

Purification of Produced Water from a Sour Oilfield in South Kuwait. 1. Oil-Water Separation and Industrial Salt Production

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Abstract

Produced water from an oil extraction site in South Kuwait was sampled after primary oil – water separation had been carried out. The produced water was filtered through a mixture of activated charcoal and esterified cellulosic material gained from spent coffee grounds as a tertiary adsorption treatment. The earth-alkaline metal ions and heavy metals were separated from the de-oiled produced water by addition of either sodium or potassium hydroxide in the presence of carbon dioxide or by direct addition of solid sodium carbonate. The resulting filtrate gave salt of industrial purity upon selective crystallization on evaporation

Keywords

Produced Water, Oil and Gas, Adsorption Filtration, Crystallization

1. Introduction (Heading 1)

Oil and gas reservoirs often contain formation water. The formation water in addition to water injected into the wells comes to the surface in the extraction process as produced water (PW). In fact, PW from oil and gas extraction is known to be one of the largest waste-streams originating from human production, amounting to 250 million barrels per day in 2020 [1]. The global average PW to oil ratio is 7:1, meaning for every barrel of oil 7 barrels of PW are obtained [2]. PW has varying concentrations of salts as well as hydrocarbons [1] [3]. It is highly corrosive, and exposes pipelines and general infrastructure to significant damage [4]-[11]. Also, it is toxic to the environment when released

untreated [12] [13] [14]. On the other hand, PW can be seen as a significant resource of water, salt and lastly of the remaining hydrocarbons [15]. For many years, also seawater has been seen as a resource for drinking water and for salt, using different types of desalination methods for the first such as multi-stage flash evaporation [17] and reverse osmosis [18], and oftentimes undertaking salt collection from salt pans for the latter [19].

Usually, in oil extraction processes, produced water (PW), oil and gas first are segregated by gravity in a three phase separator [20], before further oil separation from the water is carried out by corrugated plate interceptor (cpi) [21], hydrocyclone [22], and air flotation [23]. Membrane filtration [24] [25] or filtration through a sorbent layer [26] that may include sand [27] can be added to the purification scheme, depending on the further use of the PW. As much of the PW is produced in arid regions, research has focused on utilization of treated PW for purpose such as irrigation [28] [29] [30]. Thus far, this has been met with limited success [31]. For the most part, in regions far from the coast and from water bodies in general, treated PW is either disposed of in sub-surface disposal wells [32] or re-injected into the production well [33] to help maintain the pressure of the reservoir.

Salt has been produced from sea water going back to the Phoenicians in the 9th century BC [34] [35]. In recent times, desalination to procure fresh water has been combined to obtain salt from the reject brine in evaporation ponds, too [36] [37] [38]. The average salt content in produced water from oil and gas is 3 - 4 fold of that of seawater. An example of this is the PW used in this study (**Figure 1(a)**), Looking at the individual metal cations contributing to the salinity, it can be noted that the calcium content of PW is proportionately much higher than that in seawater. In fact, the Ca/Mg ratio found in the PW under investigation was 4.43, while the Ca/Mg ratio in seawater is 0.32 (**Figure 1(a)**). Also, with the ratio Na/K of 23.4, the average contribution of potassium in the investigated PW was slightly higher than in seawater (ratio Na/K of 27.6) (**Figure 1(a)**). These ratios should be kept in mind when contemplating the use of PW as a source of salt. Industrial salt (10 pound brine) requirements stipulate that the salt should be mostly free of the earth-alkaline metals, especially of calcium and strontium as their salts lead to scaling products [1].

The focus of this study was to purify produced water (PW) from an oilfield in South Kuwait that had already undergone a primary oil-water separation process. It is a mature field with a water cut of 1:4. Production from 40 - 60 different wells is combined to supply a central processing substation. The total field is comprised of over 1000 wells [4]. It must be noted that the composition of PW from an oil field can vary, even over short periods of time [39]. Average compositions of the two PW samples used in this study can be found in **Table 1** and **Table 2**. Graphically, the composition of PW-1 is also shown in **Figure 1(b)**. This communication can be seen as the first part of two and deals with the filtration of PW on cellulose esters gained from spent coffee grounds as the final step

of the oil-water separation step and with the production of industrial salt (10 pound brine) from the de-oiled PW after a de-calcification step.

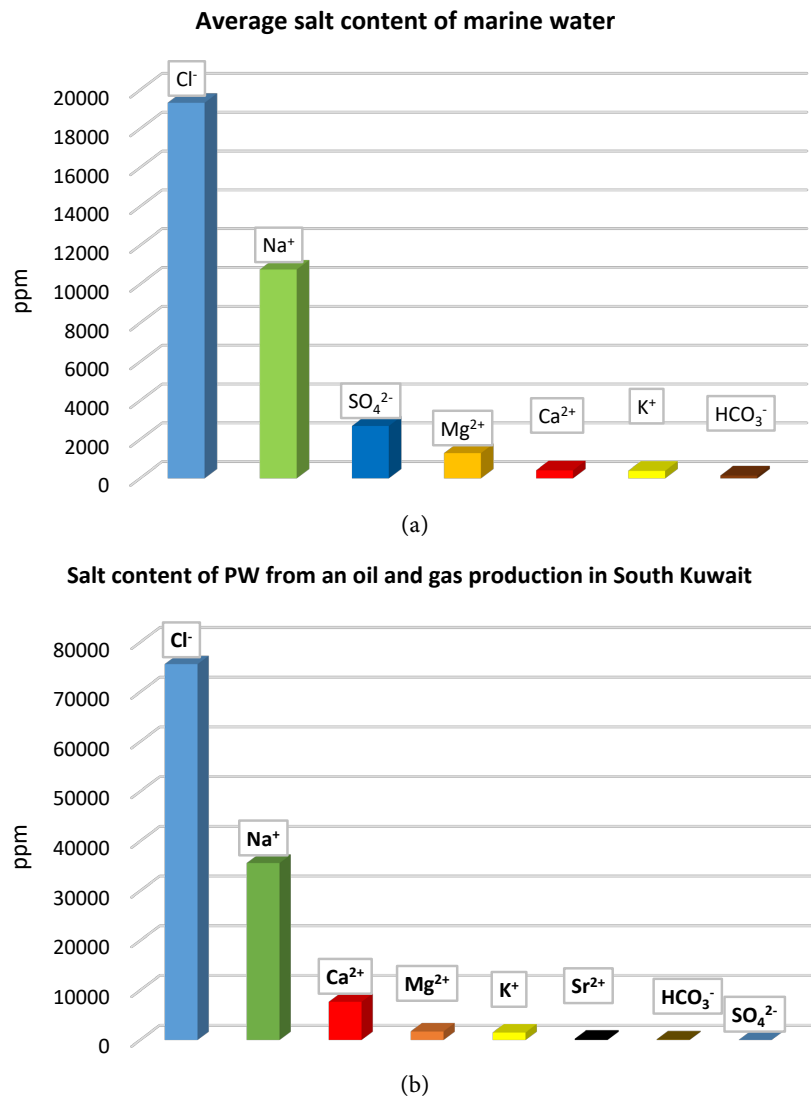


Figure 1. (a) Major ion content in seawater. Data taken from [16]; (b) Salt content with major ions in PW from an oil and gas in South Kuwait.

Table 1. Properties and ion content of PW-1, sourced from an oil production in South Kuwait—this PW was treated with SDG-octanoate (see below).

Total dissolved solids	132,780 ppm	Chloride (Cl ⁻)	75,660 pm
Sodium (Na ⁺)	35,600 ppm	Sulfate (SO ₄ ²⁻)	18 pm
Potassium (K ⁺)	1520 ppm	Bicarbonate (HCO ₃ ⁻)	140 pm
Calcium (Ca ²⁺)	7670 ppm	Silicon (Si)	12.3 ppm
Magnesium (Mg ²⁺)	1730 ppm	Total Iron (Fe)	1.36 ppm
Barium (Ba ²⁺)	2.3 ppm	Dissolved oxygen	3 ppm
Strontium (Sr ²⁺)	255 ppm	pH at 25°C	6.88

Table 2. Properties and ion content of PW-2, sourced from the same oil production site in South Kuwait 6 months after PW-1—this PW was treated either with SDG-palmitate or with SDG-acetate (see below).

