

# Purification of Produced Water from a Sour Oilfield in South Kuwait. 2. Oil-Water Separation and Crystallization of Calcium Carbonate

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## Abstract

Oil-water separation for produced water (PW) originating from an oil extraction site in South Kuwait was carried out using bleached, esterified cellulosic material from used coffee grounds. Thereafter, earth-alkaline metal ions, specifically calcium ions, of the de-oiled PW were removed by precipitation with sodium carbonate to give access to pure sodium chloride as industrial salt from the remaining PW. While the purity of the precipitated calcium carbonate (CaCO<sub>3</sub>) depends on the precipitation conditions, CaCO<sub>3</sub> of up to 95.48% purity can be obtained, which makes it a salable product. The precipitation of CaCO<sub>3</sub> decreases the amount of calcium ions in PW from 11,300 ppm to 84 ppm.

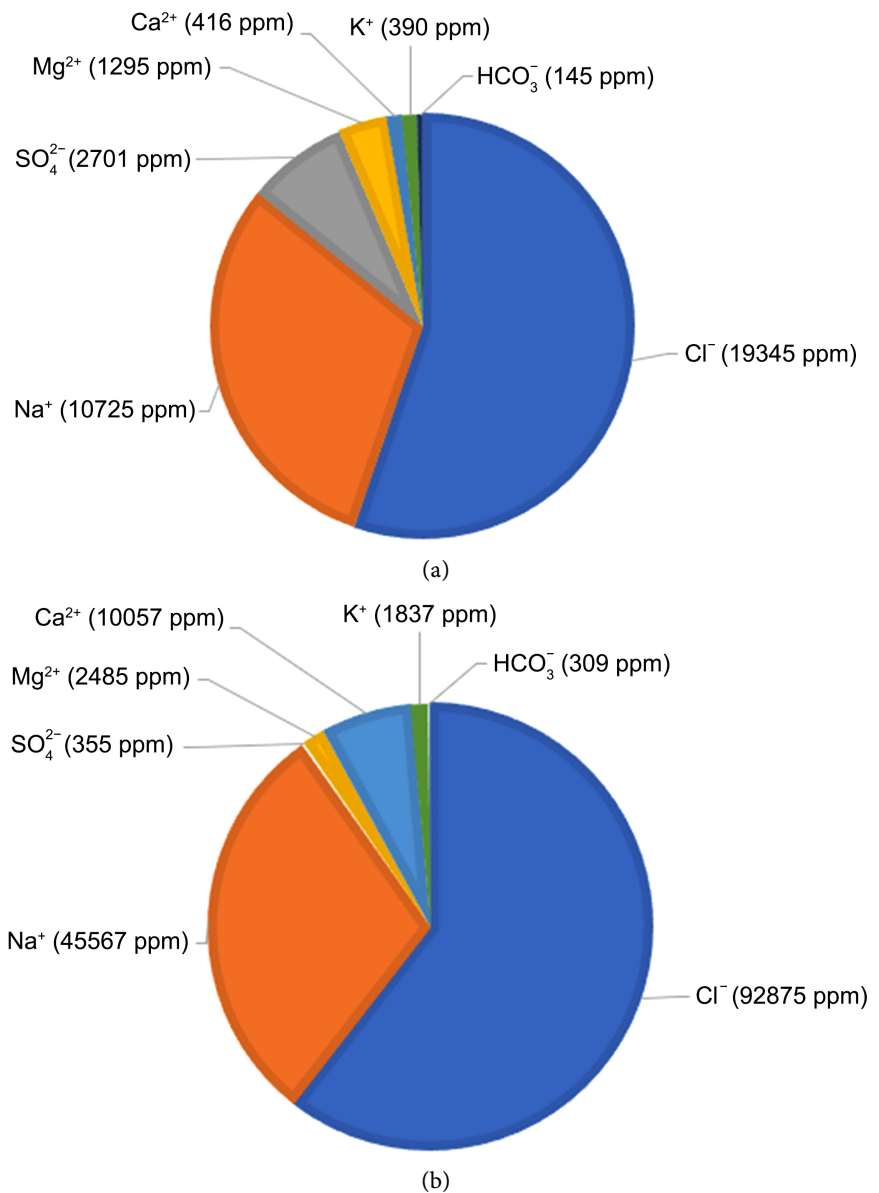
## Keywords

Produced Water, Oil and Gas, Bleached Biomass, Adsorption Filtration, Crystallization of Calcium Chloride

## 1. Introduction

Produced water (PW) is an appreciable side product of oil and gas operations, amounting to 250 million barrels per day in 2020 [1] [2]. It is predicted to reach 650 million barrels per day within the next 2 decades [3] due to the continuous maturing of the exploited oil fields and due to the development of new fields. At the moment, the global average PW to oil ratio is 7 barrels of PW for every barrel of oil [4]. PW is a very complex fluid and carries varying concentrations of

metal salts and hydrocarbons as well as additives that the operators have added for a more perfect oil/gas extraction operation [5] [6]. If released to the environment directly, PW is a potent environmental pollutant [7]-[11]. Also, PW is highly corrosive, damaging pipelines and general infrastructure of oil/gas operations [12]-[19]. If the effort is undertaken to purify PW and separate it into its components, namely into the water, sodium salt (mostly NaCl), earth-alkaline salts (mostly calcium salts, in form of calcium carbonate) and residual oil, PW can be seen as a significant resource of water, salt and a remaining hydrocarbon fraction [20], where the salts need to be separated into sodium and calcium salts for their commercial use.

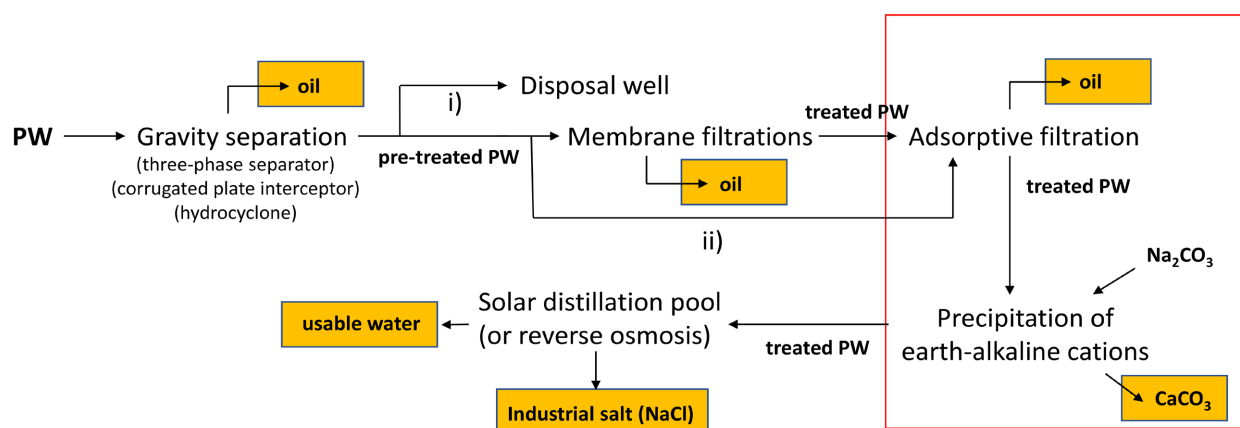


**Figure 1.** (a) Major ion content in seawater. Data taken from [21]; (b) Salt content with major ions in PW from an oil and gas operation in South Kuwait (average over 3 samplings within 2 years) [22 and current study].

