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Synthesis of calcium propionate from indigenous limestone from Swat area in Pakistan

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RESEARCH ARTICLE

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ABSTRACT

In this study, native limestone from the Swat area of Pakistan was used for the synthesis of calcium propionate. The powdered limestone was allowed to react with propionic acid and the effect of the synthesis parameters, that is, the particle size (50, 100, 150, and 200 mesh), propionic acid (10, 15, and 30 %), solid-liquid ratio (0.1:10, 0.12:1, 0.14:1, and 0.16:1), reaction time (1, 1.5, 2, and 2.5 hours) and the temperature (60, 80, 90, and 100 °C) on the percentage yield and purity of calcium propionate was studied. The results showed that the optimum synthesis parameters were 200 mesh particle size, 15% propionic acid concentration, 0.14:1 solid-liquid ratio, 2.5 hours reaction time, and 80 °C temperature. The product obtained under optimal conditions was characterized by infrared spectroscopy, thermogravimetry, and scanning electron microscopy. The results revealed that a product having ≥ 99.8% purity with 85% yield can be obtained by this process.

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1. Introduction

Pakistan is endowed with huge deposits of limestone ranging from medium to high grade, distributed in the Upper and Lower Indus basin, Peshawar basin, Hazara basin, Khyber Agency, Kohistan Island Arc, Attock–Cherat Range, Karakoram, Balochistan, and Axial Belt [1-3]. It is a sedimentary rock composed of calcium carbonate, *i.e.*, calcite mineral with some impurities such as iron, clay, magnesium, sand, organic matter, *etc.* [4]. Limestone is of great economic importance due to its wide industrial applications. It is an essential part of cement formulation and is used as crushed stone for concrete aggregates and road construction materials. It is also a fluxing agent for steel and a soil conditioner for neutralizing acidic soils. Other applications include its use in paper, plastics, rubber, tiles, paint, toothpaste, pharmacy, sugar refining, cosmetics, and abrasives. Geological formulations comprising of limestone are considered as one of the best hydrocarbon reservoirs in the world [2,4-6]. Limestone has also been reported to be a calcium source for the preparation of calcium salts [7]. Hongyi synthesized calcium chloride dihydrate from limestone [8]. El-Sherbiny *et al.* prepared a calcium carbonate nanofiller from limestone [9].

One of the most commonly used calcium salts is calcium propionate. It is found in either crystalline or powder form. It is sufficiently soluble in water, but sparingly soluble in alcohol. It finds its main use as a food preservative in breads and other baked items because of its ability to control the growth of microorganisms by preventing them from reproducing and causing a risk to human health. In fact, propionic acid is found naturally in some foods, such as certain types of cheese containing up to 1% propionic acid, which acts as a natural preservative. However, the antimicrobial property of calcium propionate has a negligible effect on yeast that makes it an ideal choice for commercial-scale products. The efficacy of propionates strongly depends on the pH of the food, where pH = 5.5 is the upper effective limit. The presence of propionate helps to improve the shelf life of food products [10-12]. Calcium propionate is usually prepared by a neutralization reaction of propionic acid with a base like calcium hydroxide, calcium oxide, calcium carbonate, egg, or oyster shell. The neutral salt thus obtained is concentrated and dehydrated to obtain the desired product [12]. Weidong *et al.* disclosed a method for preparing calcium propionate using calcium hydroxide as a calcium precursor and obtained a product of more than 99.8% purity [13].

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Table 1. Chemical analysis of limestone.

Constituents	%
Loss on ignition (LOI)	43.36
Silica (SiO_2)	0.52
Aluminum oxide (Al_2O_3)	0.25
Iron oxide (Fe_2O_3)	Traces
Calcium oxide (CaO)	55.25
Magnesium oxide (MgO)	0.46
Sodium oxide (Na_2O)	0.07
Potassium oxide (K_2O)	0.05

Similarly, Baocheng *et al.* obtained 99.1 to 100% purity calcium propionate by reaction of calcium hydroxide with propionic acid [14]. Recently, Yao and colleagues optimized the process parameters for the preparation of calcium propionate from egg shell [15].

In this research, calcium propionate was synthesized using the indigenous limestone of the Swat area of Pakistan as a source of calcium and the influence of various reaction parameters has been investigated to obtain the maximum yield and purity of the product. The obtained product was characterized by IR, TGA, and SEM techniques.

2. Experimental

2.1. Materials

Limestone ($CaCO_3$) from the Swat area of Pakistan and analytical grade propionic acid were used.

2.2. Chemical analysis of limestone

The chemical analysis of the limestone was carried out by applying the standard methods.