Total dissolved solids	193,350 ppm	Chloride (Cl^-)	110,090 pm
Sodium (Na^+)	51,500 ppm	Sulfate (SO_4^{2-})	355 pm
Potassium (K^+)	1800 ppm	Bicarbonate (HCO_3^-)	300 pm
Calcium (Ca^{2+})	11,200 ppm	Silicon (Si)	ND
Magnesium (Mg^{2+})	3050 ppm	Total Iron (Fe)	ND
Barium (Ba^{2+})	2.4 ppm	Dissolved oxygen	ND
Strontium (Sr^{2+})	460 ppm	pH at 25 °C	6.02

2. Materials and Methods

2.1. General

42 L of produced water (PW) samples, 16L of PW-1 and 26L of PW-2, were obtained from an oil extraction operation in South Kuwait. The PW had been submitted to a three-way separator and corrugated plate interceptors. Nevertheless, it still carried appreciable amounts of hydrocarbons. Spent coffee grounds (SCGs) were obtained from a selection of commercially available coffee brands. Pyridine (BDH) was dried over solid KOH and *N,N*-dimethylacetamide (Sigma Aldrich) was dried over MgSO_4 . Octanoyl chloride (Sigma Aldrich), acetyl chloride (Sigma Aldrich), and palmitoyl chloride (Sigma Aldrich) were used without further purification. Potassium hydroxide (KOH pellets, Sigma Aldrich), sodium hydroxide (NaOH pellets, BDH Analr), anhydrous sodium carbonate (soda, eurlab), activated charcoal (Sigma Aldrich, acid-washed with hydrochloric acid), hexane (Panreac) and dichloromethane (CH_2Cl_2 , Sigma Aldrich) were used as is.

Torrefaction of SCGs was carried out in a Carbolite oven. Post-reaction, samples were dried in an MMM Ecocell drying cabinet. Reaction mixtures were stirred on WiseStir magnetic stirrers. The ash contents of SCGs, the hydroxide extracted SCGs as well as the SCG-esters were determined by heating respective samples in crucibles (79C-00, Waldenwanger, Berlin) in a Carbolite oven at 600 °C for 3 h, where the mass of the resulting ash is expressed as weight % of the originally weighed-in sample. The initial produced water analysis was carried out at the CORE labs, Abu Dhabi, UAE. The ICP-OES (Inductively Coupled Plasma - Optical Emission spectroscopy) analyses of the salt crystals were carried out by CCIC Middle East FZE – Fujairah Branch. Both laboratories are accredited. For the ICP-OES measurements, an Agilent ICP-OES Model-5110 was used after digestion of the samples with HNO_3 in a microwave digester. Infrared spectra of the SCG materials, the derived esterified cellulosic materials as well as of the crystallized calcium salts were carried out as KBr pellets with a Perkin Elmer Spectrum 2 FT-IR spectrometer. TOC measurements were performed with a Shimadzu TOC-4200. For the brine surface temperature readings, a Trister® infrared thermometer TS-1/T1 was used with an initial calibration utilizing a

normal immersion glass thermometer

2.2. Preparation of Cellulosic Sorbent Material from Spent Coffee Grounds

2.2.1. Pre-Treatment of the Spent Coffee Grounds (CGS)—Obtaining Cellulosic Material from CGS

For this study, spent coffee grounds were dried by heating them overnight in a Carbolite oven at 100 °C. Thereafter, the SCG were sieved and then heated at 200 °C for 4 h to break bonds within the material and open up the structure of SCG. Thereafter, much of the lignin present in CGS was extracted with an aq. NaOH solution (3 w%, 66 °C, 3 h). For 4 g dried CGS, 3.6 g NaOH were dissolved in 116.4 g water for a 120 g aq. NaOH solution. The extracted CGS material was filtered in vacuo through a sintered glass filter and dried. Most of the extracted material is cellulosic matter. After drying, it was subjected to torrefaction at 200 °C for 2 h. Thereafter, the material was extracted with hot water (60 °C, 2h), filtered and dried once again (200 °C, 2 h). **Figure 2** shows the complete process.

2.2.2. Esterification of the CGS-Derived Cellulose

For palmitate esterification, coffee grounds (extracted with NaOH, non-sieved, 2.0 g, 12.34 mmol, one cellulose units [calcd.]) were added to a 250 mL round bottom flask, and *N,N*-dimethylacetamide (100 mL) was added. Thereafter, pyridine

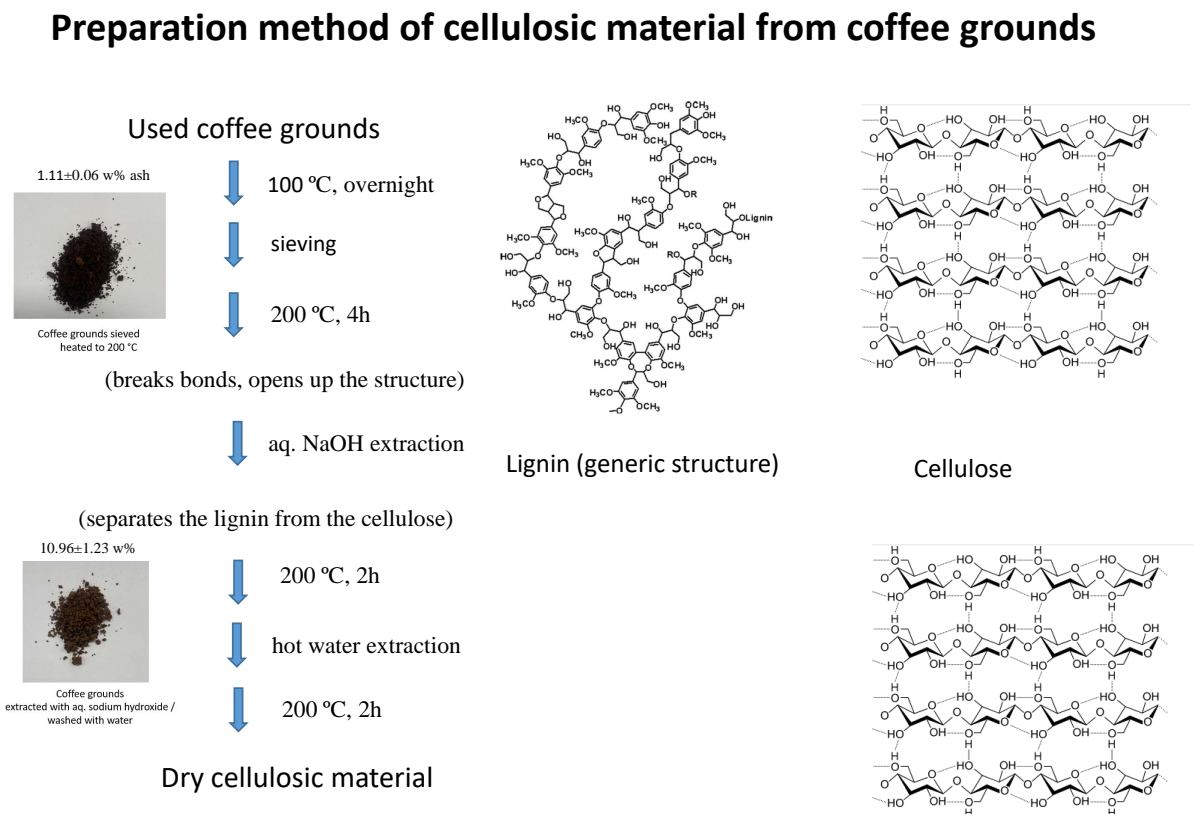


Figure 2. Sequence used to obtain cellulosic material from SCG, adopted from ref. [56] [57].