**Figure 1(a)** and **Figure 1(b)**, respectively, show the average salt contents of seawater and of PW from the SK oilfield under study in this work. It can be noted that the sodium ion ( $\text{Na}^+$ ) and chloride ( $\text{Cl}^-$ ) concentrations in PW are 4.25 and 4.80 times those of the average saltwater. In the PW under study, the calcium ion ( $\text{Ca}^{2+}$ ) content is 24.2 times that of average seawater, where calcium is the second most abundant metal cation after sodium, but before magnesium ( $\text{Mg}^{2+}$ ). Nevertheless, the magnesium concentration in PW is 1.91 times that in average seawater. Salt production from seawater as well as from other naturally occurring brines [23] has been known for a long time, going back to the Phoenicians in the 9<sup>th</sup> century BC [24] [25]. In recent times, desalination to procure fresh water has been combined to obtain salt from the rejected brine in evaporation ponds, too [26]-[28]. Salt production has also been achieved by rejecting brines of reverse osmosis processes, for instance in sea-water desalination plants [29]-[31]. In comparison, salt reclamation from PW of oil and gas operations is being carried out more seldomly.

**Figure 2** shows schematically the possibilities of purifying PW from oil and gas operations. The commercial products that can be derived from PW during the purification steps are highlighted in orange. Usually, the first step for the purification of produced water (PW) from oil and gas extraction processes is its separation into oil, gas and water with the help of a three-phase separator [32], before further oil separation from the water is carried out by corrugated plate interceptor (cpi) [33], hydro cyclone [34], and possibly air flotation [35]. Sometimes, such as is the case in the oil extraction operation in South Kuwait the PW of which is the subject of the current study, the pre-treated PW is disposed of underground, in so-called disposal wells [36].

In cases where PW is to be used for enhanced oil recovery (EOR) [37], for cooling or irrigation purposes [38]-[40], it needs to undergo further purification. Membrane filtration [41] [42] or filtration through a sorbent layer [43] that may include sand [44] can be added to the purification scheme, depending on the further use of the PW.



**Figure 2.** Schematic layout of the purification steps for PW from oil and gas operations. The processes within the red box are the focus of this work.

Looking at the salt reclamation from PW, both calcium carbonate ( $\text{CaCO}_3$ ) and sodium chloride ( $\text{NaCl}$ ) are valuable commodities. The extraction of other metal salts such as lithium, vanadium and neodymium salts would be highly lucrative [45], but for operations of this type existing technology would need to be developed further. It must be kept in mind that currently treatment of PW is not profitable or sustainable as a business model [45].

The majority of produced water (PW) from an oilfield in South Kuwait undergoes a primary oil-water separation process based on gravity separation and is subsequently disposed of in disposal wells. The space in the disposal wells is limited and the drilling of new disposal wells is costly. In addition, PW has been shown to do significant damage to the production infrastructure as it is highly corrosive [5]. Efforts have been made to come up with a sustainable solution for the PW of this oilfield, which involves more stringent treatment of the PW with concomitant extraction and separation of commercially valuable constituents from it. The oil-field 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 [5]. Recently, we have reported that the composition of PW from an oil field can vary, even over short periods of time [46]. **Tables 1-3** show the average compositions of three PW samples used in this and a previous study [22] that were taken over a period of three years.  $\text{Na}^+$  concentrations varied between 35,600 and 51,500 ppm,  $\text{Ca}^{2+}$  concentrations between 7670 and 11,300 ppm, and  $\text{Mg}^{2+}$  concentrations between 1730 and 3050 ppm.

The proposed purification of PW from the South Kuwaiti oilfield entails, apart from the existing pre-treatment by gravity separation, membrane filtration [47] and an adsorptive filtration [22] to separate the remaining oil from the water. Subsequently, the calcium of PW is separated out by precipitation as  $\text{CaCO}_3$ . Thereafter, the water is separated from the remaining salt content, mostly  $\text{NaCl}$ , by either solar pond distillation or reverse osmosis (**Figure 2**). Most of these steps have been detailed in earlier communications [22] [47] [48], where the adsorptive filtration cellulosic material from used coffee grounds (SCG) [22] [49] [50] is utilized, which has been treated with aq.  $\text{NaOH}$  to separate lignin from the cellulose of the coffee grounds. It must be noted that the price that could be obtained both for the industrial salt ( $\text{NaCl}$ ) and for the precipitated  $\text{CaCO}_3$  is an integral part of the financial sustainability of the entire PW treatment process [48].

The processes shown in **Figure 2** within the red box are the focus of this work, where the current contribution primarily deals with purity considerations in regard to the precipitated  $\text{CaCO}_3$ , where  $\text{CaCO}_3$  is precipitated from the PW under different conditions. Also, the authors tried to find out whether it would be better to bleach the SCG before esterification to give a good sorbent material. Thirdly, the authors attempted to utilize leaf material from desert squash (*Citrullus colocynthis*) as a cellulose source that after esterification could also be used as sorbent material in the adsorptive oil-water separation process.

**Table 1.** Properties and ion content of PW-1, sourced from an oil production in South Kuwait collected in November 2021—This PW was treated with SDG-octanoate/AC [21].

Total dissolved solids	132,780 ppm	Chloride (Cl <sup>-</sup> )	75,660 pm
Sodium (Na <sup>+</sup> )	35,600 ppm	Sulfate (SO <sub>4</sub> <sup>2-</sup> )	18 pm
Potassium (K <sup>+</sup> )	1520 ppm	Bicarbonate (HCO <sub>3</sub> <sup>-</sup> )	140 pm
Calcium (Ca <sup>2+</sup> )	7670 ppm	Silicon (Si)	12.3 ppm
Magnesium (Mg <sup>2+</sup> )	1730 ppm	Total Iron (Fe)	1.36 ppm
Barium (Ba <sup>2+</sup> )	2.3 ppm	Dissolved oxygen	3 ppm
Strontium (Sr <sup>2+</sup> )	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 in January 2022, 3 months after PW-1—This PW was treated either with SDG-palmitate/AC or with SDG-acetate/AC [22].

Total dissolved solids	193,350 ppm	Chloride (Cl <sup>-</sup> )	110,090 pm
Sodium (Na <sup>+</sup> )	51,500 ppm	Sulfate (SO <sub>4</sub> <sup>2-</sup> )	355 pm
Potassium (K <sup>+</sup> )	1800 ppm	Bicarbonate (HCO <sub>3</sub> <sup>-</sup> )	300 pm
Calcium (Ca <sup>2+</sup> )	11,200 ppm	Silicon (Si)	ND
Magnesium (Mg <sup>2+</sup> )	3050 ppm	Total Iron (Fe)	ND
Barium (Ba <sup>2+</sup> )	2.4 ppm	Dissolved oxygen	ND
Strontium (Sr <sup>2+</sup> )	460 ppm	pH at 25 °C	6.02

**Table 3.** Ion content of PW-3, sourced from the same oil production site in South Kuwait as in ref. [22], after treatment with bleached SDG-acetate/AC [this work]. PW3 was collected in February 2024.