2.2.1. Loss on ignition

Loss in ignition was carried out by accurately weighing about 1.0 g of ground calcium carbonate in a dried porcelain crucible in a muffle furnace at 1000-1100 °C for 30 minutes and then calculating the percentage loss in weight.

2.2.2. Impure silica/insoluble matter

The residue from loss on ignition was dissolved in 1:1 hydrochloric acid and then concentrated hydrochloric acid and nitric acid were added followed by evaporation till complete drying and again dissolving the residue in dilute hydrochloric acid followed by filtration and complete washing. This procedure was carried out for another time, and the combined precipitates were ignited and weighed to calculate the impure silica/insoluble matter.

2.2.3. Combined oxides (R_2O_3)

The combined filtrates were diluted, and the combined oxides were precipitated at alkaline pH. The precipitates were filtered, washed, and ignited for calculating the percentage of combined oxides.

2.2.4. Calcium oxide

The filtrate of combined oxides was used for the precipitation of calcium with ammonium oxalate solution. The precipitates were filtered, washed, and ignited to calculate the percentage of calcium oxide.

2.2.5. Magnesium oxide

The filtrate from the determination of calcium was used for the precipitation of magnesium with ammonium phosphate reagent. The precipitates were filtered, washed, and ignited for calculating the percentage of magnesium oxide.

2.2.6. Sodium oxide and potassium oxide

The filtrate after analyzing magnesium was used for the determination of sodium and potassium by flame photometry using the Jenway PFP-7 Flame Photometer [16].

2.3. Sample preparation

The limestone was ground to obtain various fractions of 50, 100, 150, and 200 mesh size. Batch experiments were conducted to optimize the reaction parameters such as particle size, propionic acid concentration, solid-liquid ratio, reaction time, and temperature. The effect of these variables was investigated by varying the particle size (50, 100, 150 and 200 mesh), propionic acid (10, 15, and 30%), solid-liquid ratio (0.1:10, 0.12:1, 0.14:1 and 0.16:1), reaction time (1.0, 1.5, 2.0 and 2.5 hours) and the temperature (60, 80, 90 and 100 °C). In each experiment, the weighed quantity of limestone was treated with a specific volume of propionic acid solution of known concentration. The reaction mixture was heated at an ambient temperature with continuous stirring for a limited time duration until there was no more effervescence. The mixture was filtered and evaporated to obtain a saturated solution that was cooled to obtain crystals of calcium propionate. The crystals were further dried at 100 °C to completely remove moisture.

2.4. Characterization

The product obtained by keeping the optimum conditions was characterized by infrared spectroscopy performed with Agilent Technologies infrared spectrometer. Thermal analysis was carried out from room temperature to 1000 °C at a rate of 10 °C/min using the Leco TGA701 thermogravimetric analyzer. Surface morphology was studied using the ZEISS SEM scanning electron microscope.

3. Results and discussion

3.1. Chemical analysis of limestone

The chemical analysis of limestone showed the results reported in Table 1. The results indicate that high-grade limestone was used for the present study that contains 55.25 % calcium oxide content.

3.2. Parameter optimization

3.2.1. Effect of particle size

The effect of the limestone particle size on the calcium propionate yield was investigated by varying the particle size from 50 to 200 mesh passing. Other leaching parameters were kept constant at a propionic acid concentration of 1.5 %, solid-liquid ratio 0.14:1, reaction time 2 hours, and reaction temperature 90 °C.

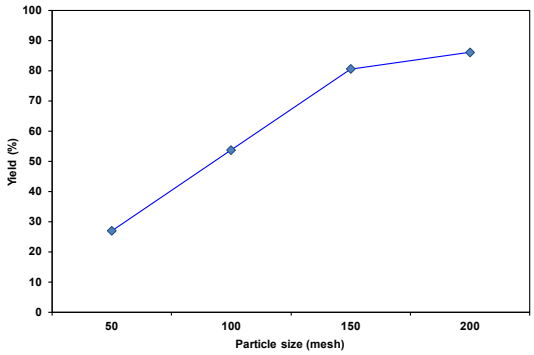

Figure 1. Effect of particle size on the percentage yield of calcium propionate.

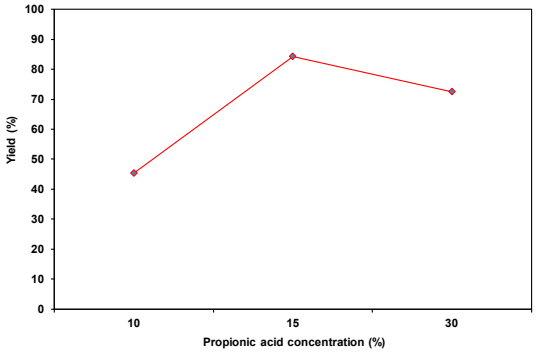

Figure 2. Effect of the concentration of propionic acid on the percentage yield of calcium propionate.