(5.14 g, 65.0 mmol) and palmitoyl chloride (15.0 g, 55.6 mmol) were added dropwise, and the resulting mixture was kept at 66°C for 4 days. Then, the mixture was cooled to 0°C, and 300 ml of cold water was added slowly to the solution (to avoid hydrolysis of the formed esters). The ensuing mixture was separated by vacuum filtration through a sintered glass funnel, then washed with dichloromethane (50 mL) and hexane (50 mL), and thereafter dried in the oven for 1 day at 37°C. (Yield = 1.70 g)

For octanoate esterification, spent coffee grounds (extracted with NaOH non-sieved, 2 g, 12.3 mmol, cellulose unit [calcd.]) were added to a 250 mL round bottom flask, and *N,N*-dimethylacetamide (100 mL) was added. Thereafter, pyridine (dried over KOH, 4.18 g, 52.84 mmol) and octanoyl chloride (7.81 g, 48.01 mmol) were added dropwise, and the resulting mixture was kept at 66°C for 4 days. Then, the mixture was cooled to 0°C, and 300 ml of cold water was added slowly to the solution (to avoid hydrolysis of the esters). The ensuing mixture was separated by vacuum filtration through a sintered glass funnel, then washed with dichloromethane (50 mL) and hexane (50 mL), and thereafter dried in the oven for 1 day at 37°C. (Yield = 2.08 g)

For acetate esterification, coffee grounds (extracted with NaOH non-sieved, 2.0 g, 12.3 mmol, one cellulose unit) were added to a 250 mL round bottom flask, and dimethylacetamide (70 mL) was added. Thereafter, pyridine (5.14 g, 65.0 mmol) and acetyl chloride (3.93 g, 50.0 mmol) were added dropwise, and the resulting mixture was kept at 66°C for 4 days. Then, the mixture was cooled to 0°C, and 300 ml of cold water was added slowly to the solution (to avoid hydrolysis of the esters). The ensuing mixture was separated through a sintered glass funnel by vacuum filtration. The filter cake was then washed with dichloromethane (50 mL) and hexane (50 mL), and thereafter dried in the oven for 1 day at 37°C. (Yield = 3.68 g).

2.3. Oil-Water Separation by Adsorptive Filtration on CGS-Esters

For the adsorptive filtration of PW, two glass columns, A (length, 35 cm, inner diameter 2.25 cm) and B (length 35 cm, inner diameter 1.70 cm) were used. Both columns have an outflow that is controlled with a Teflon[®] stop-cock. In experiment A, column A was filled with a well-mixed sorbent mixture of cellulose octanoate (2.40 g) and activated carbon (7.20 g, 1:3 w/w). In experiment B, column A was filled with a well-mixed sorbent mixture of cellulose acetate (2.40 g) and activated carbon (7.20 g, 1:3 w/w). In experiment C, column B was filled with a well-mixed sorbent mixture of cellulose palmitate (1.20 g) and activated carbon (3.60 g, 1:3 w/w). In all the experiments, sand (30 g) was added as a protective layer on top of the sorptive material. The columns were run with 1 atm pressure, initially at 1L per day (column A) and 500 mL per day (column B), respectively. The de-oiled water was collected in plastic jerry-cans, which thereafter were closed.

2.4. Salt Crystallization from De-Oiled PW

To the de-oiled PW, solid anhydrous sodium carbonate (Na_2CO_3 , 7.0 g per 200 mL de-oiled PW) was added slowly, and the resulting mixture was allowed to stir for 10 min. at rt. The precipitate was filtered off, utilizing a sintered glass filter. The filtrate was evaporated in a two stage process, one outdoors and one indoors. This option was decided upon due to the simplicity of the experimental set-up, where soil temperature as well as solar irradiation contributed to the evaporation of the majority of the water. The last part of the evaporation was carried out under controlled conditions in a drying oven at 37°C. PW was placed in open plastic containers and set outside. While experiments were performed from July to December 2023, with different temperatures in summer/autumn/winter leading to different evaporation rates, this paper focuses on work carried out in October and November 2023. Daytime temperatures in October ranged from 20°C to 34.4°C, in November from 19.4°C to 30.2°C, and in December from 18.7°C to 28.9°C (Figure 3). Typically, experiments were carried out with 500 mL of de-oiled PW. Crystals were collected directly from the evaporation pond and analyzed by ICP-OES (Agilent ICP-OES Model-5110). Alternatively, the crystals were collected by vacuum filtration using a sintered glass funnel, dissolved in a minimal amount of water, and then set for evaporation in a MMM Ecocell drying cabinet at 37°C. Crystals were collected using a sintered glass funnel. Filtrates obtained from the respective operations were re-added to the evaporation ponds.

3. Results and Discussion

3.1. Oil-Water Separation by Adsorptive Filtration on CGS-Esters

Adsorption filtration as a tertiary treatment for PW has been reviewed extensively [40] [41] [42] [43]. Biomass waste has been recognized as adequate sorption material [26] [44] [45] that is often cheaply sourced, if not always easy to be disposed of. Biomass waste can be transformed into activated carbon [46] [47], but can also be used largely unprocessed or as a scaffold for chemical transformations leading to materials with a tailored surface. Ground nut-shells, specifically walnut shells and pecan nut shells [48] [49] [50] are standardly used as sorption material in the treatment of PW, also from oil and gas. Other biomass waste materials that have been investigated include corn cobs [51], kapok (*Ceiba pentandra*) [52], sago fronds (*Cycas circinalis*) [53], biomass from the giant false agave (*Agave gigantea*) [54], and empty fruit bunches of the oil palm (*Elaeis oleifera*) [55]. In all of these cases, the biomass was processed to obtain the cellulose content. In recent years, the possibility of using spent coffee grounds (SCGs) as biowaste derived sorption material for treating oily water was communicated [56] [57] [58]. This approach separates the cellulose from the lignin by aq. hydroxide extraction, and then optionally derivatises the so-obtained cellulose by either esterification or silylation. As SCGs are a major accumulating biowaste that is readily available, with globally 6 million tons produced annually

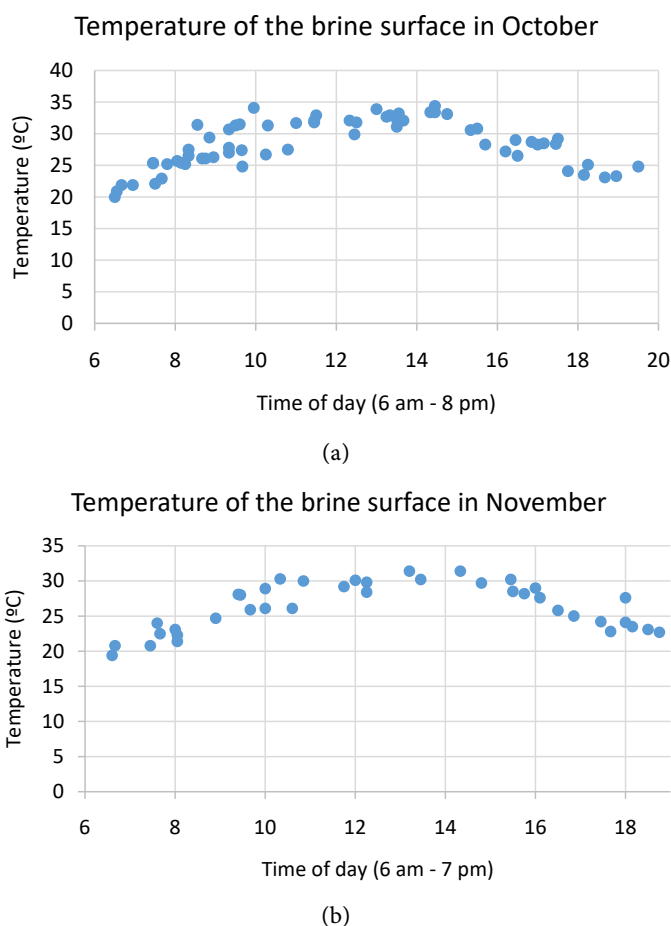


Figure 3. Surface temperatures of the brine in the evaporation ponds in October and November.