Sodium (Na <sup>+</sup> )	49.600 ppm	Strontium (Sr <sup>2+</sup> )	416 pm
Potassium (K <sup>+</sup> )	2192 ppm	Aluminum (Al <sup>3+</sup> )	0.30 pm
Calcium (Ca <sup>2+</sup> )	11,300 ppm	Cobalt (Co), lead (Pb), manganese (Mn), nickel (Ni)	<0.1 ppm
Magnesium (Mg <sup>2+</sup> )	2676 ppm	Total Iron (Fe)	ND

## 2. Materials and Methods

### 2.1. General

8.5 L of a produced water (PW) sample was obtained from an oil extraction op-

eration in South Kuwait. The PW had been submitted to oil-water separation with a three-way separator and with 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<sub>4</sub>. Acetyl chloride (Sigma Aldrich) was used without further purification. Commercial Clorox® was used as bleaching agent. It had a sodium hypochlorite (NaOCl) content of 3.5 w%. Potassium hydroxide (KOH pellets, Sigma Aldrich), sodium hydroxide (NaOH pellets, BDH Analr), anhydrous sodium carbonate (soda, eurolab), activated charcoal (Sigma Aldrich, acid-washed with hydrochloric acid), hexane (Panreac) and dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>, Sigma Aldrich) were used as is. Water used to make solutions and to wash the precipitated salts was AlAinwater® of drinking water quality.

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 the commercial activated charcoal (AC), SCG, the hydroxide extracted SCG, the bleached SCG as well as the bleached SCG-ester 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 preparation of the SCG material used as the starting material for the bleaching process was described previously [22]. The ICP-OES (Inductively Coupled Plasma-Optical Emission Spectroscopy) analyses of the salt crystals were carried out by CCIC Middle East FZE-Fujairah Branch. The laboratory is accredited. For the ICP-OES measurements, an Agilent ICP-OES Model-5110 was used after the digestion of the samples with HNO<sub>3</sub> in a microwave digester. Infrared spectra of the SCG materials and the derived esterified cellulosic materials were carried out as KBr pellets with a Perkin Elmer Spectrum 2 FT-IR spectrometer. TOC measurements were performed with a Shimadzu TOC-4200.

## **2.2. Preparation of the Bleached Cellulosic Sorbent Material from Spent Coffee Grounds**

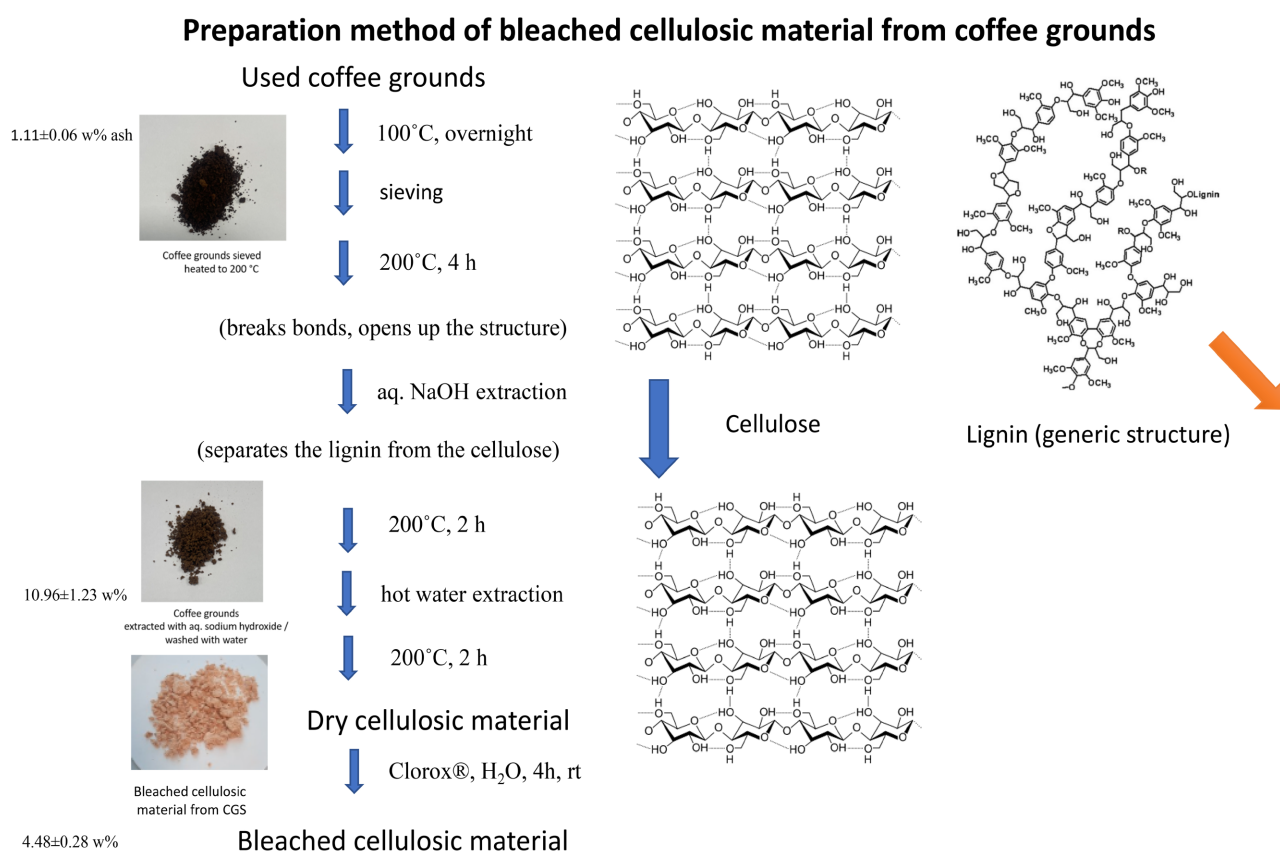
### **2.2.1. Preparation of Bleached SCG from Torrified SCG**

To a suspension of hydroxide extracted and dried SCG (10 g) in H<sub>2</sub>O (150 mL) was given Clorox® (50 mL) and the resulting mixture was stirred for 5 h at rt. Thereafter, the mixture was filtered through a sintered glass filter. Thereafter, the filter cake was transferred to a metal sieve with a mesh size of 125 µm, and the obtained mass was thoroughly washed with 3 × 25 mL H<sub>2</sub>O and dried for 10 h at 37°C. Yield 5.55 g. (Figure 3)

### **2.2.2. Esterification of the Bleached SCG-Derived Cellulose**

Coffee grounds (extracted with NaOH, non-sieved, 1.0 g, 6.15 mmol, one cellulose unit, bleached) were added to a 250 mL round bottom flask, and dimethyla-

cetamide (35 mL) was added. Thereafter, pyridine (2.6 g, 32.5 mmol) and acetyl chloride (2.0 g, 25.0 mmol) were added dropwise, and the resulting mixture was kept at 66°C for 3 days. Then, the mixture was cooled to 0°C, and 150 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 (30 mL) and hexane (30 mL), and thereafter dried in the oven for 1 day at 37°C. (Yield = 1.11 g).



**Figure 3.** Sequence used to obtain bleached cellulosic material from SCG, adapted from ref. [49] [50]. The preparation of cellulosic material from SCG has also been described elsewhere [22].

### 2.2.3. Esterification of Cellulosic Material Derived from Leaves of *Citrullus colocynthis*

Crushed leaves of *Citrullus colocynthis* (extracted with ethanol and with aq. NaOH, bleached, 1.0 g, 6.15 mmol, one cellulose unit) were added to a 250 mL round bottom flask, and dimethylacetamide (35 mL) was added. Thereafter, pyridine (2.6 g, 32.5 mmol) and acetyl chloride (2.0 g, 25.0 mmol) were added dropwise, and the resulting mixture was kept at 66°C for 3 days. Then, the mixture was cooled to 0°C, and 150 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 (30 mL) and hexane (30 mL), and thereafter dried in the oven for 1 day at 37°C (Yield = 1.10 g).

