutes produced insignificant results. To determine the effect between variations is significant or not, it can be proven by the p-value. A p-value of less than 0.05 indicates that the relation between variables is significant [12]. The response between salt content and salt recovery at the extraction time of 10 and 15 minutes as well as 15 and 30 minutes is not significant, as evidenced by the p-value above 0.05. Hence, the extraction time variable was not effectively influencing the extraction process. The insignificant difference between the extraction times indicates the quality of the residual salt is not determined by the extraction time, but by the ratio of methanol.

3.3 Spectroscopy analysis of GP and residual salt

FTIR analysis of the GP samples was performed at wavelengths of 4000 - 500 cm⁻¹. FTIR is based on peaks that indicate the characteristics and functional groups of a sample. Figure 5 obtained peak observed as glycerol molecular bonds, at 3292 cm⁻¹ absorption of hydroxyl group -OH, 2874 cm⁻¹ symmetrical stretch CH₂ and 1411 cm⁻¹ bent stretch CH₂. The characteristic peaks between 1300 and 1000 cm⁻¹ show the presence of C-O bonds, at 1113 cm⁻¹ and 1036 cm⁻¹, respectively in the form of C-O strain of secondary alcohol and C-O of primary alcohol. The strain at 925, 853 and 650 cm⁻¹ are respectively the vibration of C-C strain, C-C-O symmetrical strain and glycerol OH aggregates [9]. Impurities in GP are shown at peaks of 1800-1500 cm⁻¹, which are at an absorption of 1586 cm⁻¹ related to the COO⁻ strain, representing soap impurities [13].

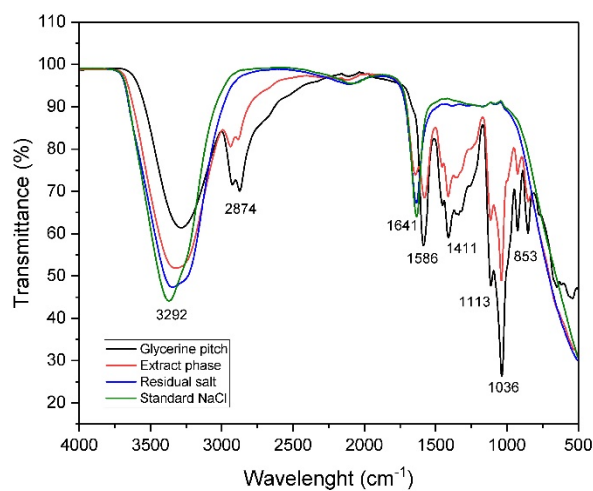


Fig. 5. Spectrum FTIR glycerine pitch, extract phase, residual salt and standard NaCl.

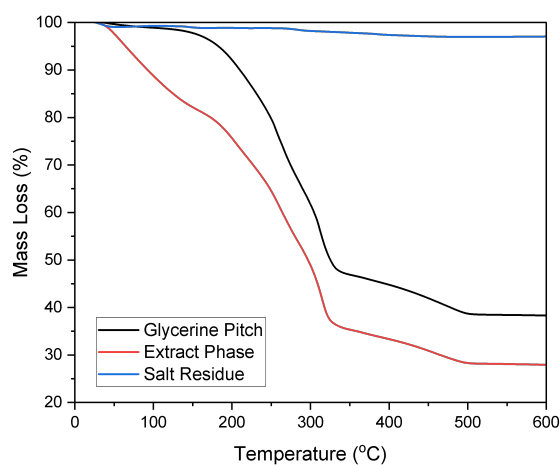


Fig. 6. TGA curve glycerine pitch, extract phase and residual salt.

3.4 Thermal analysis of GP and residual salt

According to the TGA curve, the three samples showed three phases of mass loss, for the GP sample, the mass loss at temperatures below 200 °C showed a water elimination of 12.75%, followed by 33.78% and 38.53% for the extract and residual salt phase samples, respectively. The percentage of mass loss in the extract sample is due to methanol and water content. Mass loss in the second phase was observed in the range of 200 - 360 °C with the main decomposition of glycerol [14], for GP and extract 78.38 and 59.91%, respectively. The residual salt experienced a second phase mass loss of 54.45% in the range of 200 - 420 °C. The third phase mass loss was composed of degradation of impurities in the form of soaps, residues from the initial degradation of glycerol in the form of acrolein and fatty acids and esters in the range of 420 - 600 °C. For residual salts, the observed mass loss up to 600 °C was only 7.02%, indicating the low content of these impurities. The remaining mass residues for the GP sample, extract phase and residual salt were 38.30, 27.94 and 97.05% respectively.