[59], we opted to adapt the protocol described in ref. 56 and 57. An additional advantage of SCGs is that it is already in powdered form. After drying at 100 °C, CGS was subjected to extraction with 3w% aq. NaOH solution. It is here that much of the lignin which contains phenolic groups is separated from the remaining material, which is mostly cellulosic, by entering the aqueous phase as lignin salt. In this step, hemicellulose is partially also extracted as hemicellulose can be hydrolyzed by aqueous base more easily than cellulose. The cellulosic material was filtered off and dried. During the extraction process, 37.3% - 44.7% of the mass of the material was lost. The water used in the extraction process can be recycled by distillation. We obviated a bleaching process of the material with sodium hypochlorite (NaOCl).

Analysis of the infrared spectra of the original, dried SCGs and the extracted, dried SCGs reveal a number of differences, one of the main being the disappearance of the IR band at 1744 cm^{-1} , which is attributed to ester functions present in the lignin and potentially to polysaccharide pectins, the latter of which are less likely to be present in spent coffee grounds (Figure 4). The absorption of the ester carboxyl group has been studied both in lignin isolated from natural sources [60], in synthetically modified, esterified lignins [61] as

well as in esterified lignin components [62] and the absorption ranges between 1717 cm^{-1} and 1760 cm^{-1} , with 1744 cm^{-1} signaling an aliphatic ester function. The infrared spectrum shown in **Figure 4(b)** matches infrared spectra of cellulose from the literature [63]. Next, the cellulosic material was subjected to esterification reactions to produce a hydrophobic surface of an appreciable thickness. A larger number of procedures are known for the preparation of cellulosic esters [64], some of which use *N,N*-dimethylacetamide (DMAc) as solvent. The authors opted to use acyl chlorides as reagents in DMAc as solvent and pyridine as catalyst and HCl scavenger (**Figure 5**), obviating the use of the known DMAc-LiCl system [65]. The resulting cellulosic esters were filtered, washed with CH_2Cl_2 - hexane and dried. IR spectra of the esters (**Figure 5**) showed the characteristic ester carboxyl band at 1748 cm^{-1} . A comparison of the IR spectrum of the cellulose acetate (**Figure 6(a)**) obtained showed that it exactly matches the IR spectrum of commercially available cellulose acetate [66]. The ash (mostly inorganic) content of the sieved and dried SCGs was found to be

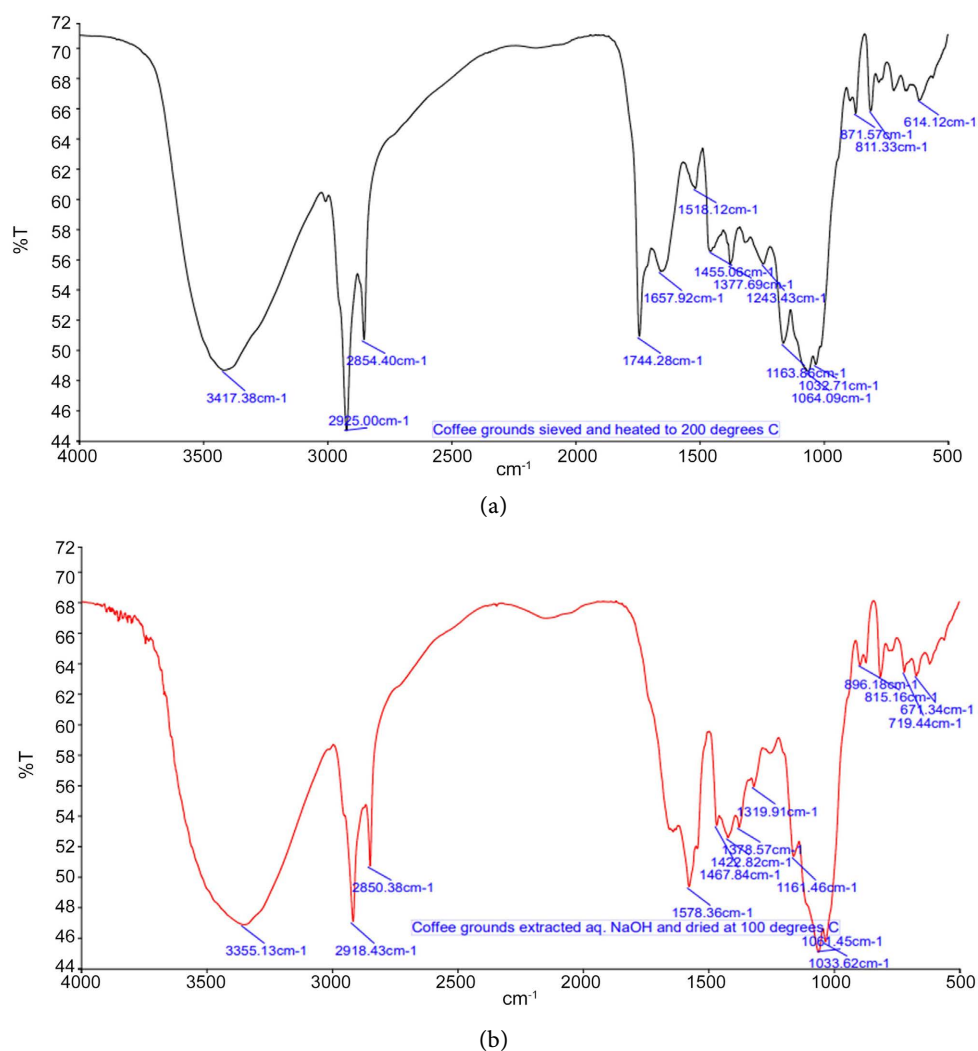


Figure 4. (a) FT-IR spectrum of sieved and dried CGS; (b) FT-IR spectrum of dried CGS after extraction with 3 w% aq. NaOH solution.

1.11 ± 0.06 w%. After the SCGs were extracted with 3w% aq. NaOH to separate out the lignin, the ash content of the remaining cellulosic material was measured at an appreciable 10.96 ± 1.23 w%. This value was seen to be significantly decreased upon acylation of CGS, with 4.86 w% ash content for cellulose palmitate and 0.26 w% ash content for cellulose acetate. It is believed that salts including remaining sodium ions were still attached to the extracted CGS, which were then released upon reaction of the hydroxyl groups with the acyl chlorides.