### 2.3. Oil-Water Separation by Adsorptive Filtration on Bleached SCG-Acetate

For the adsorptive filtration of PW, a glass column (length 35 cm, inner diameter 1.70 cm) was used. The column was filled with a well-mixed sorbent mixture of cellulose acetate (1.20 g) and activated carbon (3.60 g, 1:3 w/w). Sand (30 g) was added as a protective layer to the top of the sorptive material. The column was run with 1 atm pressure, initially at 500 mL per day. The de-oiled water was collected in plastic jerry cans, which thereafter were closed. PW (8.5 L) was filtered through the column. TOC measurements of the filtered PW were performed with a Shimadzu TOC-4200. The TOC of the filtered water was measured to be below 50 ppm. The metal cationic content of the filtered PW was determined by ICP-OES and is shown in **Table 3**.

### 2.4. Salt Crystallization from De-Oiled PW

#### **CaCO<sub>3</sub> Crystallization from De-Oiled PW Using Conc. aq. Solutions of Na<sub>2</sub>CO<sub>3</sub>**

1) At room temperature, solid Na<sub>2</sub>CO<sub>3</sub> (7.00 g) was added within 30 sec. to stirred de-oiled PW (200 mL). The mixture was stirred for a further 10 min. at rt and then filtered through a glass filter. The filter cake was washed with H<sub>2</sub>O (50 mL) and subsequently dried in an MMM Ecocell drying cabinet at 37°C (14 h) to give a white crystalline solid, (yield: 5.83 g). The filtrate and washings were kept separate, where the filtrate was analyzed further.

2) At room temperature, solid Na<sub>2</sub>CO<sub>3</sub> (5.00 g) was added dropwise within 30 sec. to stirred de-oiled PW (200 mL). The mixture was stirred for a further 10 min. at rt and then filtered through a glass filter. The filter cake was washed with H<sub>2</sub>O (50 mL) and subsequently dried in an MMM Ecocell drying cabinet at 37°C (14 h) to give a white crystalline solid (yield: 4.95 g). The filtrate and washings were kept separate, where the filtrate was analyzed further.

3) At room temperature, solid Na<sub>2</sub>CO<sub>3</sub> (3.00 g) was added dropwise within 30 sec. to stirred de-oiled PW (200 mL). The mixture was stirred for a further 10 min. at rt and then filtered through a glass filter. The filter cake was washed with H<sub>2</sub>O (50 mL) and subsequently dried in an MMM Ecocell drying cabinet at 37°C (14 h) to give a white crystalline solid (yield: 2.56 g). The filtrate and washings were kept separate, where the filtrate was analyzed further.

4) At room temperature, an aqueous solution of Na<sub>2</sub>CO<sub>3</sub> (7.00 g in 50 mL H<sub>2</sub>O) was added dropwise within 5 min. to stirred de-oiled PW (200 mL). The mixture was stirred for a further 10 min. at rt and then filtered through a glass filter. The filter cake was dried in an MMM Ecocell drying cabinet to give a white crystalline solid (yield: 5.77 g). This experiment was repeated with the difference that the filter cake was washed with H<sub>2</sub>O (50 mL) to give a white crystalline solid (yield: 5.75 g). The filtrate and washings were kept separate, where the filtrate was analyzed further.

5) At room temperature, an aqueous solution of Na<sub>2</sub>CO<sub>3</sub> (5.00 g in 35 mL

H<sub>2</sub>O) was added dropwise within 5 min. to stirred de-oiled PW (200 mL). The mixture was stirred for a further 10 min. at rt and then filtered through a glass filter. The filter cake was dried in an MMM Ecocell drying cabinet to give a white crystalline solid (yield: 4.91 g).

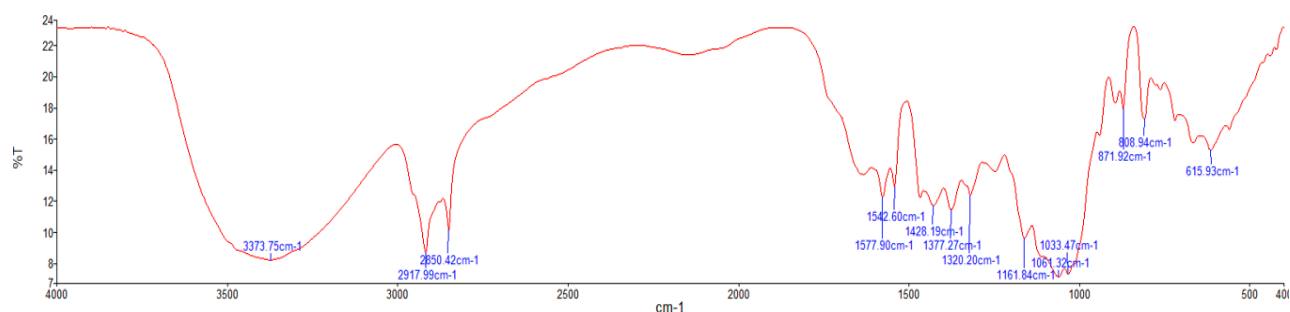
6) At room temperature, an aqueous solution of Na<sub>2</sub>CO<sub>3</sub> (3.00 g in 21 mL H<sub>2</sub>O) was added dropwise within 5 min. to stirred de-oiled PW (200 mL). The mixture was stirred for a further 10 min. at rt and then filtered through a glass filter. The filter cake was dried in an MMM Ecocell drying cabinet to give a white crystalline solid (yield: 2.47 g).

The samples from experiments 1.4.1.1-1.4.1.3 and 2.4.1.1-2.4.1.3 were stored in small plastic containers and sent within the week of the experiment to CCIC, Fujairah, for ICP analysis.