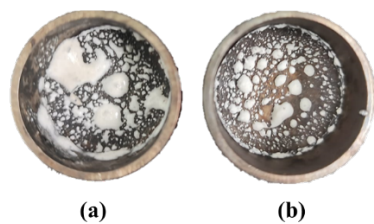


Fig. 7. Combustion ash (a) glycerine pitch, (b) extract phase.

The combustion potential of organic waste has been analysed and it was found that GP waste and organic phase waste after extraction have calorific values of 3171 and 3052 cal/g, respectively, producing white ash and a dense texture (see Fig. 7). The heat of combustion is half other fossil fuels but comparable to other types of biomass, such as wood, straw, wood fibres and sawdust.

3.5 Chemical composition of residual salt

Total organic carbon (TOC) is measured in the form of total carbon (TC) and inorganic carbon (IC) and TOC, obtained from the subtraction of TC and IC. Table 5 shows that the TOC value decreased significantly between GP and residual salt from 345.70 ppm to 44.26 ppm, respectively. It is proved that the extraction process is optimal, where methanol tends to bind organic substances such as glycerol to the liquid phase from residual salt.

Table 5. Results of chemical composition analysis of pitch glycerine and residual salt

Analysis	Glycerine pitch	Residual salt
TOC, ppm	345.70	44.26
Glycerol content, %	18.76	N.D.

Salt content, %	21.64	80.60
Moisture content, %	0.19	0.65
Ash content, %	23.80	88.72
MeOH content, %	N.D.	N.D.

The GP extraction process was able to separate the residual salt from organic impurities and increase the purity of the salt. Purity as NaCl salt increased from 21.64% to 80.60%. It also increased ash content and eliminated glycerol content. Based on the chemical composition, the residual salt from GP purification was potentially used for fertilizer mixture.

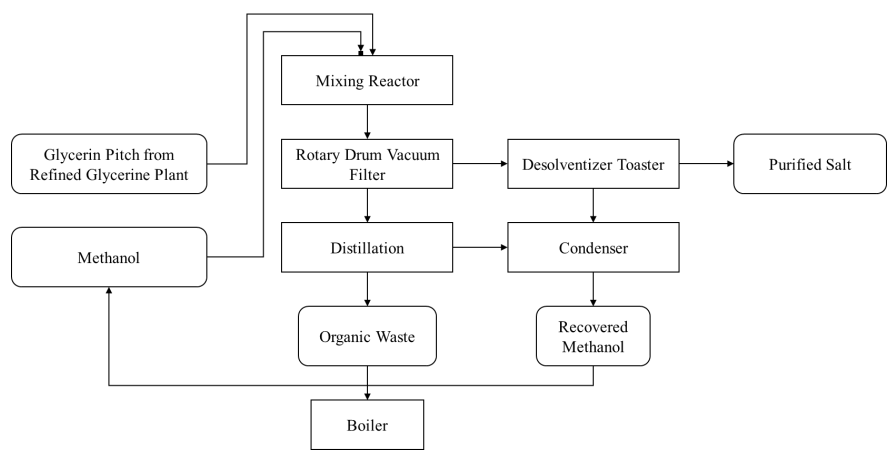


Fig. 8. Block diagram of integration process of separation and purification of residual salt from glycerine pitch.

The block diagram of the process of refining residual salt from GP has been established with the operating conditions determined after optimizing the variables of ratio and extraction time. Figure 8 shows a summary of process block diagram that has been integrated to optimize the process. Glycerine Pitch is supplied from the refined glycerine plant at a temperature of 160-165°C and enters with methanol and maintained at 60°C. The extraction process separates the residual salt with its organic phase dissolved with methanol. The next process was to separate the solid and liquid phases using a rotary drum vacuum filter (RVDF) with 10 µm filter specifications. After the residual salt was separated, it subsequently entered the evaporation process on the desolventizer toaster (DT) to evaporate the methanol content that was followed to a maximum of 0.01% and produced residual salt with high purity and white color. The organic liquid phase enters the distillation process for methanol recovery and the organic waste was burned in the boiler.

4 Conclusions

The process of separation and purification of residual salt from GP can be done by solid-liquid extraction using polar solvents. Methanol solvent was chosen as the optimum solvent with the highest average absorbance of 3.53, purity of 80.60 and visual white color of the residual salt produced. The optimization process with OFAT resulted in optimum extraction conditions at a ratio of 1:5. While the extraction time has no significant effect ($p>0.05$). The chemical composition of GP and residual salt showed a significant decrease in TOC value, high purity and low impurity content making the application of residual salt as a fertilizer mixture is feasible. The integrated process of separation and purification of residual salt was applicable, with the additional data of combustion of GP and organic phase in the boiler produced calories of 3171 and 3052 cal/g respectively as final treatment of the waste generated.

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