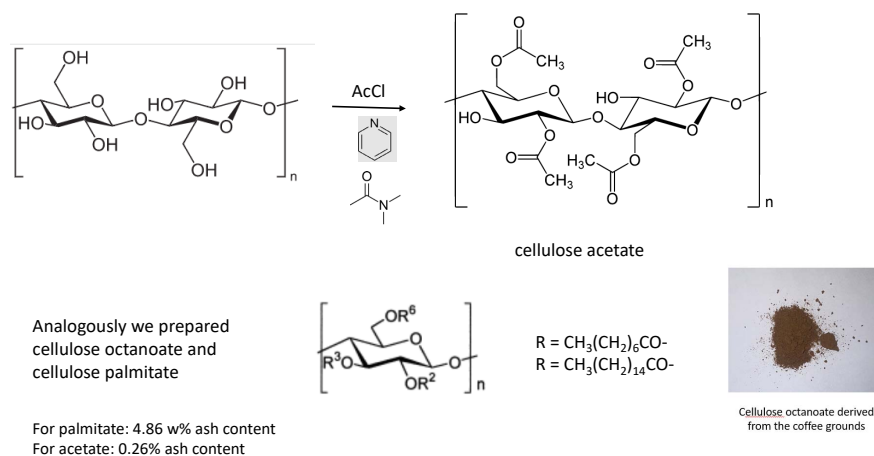
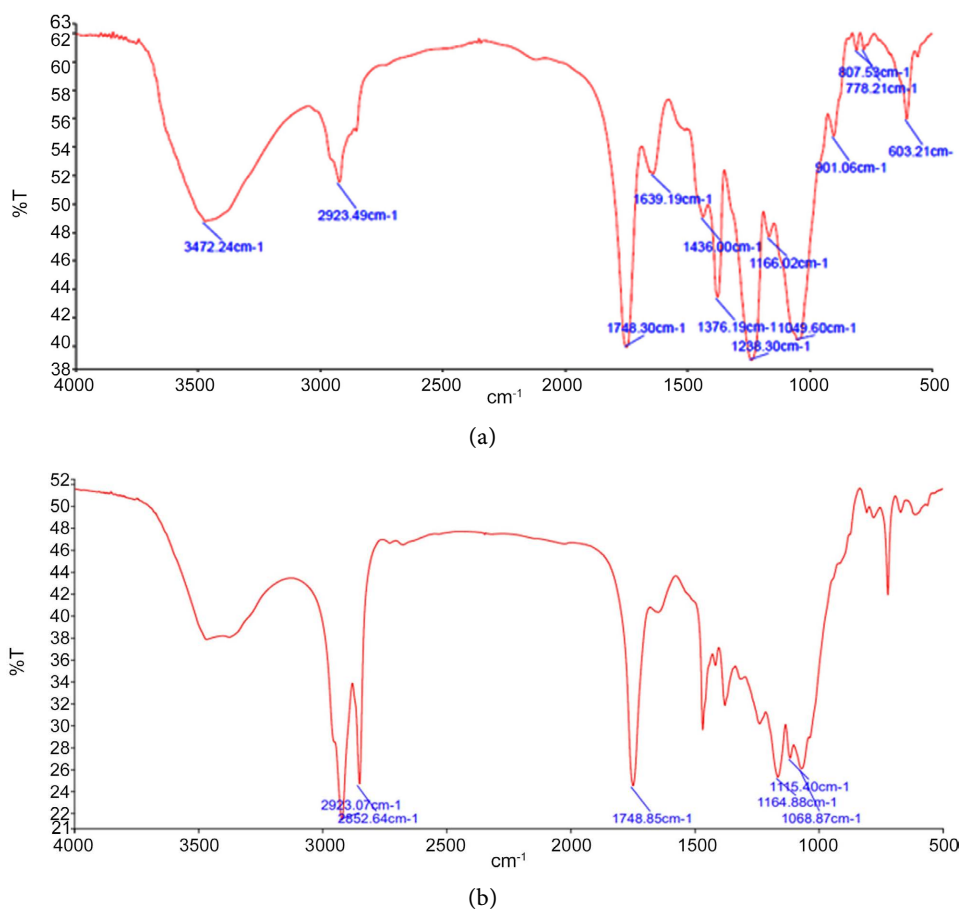


Figure 5. Esterification of the cellulosic material obtained from SGCs



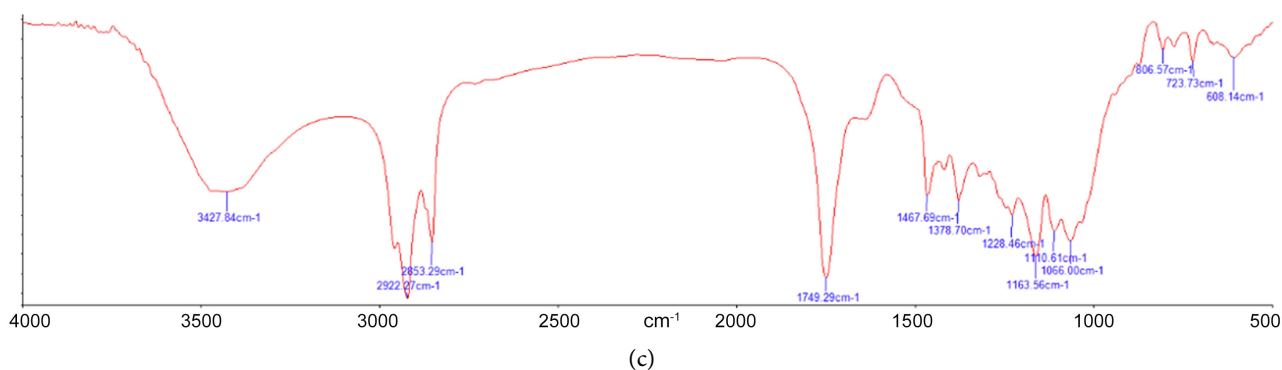


Figure 6. FT-IR spectra of cellulosic esters. (a) cellulose acetate; (b) cellulose palmitate; (c) cellulose octanoate.

For the adsorptive filtration (**Figure 7**), two glass columns were used, both 35 cm in length, but one with an inner diameter of 2.25 cm (column A) and the other with an inner diameter of 1.70 cm (column B). Column A was filled with cellulosic ester (octanoate or acetate, 2.40 g) and commercially available activated carbon (7.20 g), column B was filled with cellulose palmitate (1.20 g) and activated carbon (3.60 g). To the sorbent layer was added a layer of sand (30 g/15 g) as protection. Thereafter, PW was subjected to adsorptive filtration on these mixed sorbents, with 15.2 L PW-1 run over the cellulose-octanoate/AC column, 17.1 L PW-2 run over the cellulose-acetate/AC column, and 7.7 L PW-2 run over the cellulose-palmitate/PW column. One reason that a mixture of cellulose-ester and AC was used rather than cellulose-ester alone was the worry that due to the small particle size sole use of cellulose ester might lead to clogging once enough oil had been adsorbed. The small particle size of the sorbent and the use of sand as protective layer made back-washing unsuitable for this set-up, in contrast to using walnut shell granules as sorbent material [50] [67] [68]. Thus, clogging, even for the mixed sorbent, limits the amount of PW that can be treated per g sorbent material rather than a perceived concentration of effluent oil at the column outflow in form of an oil effluent breakthrough. The TOC of the effluent water was measured to be below 50 ppm. In the case of using cellulose-octanoate/AC as sorbent for the filtration of 15.2 L of PW 14.2 mL oil could be retained. This oil could be recovered, partly by squeezing out the oil from the sorbent material. The oil showed a density of 0.9586 g/mL corresponding to an API gravity of 16.02. The sulfur content of the recovered oil was found to be 5.42%. While PW is now de-oiled, the salt content has remained the same. This was true for PW-1 filtered over CGS-octanoate and for PW-2 filtered over CGS-acetate or CGS-palmitate.

3.2. Salt Crystallization

After de-oiling the PWs, the salt inherent in PWs was to be precipitated as industrial salt. As the adsorptive filtration of PW does not change its inorganic ion content, **Table 1** shows the approximate ion concentration in the PW under study, after being de-oiled by adsorptive filtration over CGS-octanoate and **Table**

2 shows the approximate ion concentration of PW-2 after being de-oiled either by CGS-acetate or CGS-palmitate. The density of PW-2 at this stage was ca. 1.113 g/mL. After de-oiling, PWs maintain high Ca [7670 ppm for PW-1], Mg [1730 ppm for PW-1] and Sr [255 ppm for PW-1] concentrations. All of these divalent earth-alkaline metals form salts that are scalants, and their presence in industrial salt (10 pound brine) is unwanted. Thus, their concentration needs to be reduced significantly. The overall idea was to remove the earth-alkaline ions as carbonates under necessarily basic conditions, acidify the filtrate and subject the filtrate to evaporation, first in an outdoor evaporation pond. **Figure 8** shows the overall process schematically.