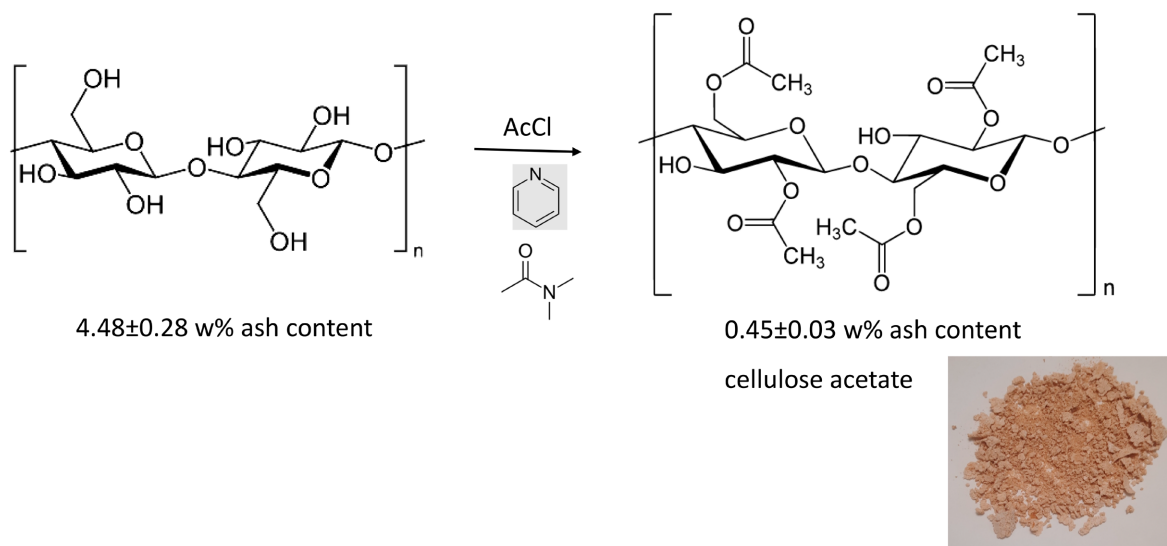
### 3. Results and Discussion

#### 3.1. Oil and Water Separation by Adsorptive Filtration

The preparation of non-bleached, torrefied (treated) SCG had been published previously [22], see also ref. [49] [50]. The subsequent bleaching of the SCG was achieved easily by the addition of commercial Clorox® to a suspension of treated SCG. That reaction could be made out visually by the significant lightening of the color of the material. After stirring the mixture for 5h rt, it was filtered through a glass filter. Filtration proved to be slow, and the material needed to be washed copiously. For this, the material was transferred to a 125 µm metal sieve. Very often, organic materials have inorganic salts incorporated or adhering to the surface. A measure of the inorganic content of the material is the ash content, where the material is heated to 600°C and the organic material is combusted, leaving the inorganics as ash. Here, it can be seen that the treatment of organic material with inorganic salts can contaminate the surface of the material, where the adhering inorganic salts cannot be removed completely by successive washings. In this regard, the ash content of the SCG material was measured after each treatment. At the outset, SCG, after torrefaction, had an ash content of  $1.11 \pm 0.06$  w% (Figure 4). The ash content of SCG increased significantly to  $10.96 \pm 1.23$  w% (Figure 4) after basic extraction of the material with aq. NaOH to remove the lignin fraction from the material. Here, it could be imagined that sodium ions still remain with the extracted SCG. After the bleaching process, the ash content of the material halved to  $4.48 \pm 0.28$  w% (Figure 5), most likely due to successive washings. Interestingly, the subsequent esterification of the bleached SCG decreased the ash content to a negligible level ( $0.45 \pm 0.03$  w%, Figure 5), indicating the ash content of the extracted SCG most likely is due to sodium ions associated with hydroxy groups of the sugar units of the cellulosic material. The esterification of these hydroxy groups releases the sodium ions. The commercial-activated AC was found to have an ash content of  $8.00 \pm 0.16$  w%.

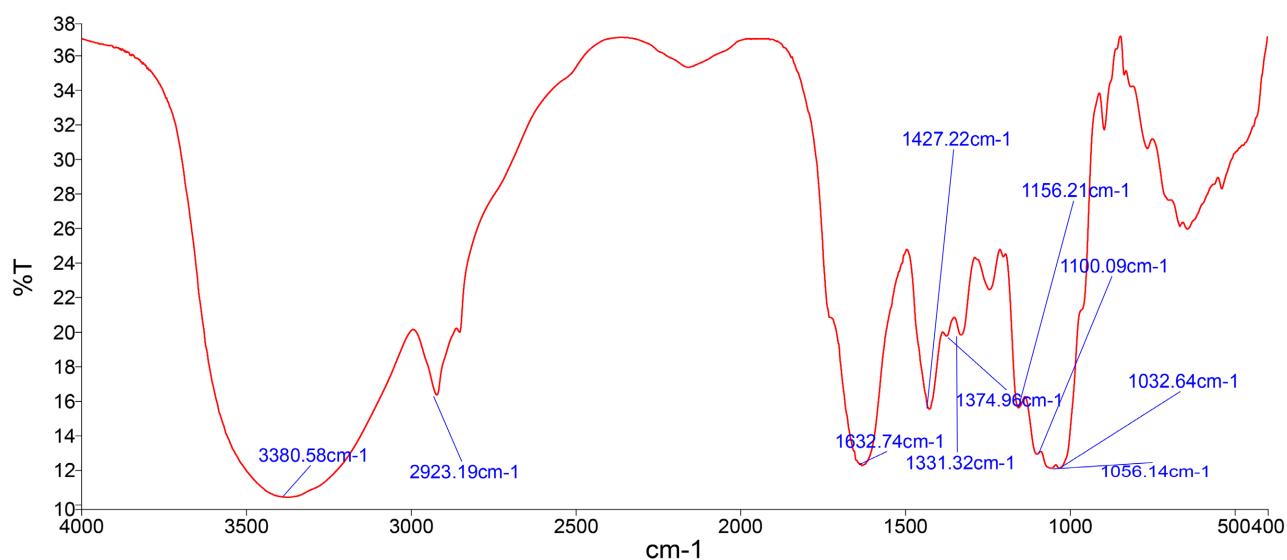


**Figure 4.** Infrared spectrum of bleached SCG.

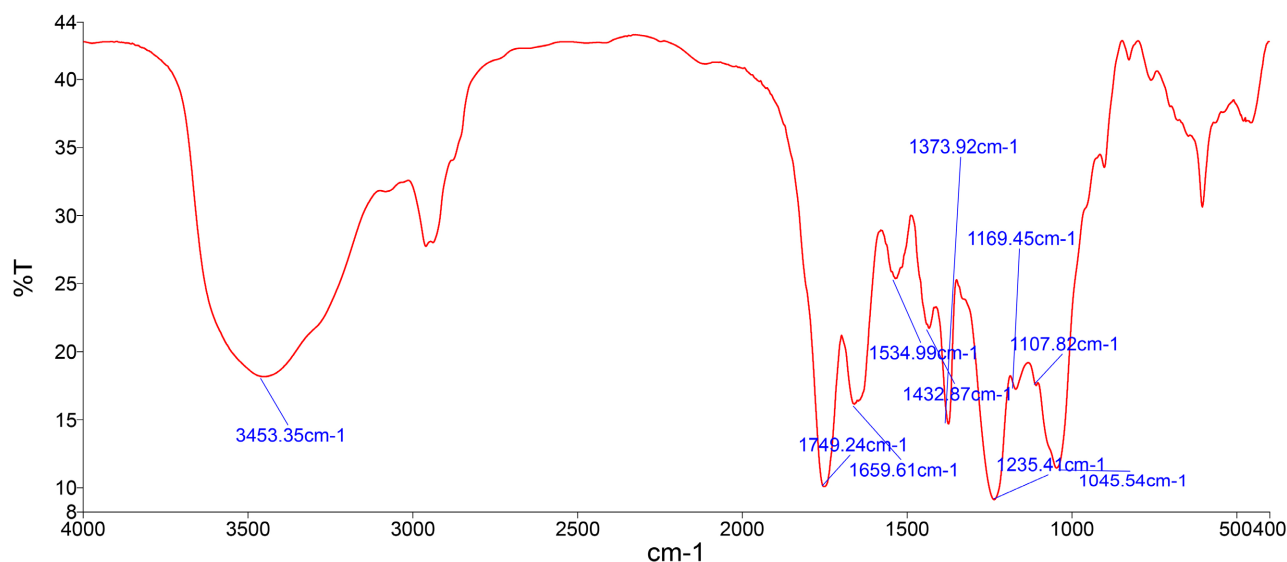


**Figure 5.** Esterification of cellulose with acetyl chloride in the presence of pyridine.

As a second source of cellulosic sorption material, the authors looked at the leaves of *Citrullus colocynthis*, a vine plant that grows on arid lands. It is known under a number of names such as Abu Jahl's melon, colocynth, bitter apple and the vine of Sodom. In the UAE, it is also called the desert gourd or desert squash. *Citrullus colocynthis* leaves were collected in Tohwayya Wadi, Al Ain. The leaves were washed and subsequently dried for two weeks at rt and crushed in a mortar. Thereafter, they were stirred in ethanol to extract small organic molecules including chlorophyll. Then, the leaves were dried at 37°C. Thereafter, they were subjected to basic extraction of the material with aq. NaOH to remove the lignin fraction from the cellulosic material (Figure 6). Thereafter, the leaves were heated to 200°C and ground. They were bleached with an aq. solution of Clorox®, filtered and washed with water. Subsequently, they were dried at 120°C over 16 h. Finally, they were submitted to esterification with acetyl chloride (AcCl). The IR spectral data showed an incomplete esterification of the material (Figure 7). Therefore, the material was submitted to a second esterification under the same conditions, however, it could be noted that esterification of all hydroxy functions of the cellulosic material could not be achieved. Therefore, further studies with this material were not carried out.



**Figure 6.** Cellulosic material from leaves of *Citrullus colocynthis* after extraction with ethanol (EtOH) and subsequently with aq. NaOH.



**Figure 7.** Partially acetylated cellulosic material from leaves of *Citrullus colocynthis*.

### 3.2. Precipitation of Earth-Alkaline Metal Ions from Produced Water - Effect of the Precipitation Method on the Purity of the Precipitated $\text{CaCO}_3$

A number of papers have been reported on the crystallization of  $\text{CaCO}_3$  from aqueous solutions [51], including in the presence of other ions [52]. Crystallization can be induced by a liquid-liquid system where both  $\text{Ca}^{2+}$  and  $\text{CO}_3^{2-}$  ions are present [53] or by the gas-liquid system where carbon dioxide ( $\text{CO}_2$ ) is bubbled through a solution of  $\text{Ca}(\text{OH})_2$  or  $\text{CaCl}_2$  [54]-[56] in the presence of ammonium hydroxide or amine-containing solutions [57] [58].

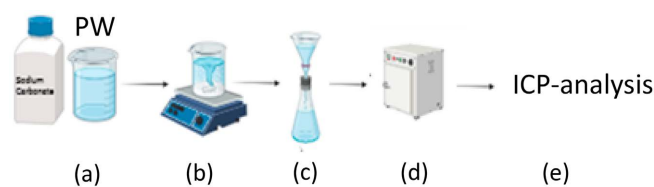
In the current study, the de-oiled PW which had been filtered through a column of AC and bleached SCG-Ac, was treated with either solid  $\text{Na}_2\text{CO}_3$  or a

concentrated aqueous solution of  $\text{Na}_2\text{CO}_3$ . The major concentrations of earth-alkaline cation in the PW before the treatment with  $\text{Na}_2\text{CO}_3$  are given in **Table 4**.

**Table 4.** Concentration of earth-alkaline ions in PW after de-oiling by adsorptive filtration over bleached SCG-OAc/AC.

Earth-alkaline ion	Abundance
Calcium ( $\text{Ca}^{2+}$ )	11300 ppm
Magnesium ( $\text{Mg}^{2+}$ )	2676 ppm
Strontium ( $\text{Sr}^{2+}$ )	416 pm

In the first series of experiments, solid  $\text{Na}_2\text{CO}_3$  (3 g, 5 g, 7 g, all for 200 mL PW) was added to PW within 30 seconds. The precipitate formed was filtered after 10 min., washed with  $\text{H}_2\text{O}$  (50 mL) and dried over  $37^\circ\text{C}$ . Filtrate and washings were kept separate, Thereafter, the cationic composition of the precipitated salt was obtained by ICP-OES analysis (**Figure 8**). **Tables 5-7** and **Figures 9-11** show the remaining content of earth-alkaline metal ions in the treated PW after the filtration of the precipitated metal carbonates. After the addition of 3 g  $\text{Na}_2\text{CO}_3$ /200mL PW, the calcium ion concentration dropped from 11,300 ppm to 4413 ppm. After the addition of 5 g  $\text{Na}_2\text{CO}_3$ /200mL PW, the  $\text{Ca}^{2+}$  concentration in PW diminished to 1647 ppm, dropping to 84.0 ppm after the addition of 7 g  $\text{Na}_2\text{CO}_3$ /200mL PW. Interestingly, magnesium as the second most important earth-alkaline metal found in the studied PW is not as easily crystallized as  $\text{CaCO}_3$  so there is some separation of calcium from magnesium possible, although magnesium remains the most dominant contaminant in the precipitated  $\text{CaCO}_3$  crystals. The solubility products of calcium carbonate, magnesium carbonate, and strontium carbonate are  $4.96 \times 10^{-9}$ ,  $6.82 \times 10^{-6}$ , and  $5.60 \times 10^{-10}$ , respectively [59]. Clearly, magnesium carbonate is more soluble in water than calcium carbonate, with the solubility products of the two magnesium carbonate hydrates  $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$  and  $\text{MgCO}_3 \cdot 5\text{H}_2\text{O}$  tabulated as  $2.38 \times 10^{-6}$  and  $3.79 \times 10^{-6}$ , respectively [59]. Only after most of the calcium content in PW has crystallized as  $\text{CaCO}_3$  and added sodium carbonate delivers further carbonate ions does magnesium start crystallizing more abundantly (**Figure 11**).



**Figure 8.** Schematic presentation of the treatment of PW with  $\text{Na}_2\text{CO}_3$  to precipitate  $\text{CaCO}_3$  and other earth-alkaline carbonates (a) addition of  $\text{Na}_2\text{CO}_3$  to PW; (b) stirring of the resulting solution with precipitation ensuing; (c) filtration of solid earth alkaline carbonates; (d) drying of the solid at  $37^\circ\text{C}$  in a drying cabinet; (e) ICP-analysis.

**Table 5.** Concentration of earth-alkaline ions in PW after addition of 3 g Na<sub>2</sub>CO<sub>3</sub> (solid) for every 200 g PW.

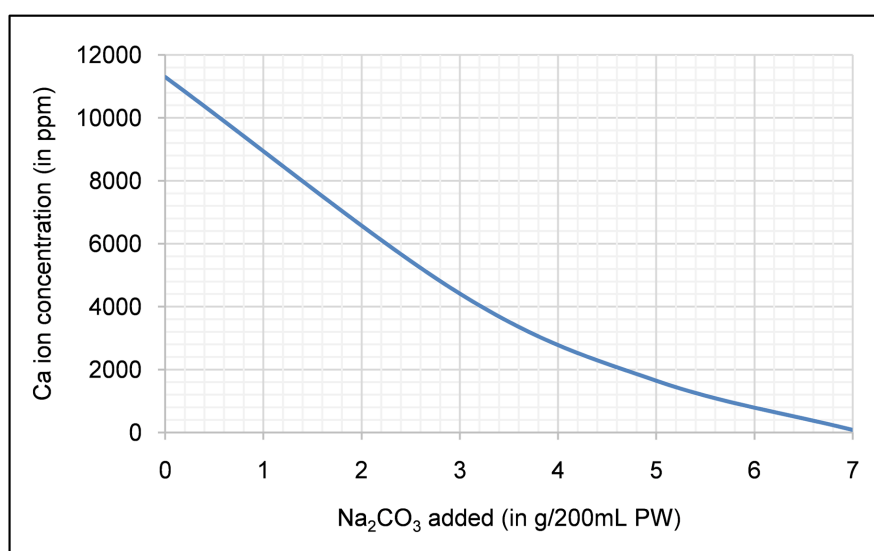
Earth-alkaline ion	Abundance
Calcium (Ca <sup>2+</sup> )	4413 ppm
Magnesium (Mg <sup>2+</sup> )	2483 ppm
Strontium (Sr <sup>2+</sup> )	285.3 ppm