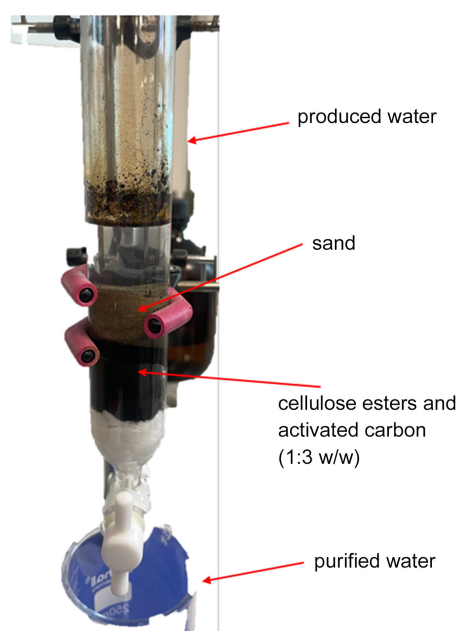


Figure 7. Adsorptive filtration of PW

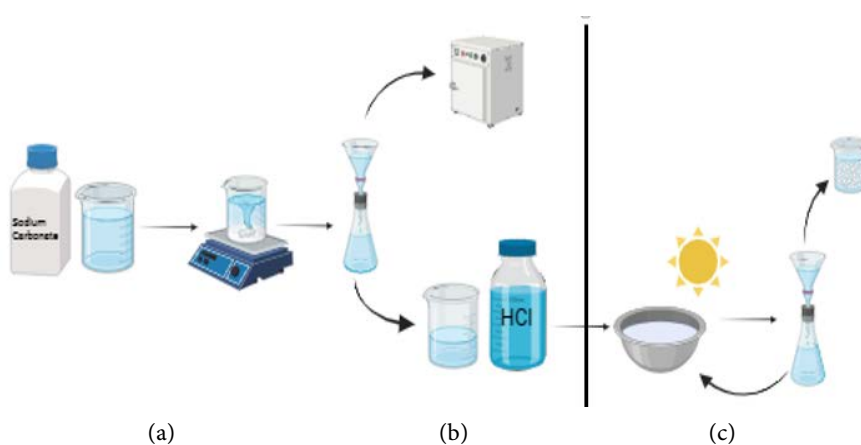


Figure 8. Schematic representation of the crystallization of industrial salt: (a) dry Na_2CO_3 was added to de-oiled PW and the precipitated CaCO_3 filtered off; (b) small amounts of conc. HCl are added to adjust the pH of the filtrate; (c) filtrate is set into an outdoors evaporation pond.

To achieve a carbonate concentration in solution in order to remove the earth-alkaline metal species as carbonates can be achieved principally in two different ways – 1) by saturation of the aq. solution with CO_2 which could be obtained as part of flue gases from a separate process or 2) by the addition of solid, but water-soluble alkali metal carbonates. In both cases, it must be noted that in an equilibrium the carbonate concentration in the aq. solution is pH dependent as shown in **Figure 9**, with the equilibria shown in **Figure 10** playing a role. In the case of adding solid alkali metal carbonates to the solution it can be expected that the reaction to the little soluble earth alkaline metal carbonates such as calcium carbonate (CaCO_3) is faster than the carbonic acid/bicarbonate/carbonate equilibrium can establish itself.

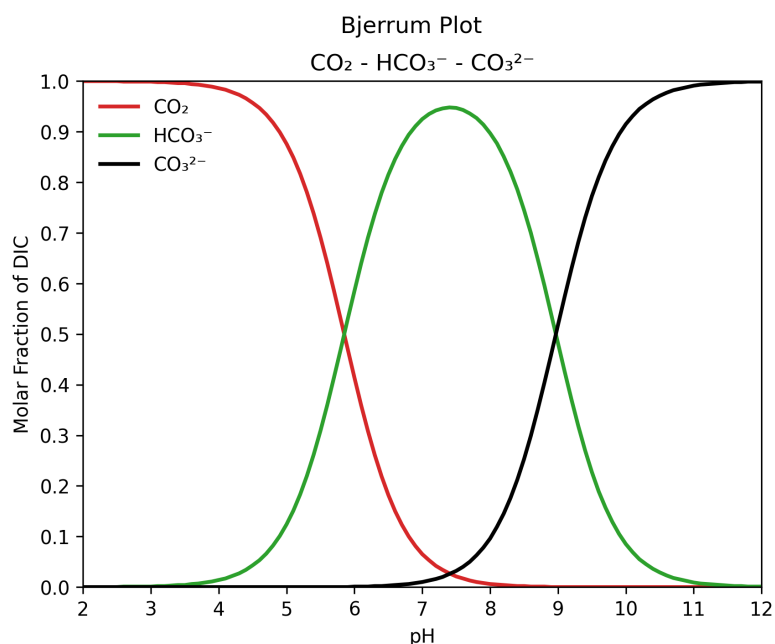
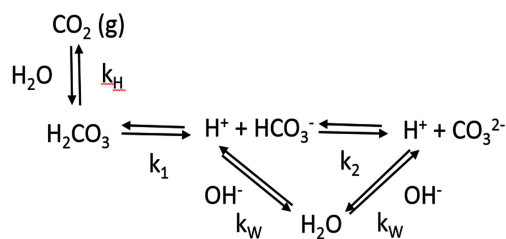


Figure 9. Different relative amounts of CO_2 (g)/ H_2CO_3 , HCO_3^- and CO_3^{2-} in solution at different pH values of the solution [adopted from ref. [70] [71]]. The Bjerrum plot was drawn by Tim Thiemann, Hannover, using PyCO2SYS to calculate the carbonate system, NumPy for data modification and Matplotlib for data visualization.



$$k_H = 10^{-1.47}; k_1 = 10^{-6.35}; k_2 = 10^{-10.33}; k_W = 10^{-14}$$

Figure 10. Some of the equilibria that are at play in an aq. solution in contact with CO_2 gas [adopted from ref. [69]].

When adding aq. 1N KOH to PW, both in presence and in absence of CO₂, the pH of the analyte moves to about pH 10, where it then remains upon further addition of aq. KOH for a time (**Figure 11**). It is here that reactions take place with the earth-alkaline metal ions, where metal hydroxides are formed in the absence of CO₂ and a mixture of metal carbonates and metal hydroxides are formed in the presence of CO₂ (see below). The low solubility of both carbonates and hydroxides mean that all added hydroxide ions are bound up in the precipitated metal salts. Only upon reaction completion does the pH increase upon further addition of KOH. It should be noted that the addition of aq. KOH to synthetic aq. sodium chloride solution of a concentration similar to that in PW shows no such buffering zone in respect to change of pH.

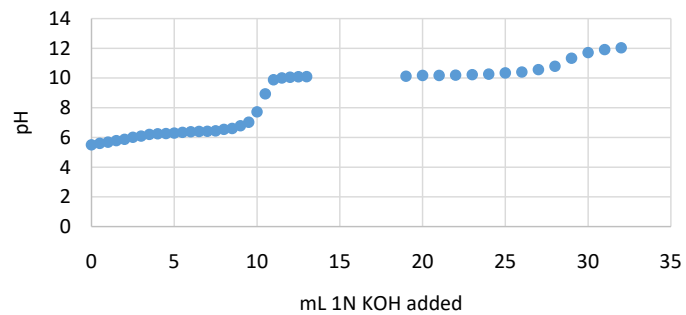
Indeed, adding aq. 1N KOH or aq. 1N NaOH solutions dropwise to the PW in the presence of CO₂ leads to a rapid crystallization of a colorless solid which becomes more pronounced with increased pH. Filtration yields a colorless solid, that is hygroscopic, which indicated that a certain amount of Ca(OH)₂ would be found in the mixture. Indeed, the IR spectrum shows a strong band for the OH stretching vibration of Ca(OH)₂ at 3700 cm⁻¹. The CO stretching vibration of CaCO₃ at 1445 cm⁻¹ is less in evidence (**Figure 12(a)**). If the mixture is stirred under CO₂ for a further 6 h, Ca(OH)₂ converts to Ca(CO)₃, driven also by the different solubilities of the salts [solubility product $K_{sp(25^{\circ}C)} \text{CaCO}_3 = 4.96 \times 10^{-9}$; $K_{sp(25^{\circ}C)} \text{Ca(OH)}_2 = 4.68 \times 10^{-6}$] [72].

Figure 12(b) shows the IR spectrum of the filtered solid collected afterwards, clearly showing that CaCO₃ is by now the main constituent. The solid was also analyzed by completely dissolving it in HCl and subsequently determining the total hardness of the solution by standard titration with ethylenediaminetetraacetic acid (EDTA) [73] with the idea that the w% of Ca in Ca(OH)₂ is quite different from that in CaCO₃.