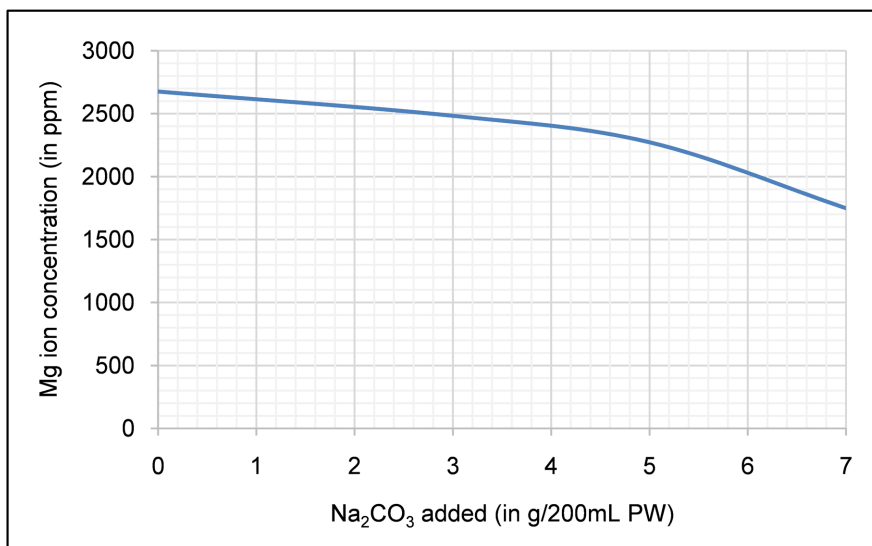
**Table 6.** Concentration of earth-alkaline ions in PW after addition of 5 g Na<sub>2</sub>CO<sub>3</sub> (solid) for every 200 g PW.

Earth-alkaline ion	Abundance
Calcium (Ca <sup>2+</sup> )	1647 ppm
Magnesium (Mg <sup>2+</sup> )	2273 ppm
Strontium (Sr <sup>2+</sup> )	189.2 ppm

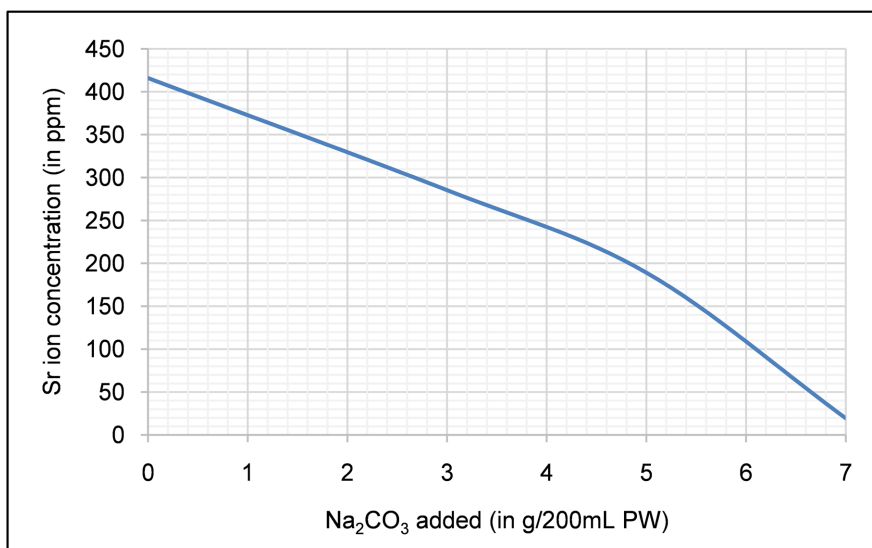
**Table 7.** Concentration of earth-alkaline ions in PW after addition of 7 g Na<sub>2</sub>CO<sub>3</sub> (solid) for every 200 g PW.

Earth-alkaline ion	Abundance
Calcium (Ca <sup>2+</sup> )	84.0 ppm
Magnesium (Mg <sup>2+</sup> )	1749 ppm
Strontium (Sr <sup>2+</sup> )	19.5 ppm

**Figure 9.** Calcium concentration in de-oiled PW as a function of added solid Na<sub>2</sub>CO<sub>3</sub>.



**Figure 10.** Magnesium concentration in de-oiled PW as a function of added solid Na<sub>2</sub>CO<sub>3</sub>.



**Figure 11.** Strontium concentration in de-oiled PW as a function of added solid Na<sub>2</sub>CO<sub>3</sub>.

**Tables 8-14** show the purity of the crystallized CaCO<sub>3</sub> obtained under different conditions. The purity of the crystallized CaCO<sub>3</sub> is high with the first additions of solid Na<sub>2</sub>CO<sub>3</sub> and then drops: 94.41 w% (upon addition of 3 g Na<sub>2</sub>CO<sub>3</sub>, 89.47 w% (upon addition of 7 g Na<sub>2</sub>CO<sub>3</sub>) as also shown in **Table 8**, **Table 10** and **Table 12**. The same holds true when adding a concentrated aqueous solution of Na<sub>2</sub>CO<sub>3</sub>: 92.26 w% (upon addition of conc. aq. Na<sub>2</sub>CO<sub>3</sub> [3 g in 21 mL H<sub>2</sub>O]), 89.76 w% (upon addition of conc aq. Na<sub>2</sub>CO<sub>3</sub> [7 g in 35 mL H<sub>2</sub>O]) as shown in **Table 9** and **Table 13**.

Apart from magnesium, the calcium carbonate precipitate also showed a significant amount of sodium. As sodium salts are quite soluble in water, CaCO<sub>3</sub> crystallized with 5 g solid Na<sub>2</sub>CO<sub>3</sub>/200mL PW was taken up in water (75 mL) af-

ter filtration, and the resulting slurry was stirred at 75°C for 30 min and subsequently filtered. Interestingly, the CaCO<sub>3</sub> precipitate before and after this treatment gave the same CaCO<sub>3</sub> content (92.57 w% vs. 92.58 w%), as shown in **Table 10** and **Table 11**. The authors believe that this could be due to encapsulation of sodium salts by the crystallizing CaCO<sub>3</sub>, where the sodium carbonate crystallites serve as seeding points for the crystallization, and where a concentration gradient in carbonate would be expected from the dissolving sodium carbonate crystallite outwards.

To have a more uniform concentration of carbonate throughout the solution during the crystallization process, a conc. aq. solution of Na<sub>2</sub>CO<sub>3</sub> was added dropwise to PW in a separate series of experiments (**Table 9**, **Table 13**, and **Table 14**). However, the purity differences between the CaCO<sub>3</sub> crystallized by addition of solid Na<sub>2</sub>CO<sub>3</sub> and by addition of a concentrated aqueous solution of Na<sub>2</sub>CO<sub>3</sub> were not markedly different (92.26 w% vs. 94.41 w%), as seen from **Table 11** and **Table 12**. Washing of the filter cake with minimal amounts of H<sub>2</sub>O in the latter procedure did change the purity of the precipitated CaCO<sub>3</sub> (95.48 w% purity vs. 92.58 w% purity), as can be seen in **Table 13** and **Table 14**. Here, most likely Na<sub>2</sub>CO<sub>3</sub> attached to the surface of the CaCO<sub>3</sub> crystals is removed, decreasing the Na<sub>2</sub>CO<sub>3</sub> content from 4.65 w% to 1.30 w%.

**Table 8.** Purity of CaCO<sub>3</sub> precipitated with 7 g solid Na<sub>2</sub>CO<sub>3</sub> (for 200 mL PW).

Metal carbonate	w%	Metal carbonate	w%
CaCO <sub>3</sub>	89.47 w%	K <sub>2</sub> CO <sub>3</sub>	0.047 w%
SrCO <sub>3</sub>	2.00 w%	Na <sub>2</sub> CO <sub>3</sub>	3.21 w%
MgCO <sub>3</sub>	5.26 w%	Others	0.013 w%

**Table 9.** Purity of CaCO<sub>3</sub> precipitated with a conc. aq. solution of Na<sub>2</sub>CO<sub>3</sub> (7 g Na<sub>2</sub>CO<sub>3</sub> in 35 mL H<sub>2</sub>O for 200 mL PW).

Metal carbonate	w%	Metal carbonate	w%
CaCO <sub>3</sub>	89.76 w%	K <sub>2</sub> CO <sub>3</sub>	0.049 w%
SrCO <sub>3</sub>	1.83 w%	Na <sub>2</sub> CO <sub>3</sub>	3.09 w%
MgCO <sub>3</sub>	5.22 w%	Others	0.051 w%

**Table 10.** Purity of CaCO<sub>3</sub> precipitated with 5 g solid Na<sub>2</sub>CO<sub>3</sub> (for 200 mL PW).

Metal carbonate	w%	Metal carbonate	w%
CaCO <sub>3</sub>	92.57 w%	K <sub>2</sub> CO <sub>3</sub>	0.043 w%
SrCO <sub>3</sub>	1.51 w%	Na <sub>2</sub> CO <sub>3</sub>	1.89 w%
MgCO <sub>3</sub>	3.93 w%	Others	0.057 w%

**Table 11.** Purity of CaCO<sub>3</sub> precipitated with 5 g solid Na<sub>2</sub>CO<sub>3</sub> (for 200 mL PW), then washed with hot water (75 mL, 75 °C).

Metal carbonate	w%	Metal carbonate	w%
CaCO <sub>3</sub>	92.58 w%	K <sub>2</sub> CO <sub>3</sub>	0.032 w%
SrCO <sub>3</sub>	1.51 w%	Na <sub>2</sub> CO <sub>3</sub>	1.86 w%
MgCO <sub>3</sub>	3.93 w%	Others	0.088 w%

**Table 12.** Purity of CaCO<sub>3</sub> precipitated with 3 g solid Na<sub>2</sub>CO<sub>3</sub> (for 200 mL PW).

Metal carbonate	w%	Metal carbonate	w%
CaCO <sub>3</sub>	94.41 w%	K <sub>2</sub> CO <sub>3</sub>	0.058 w%
SrCO <sub>3</sub>	1.27 w%	Na <sub>2</sub> CO <sub>3</sub>	1.28 w%
MgCO <sub>3</sub>	2.82 w%	Others	0.162 w%

**Table 13.** Purity of CaCO<sub>3</sub> precipitated with a conc. aq. solution of Na<sub>2</sub>CO<sub>3</sub> (3 g Na<sub>2</sub>CO<sub>3</sub> in 21 mL H<sub>2</sub>O for 200 mL PW).

Metal carbonate	w%	Metal carbonate	w%
CaCO <sub>3</sub>	92.26 w%	K <sub>2</sub> CO <sub>3</sub>	0.0833 w%
SrCO <sub>3</sub>	1.13 w%	Na <sub>2</sub> CO <sub>3</sub>	4.65 w%
MgCO <sub>3</sub>	1.84 w%	Others	0.037 w%

**Table 14.** Purity of CaCO<sub>3</sub> precipitated with a conc. aq. solution of Na<sub>2</sub>CO<sub>3</sub> (3 g Na<sub>2</sub>CO<sub>3</sub> in 21 mL H<sub>2</sub>O for 200 mL PW), precipitate washed with H<sub>2</sub>O (50 mL).

Metal carbonate	w%	Metal carbonate	w%
CaCO <sub>3</sub>	95.48 w%	K <sub>2</sub> CO <sub>3</sub>	0.058 w%
SrCO <sub>3</sub>	1.17 w%	Na <sub>2</sub> CO <sub>3</sub>	1.30 w%
MgCO <sub>3</sub>	1.90 w%	Others	0.092 w%

Apart from being used as construction material, calcium carbonate is used in the production of paints, paper and textiles. It is also used as a filling material in plastics [60] [61] and rubber products such as tires, influencing the mechanical properties of the materials [61]. Furthermore, it finds applications in the adhesive industry and the pharmaceutical industry [62]. Also, in the oil and gas industry calcium carbonate is used as a constituent of drilling fluid [63]. The purity of calcium carbonate is an important factor in the pricing of the material, with typical prices for bulk CaCO<sub>3</sub> for non-industrial uses in the UAE ranging from US\$ 0.4/kg CaCO<sub>3</sub> to US\$ 9.6/kg CaCO<sub>3</sub>. The average import price of CaCO<sub>3</sub> in-

to the UAE stood at US\$ 0.22/kg CaCO<sub>3</sub> in 2022.

#### 4. Recommendations and Outlook

The study showed that PW pre-treated with a three phase separator could be de-oiled effectively by adsorptive filtration over a mixture of activated charcoal and cellulose acetate, where the cellulosic material was obtained from spent coffee grounds, subjected to aq. NaOH extraction and bleaching. The effectiveness of the sorbent material was similar to that derived from non-bleached cellulosic material from SCGs. As the bleaching process only gives a yield of 55.5% and the bleaching itself and subsequent thorough washing of the bleached cellulosic material leads to added liquid waste, the recommendation is to obviate the bleaching process. The authors tried to use leaves of the desert gourd (*Citrullus colocynthis*) as source of cellulosic material. The leaves were dried, extracted with ethanol, subsequently with aq. NaOH and finally bleached. The acetylation of the material with acetyl chloride in *N,N*-dimethylacetamide in the presence of pyridine did not lead to fully acetylated cellulose. Therefore, the material was foregone as sorbent for the adsorptive filtration of PW. This, however, does not preclude using other esterified biomass material in the future.

After the de-oiling process, PW was subjected to the addition of Na<sub>2</sub>CO<sub>3</sub> with which CaCO<sub>3</sub> precipitated from the solution. Here, it was noted that the purity of the precipitated CaCO<sub>3</sub> diminished with a continued addition of Na<sub>2</sub>CO<sub>3</sub>. Therefore, it is advisable to carry out the precipitation of CaCO<sub>3</sub> from PW in batches, where a high purity of CaCO<sub>3</sub> is maintained with the addition of up to about 43w% of the amount needed to complete the precipitation of the CaCO<sub>3</sub> present in the PW.

While the above results are promising, it is important to look at a scale-up of the overall process in the near future.

#### 5. Conclusion

PW from an oil and gas operation situated in South Kuwait that was pre-treated with a three-phase separator was de-oiled by adsorptive filtration. Thereafter, the earth-alkaline metal ions were removed from the filtrate by precipitation as carbonates. Calcium carbonate with a purity as high as 95.48 w% could be obtained from the de-oiled PW by precipitation upon addition of Na<sub>2</sub>CO<sub>3</sub>. Together with the industrial salt (NaCl) that can be obtained in a purity of 99.2 w%, as communicated in an earlier publication, the possibility of attaining CaCO<sub>3</sub> in a purity of 95.5 w% during the purification of PW contributes to the potential of making the treatment of PW from oil and gas a financially sustainable operation by generating products of commercial value.

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measurements to determine the cation content of the crystallized salt.

## Conflicts of Interest

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

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