Well realizing that EDTA also complexes Sr²⁺ and Mg²⁺, the results nevertheless clearly show that Ca(OH)₂ comprises less than 5% of the material, although a OH-band is still visible at 3700 cm⁻¹ in the infrared spectrum. Upon addition of solid Na₂CO₃ to PW (7 g for every 200 mL PW), precipitation is very rapid. In the case of an addition of Na₂CO₃ all at once to PW, the filtered solid shows up to 10.8 w% Na in the sample, in addition, 3.5 w% Mg can be found in the solid as well as Sr (8620 ppm) and K (3050 ppm). Upon a portion-wise addition of Na₂CO₃ to PW, lasting a minute, 2.28 - 2.32 w% of Na were found in the filtered solid, Here, also Mg (3.41 w%) and Sr (1.06 w%) were observed. When the filter cake was washed with a minimum amount of water (20 mL per 50 g precipitate), the amount of Na in the CaCO₃ can be reduced to 1.27 w%. It can be expected that all earth alkaline metals precipitate predominately as carbonates. If this is the case, more than 94% of the precipitated calcium is in form of calcium carbonate. At this point, the spectrum of the solid also lacks the tell-tale absorption band in the infrared at 3700 cm⁻¹ for Ca(OH)₂, signaling its absence (**Figure 13**). In addition, most of the heavy metal content can be removed from PW in this way. In various experiments of adding Na₂CO₃ to de-oiled PW, heavy metals

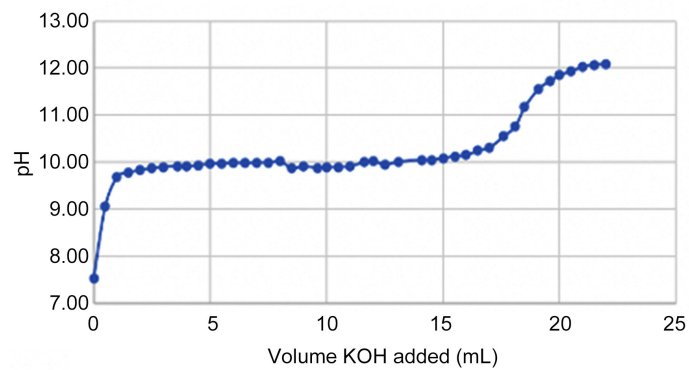
could be noted in the precipitate such as Cu (3.8 - 8.9 ppm), Mn (up to 4.5 ppm), and Ni (up to 6.7 ppm), while the concentrations of these metals in the NaCl crystals gained from the filtered PW were all found to be <0.1 ppm (see below).

Titration 60 mL produced water and 60 mL water sat. with CO₂ with 1N KOH



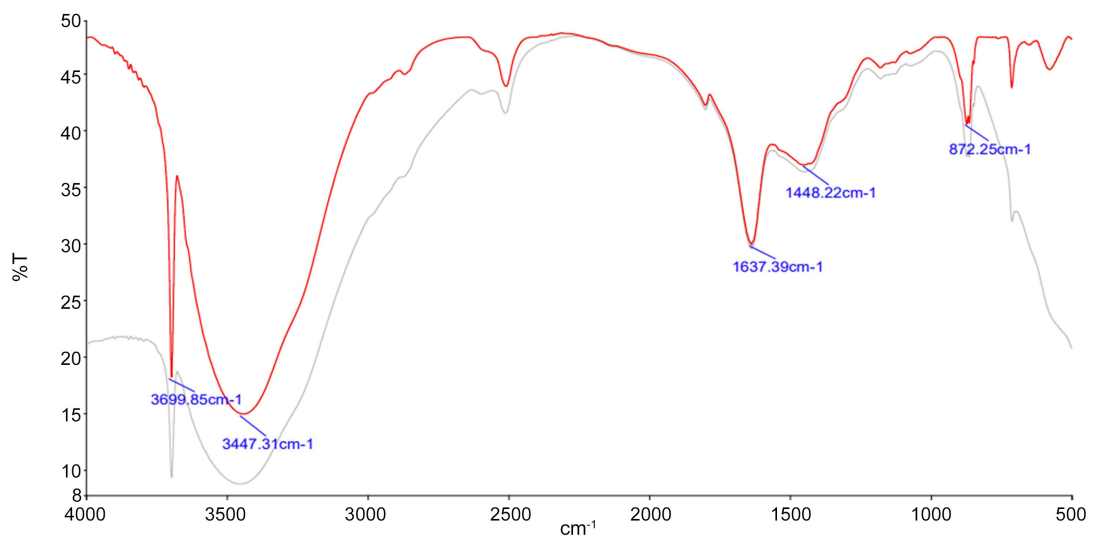
(a)

Titration of KOH VS Produced Water



(b)

Figure 11. (a) Titration of a mixture of PW and CO₂ saturated water with 1N KOH. (b) Titration of PW with 1N KOH.



(a)

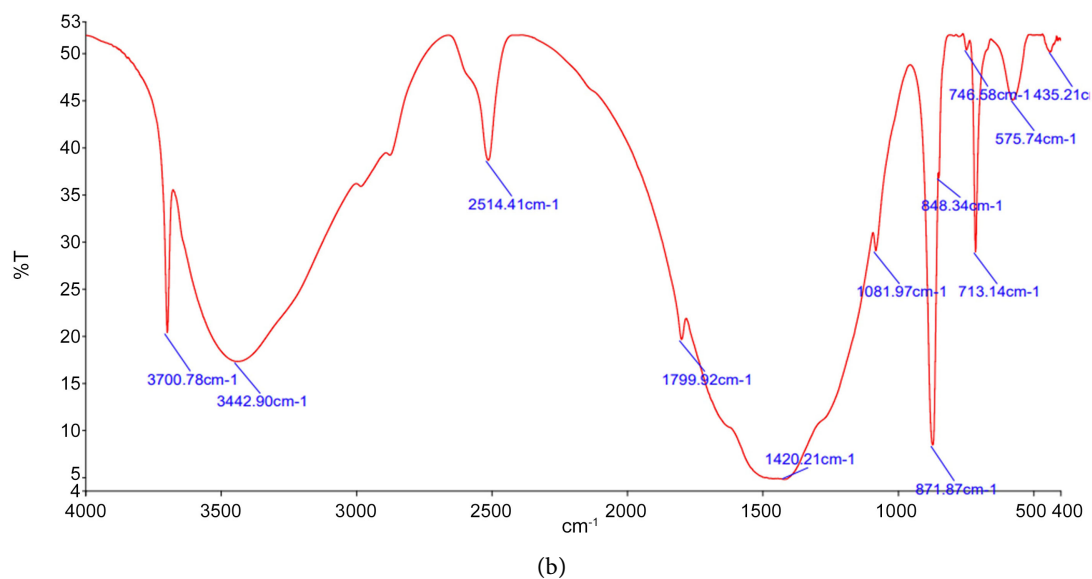


Figure 12. (a) FT-IR spectrum of the precipitate formed when adding 1N KOH to PW in the presence of CO₂ (immediate filtration); (b) FT-IR spectrum of the same precipitate when stirred for 6 h (rt) in the aq. solution in the presence of CO₂.

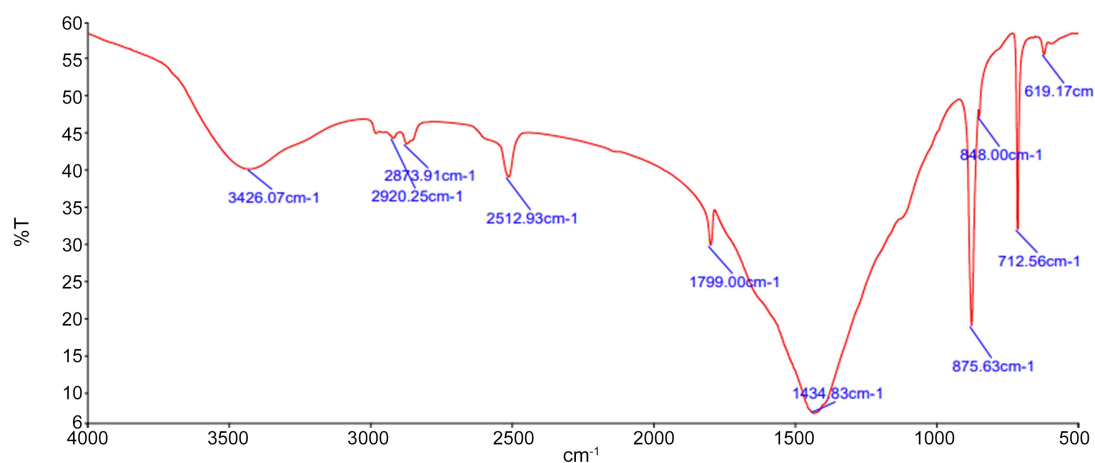


Figure 13. FT-IR spectrum of precipitated CaCO₃ after addition of Na₂CO₃ to de-oiled PW.

Crystallization of salt by evaporation of the filtered and slightly acidified PW gave sodium chloride (NaCl) crystals in their typical cubic shape (Figure 14). The first harvesting was performed after evaporation of 37.5 vol% of the PW-1, the second harvesting after evaporation of overall 67.5 vol% of PW-1, and the final harvesting was carried out after evaporation of 38.7 vol% of the remaining PW-1, leaving 20 vol% PW-1 at the end. Direct evaporation of PW without removal of calcium ions via the carbonate process gave calcium concentrations in the salt crystals of 200 - 400 ppm and magnesium concentrations of 130 - 150 ppm in the first harvest. The last harvest gave salt crystals with a calcium (Ca) concentration of 5100 pm, a magnesium (Mg) concentration of 1490 ppm and a strontium (Sr) concentration of 185 - 190 ppm. In addition, heavy metals such as copper (Cu, 0.56 ppm) and manganese (Mn, 0.36 ppm) could be found.

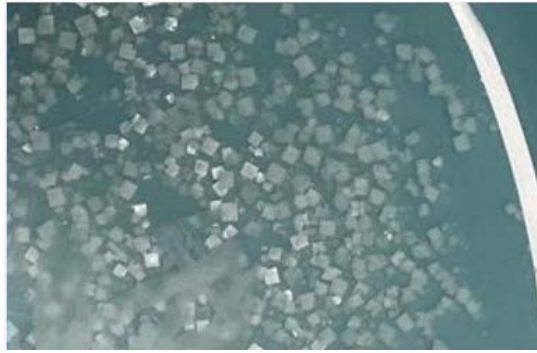


Figure 14. Salt crystals formed during the evaporation process showing their typical cubic shape.

The first harvest of PW-1 where calcium had been removed by the carbonate method showed Ca concentration of 32 - 46 ppm, with potassium (K) at 39 - 105 ppm, Mg at 54 - 95 ppm and Sr at 2.4 ppm and with lead (Pb), Cu, Mn and nickel (Ni) at <0.1 ppm. The purity of NaCl salt obtained was calculated to be 99.2 w%. The final harvest of the decalcified PW-1 gave a Ca concentration of 220 ppm. Also in evidence were Mg (190 ppm), K (123 ppm) and Sr (11.8 ppm). All heavy metal conc. (Cu, Pb, Mn, Ni) were found to be below 0.1 ppm.

Salt crystals from PW treated with aq. NaOH or aq. KOH in the presence of CO₂, where the solid precipitate formed was immediately filtered after addition of the base, still showed relatively high values of Ca (up to 420 ppm) even in the first harvest due to the fact that in this case there is still an equilibrium that establishes itself among Ca(OH)₂ and CaCO₃ via the species CO₂, HCO₃⁻ and CO₃²⁻.

NaCl production was also carried out with PW-2, de-oiled by adsorptive filtration on CGS-palmitate. Here, de-oiled PW was evaporated in 500 mL batches, Here, the first harvest was taken after the brine was reduced to 50 vol%, the second harvest when it was reduced to 26.0 vol% and the third harvest when it was reduced to 16.0 vol%. **Table 3** shows the content of the obtained salt, where the composition and NaCl purity was calculated upon subtraction of the moisture content of the samples.

4. Benefits of PW Treatment, Industrial Salt Specifications and Industrial Salt Market

Untreated PW from oil extraction poses substantial environmental risks, including contaminant discharge with adverse effects on ecosystems, both terrestrial and aquatic, and has potential health risks for humans and wildlife. Especially direct disposal exacerbates soil and water contamination, impacting vegetation, aquatic life, and overall ecosystem health. In contrast, treating PW offers significant environmental and economic advantages. The treatment reduces contaminants, minimizes environmental impact, and transforms a waste product into a valuable resource, aligning with principles of resource efficiency and sustainable industrial practices.

Table 3. Salt composition of harvests 1-3 of PW-2, de-oiled by adsorptive filtration on CGS-palmitate, subsequent treatment with solid Na_2CO_3 and slow evaporation of the residual brine.

harvest	1 st harvest	2 nd harvest	3 rd harvest
Amount of salt harvested	36.7 g	27.6 g	24.6 g
Amount of residual brine	50.0 vol%	26.0 vol %	16.0 vol%
NaCl (purity)	99.73%	99.73%	99.51%
Ca ²⁺	693 ppm	578 ppm	769 ppm
Mg ²⁺	313 ppm	212 ppm	426 ppm
Sr ²⁺	8.0 ppm	4.9 ppm	10.0 ppm
K ⁺	80.5 ppm	26.8 ppm	440 ppm

In oil and gas operation where PW is sent into discharge wells or is re-injected into the production zone, non-treated PW corrodes the piping infrastructure. While that is also true for the production tubing [4], intermittent treatment of PW before disposal or re-injection can reduce corrosion on that side of the infrastructure, limiting the expensive replacing of the piping infrastructure.

Table 4 shows the specifications of industrial salt. It can be noted that the salt obtained from PW of a South Kuwaiti oil and gas operation through gravity oil-water separation, adsorptive filtration and precipitation by evaporation is with the specifications of grade 2 industrial salt. The global industrial salt market has been reported to be worth 14.2 billion USD in 2020 and is expected to reach 19.4 billion USD in 2023. In the GCC region, industrial salt is used in the building material and glass industries [74]. Therefore, an urgency to further treat the industrial salt to achieve table salt quality for the purpose of product marketing is not present.

Treating PW appears to be a comprehensive solution, offering substantial economic and environmental benefits. If adopted, Kuwait has the potential to become a significant player in industrial salt production, with an estimated annual output of around 15,666,700 metric tons. However, it must be noted that for the above discussed process, 180 g Na_2CO_3 (soda) are used per 1 kg of industrial salt produced. With a price of US\$ 50 per ton of industrial salt and of US\$ 150 per ton of soda, the process is economically attractive then, when the calcium carbonate (CaCO_3) that is precipitated can also be used commercially such as a raw primary substance for building materials, as a constituent of cement, as a component in drilling fluids in the oil and gas industry and as a component in many plastic composites. Currently, the purity of the precipitated CaCO_3 in the here-described process is 87.3%, which is not yet adequate for some of the above named uses.

In essence, the treatment of PW delivers economic advantages through cost reduction and revenue increase while concurrently fostering both operational efficiency and environmental sustainability. It must be noted that while in this

Table 4. Specifications of industrial salt [75] [76].

Characteristics	Grade 1	Grade 2	Our samples from PW-1
Moisture content (max. w%)	1	4	less than 1.5
NaCl content (min. w%)	99.5	98.5	99.2
Ca ²⁺ content (min. w%)	0.03	0.2	32 - 46 ppm
Mg ²⁺ content (w%)	0.01	0.1	54 - 95 ppm
Water insoluble matter (in w%)	0.2	0.6	<0.1

work there was no focus on obtaining purified water from PW as the evaporation was not carried out in closed systems, the here-described process can be integrated into a closed system where apart from industrial salt production purified water would be obtained such as in the combination of the process with a solar still [77] [78] [79].

5. Conclusion

PW from an oil and gas operation situated in South Kuwait was used to produce industrial salt with a reproducible NaCl purity of at least 99.2 w%, when subjecting PW, which had been submitted previously to gravity oil-gas-water separation, to sorption filtration on a mixture of cellulosic esters derived from spent coffee grounds and commercial activated carbon, subsequently to decalcification using solid sodium carbonate and finally selective crystallization in evaporation process. It could be shown that scale-forming earth-alkaline metals that include strontium and magnesium could be retained in the calcium carbonate precipitated during the decalcification process as could heavy metals present in PW, leaving the remaining salt devoid of these contaminating materials.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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