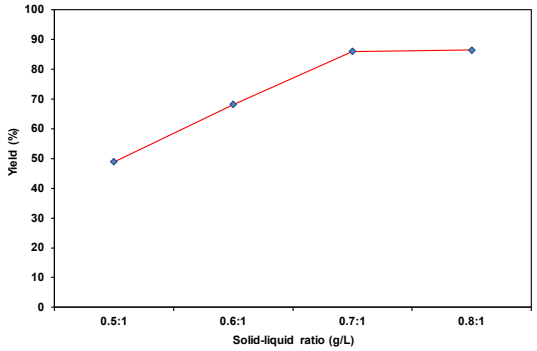

Figure 3. Effect of the solid-liquid ratio on the percentage yield of calcium propionate.

The results are plotted in Figure 1, which shows a regular increase in the calcium propionate yield with the decrease in the size of the limestone particles. When the particle size decreased from 50 to 100 mesh passing, the yield increased from 26.87 to 53.75% followed by 80.60 and 86.10% at 150 and 200 mesh size, respectively. These results revealed that the reaction rate of limestone with propionic acid and its conversion to calcium propionate increased with the finer particle size, and hence, the maximum yield was obtained at the finest limestone size. Therefore, 200 mesh of limestone was found to be the optimum particle size to carry out the present study.

3.2.2. Effect of propionic acid concentration

The effect of propionic acid concentration on the calcium propionate yield was studied by varying its concentration from 10 to 30 % keeping all other reaction parameters constant, and the results are illustrated in Figure 2. The figure shows that with an increase in the concentration of propionic acid, the yield first increases to a maximum of 84.25% since a 15% concentration containing a sufficient quantity of propionic acid leads to the completion of reaction. However, as the concentration of propionic acid increased to 30%, the calcium propionate yield subsequently decreased to 72.51% due to the decrease in solubility with its saturation in the aqueous solution. Therefore, 15% of propionic acid was selected as the optimal concentration for the preparation of calcium propionate from limestone.

3.2.3. Effect of solid-liquid ratio

To investigate the effect of the solid-liquid ratio on calcium propionate yield, synthesis experiments were carried out in solid-liquid ratios 0.1: 1, 0.12: 1, 0.14: 1 and 0.16: 1 for the limestone and propionic acid solution, while other parameters were kept invariable and the results are demonstrated in Figure 3. The figure shows that as the solid-liquid ratio increased, the percentage yield of calcium propionate also increased. It shows a profound increase from 0.1:1 to 0.12:1 *i.e.* 48.89 to 68.23%

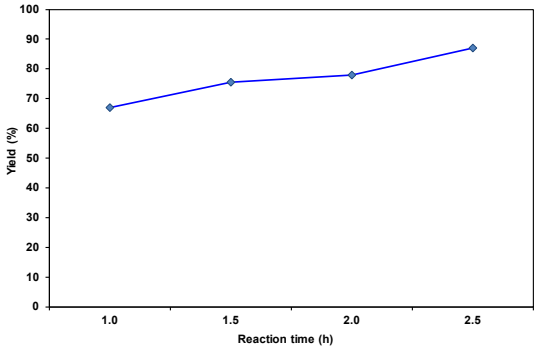

Figure 4. Effect of the reaction time on the percentage yield of calcium propionate.

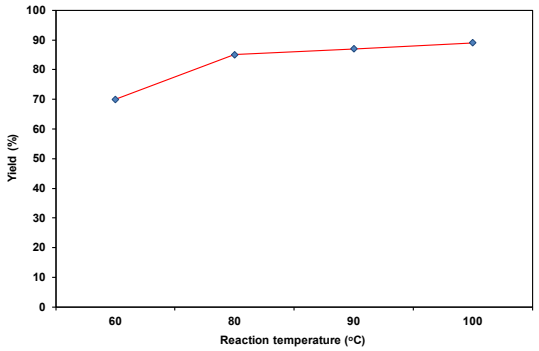

Figure 5. Effect of the reaction temperature on the percentage yield of calcium propionate.

and then again reached 86.04% in the 0.14:1 ratio. However, an additional increase in the solid-liquid ratio to 0.16:1 showed stability in the percentage yield, that is, 86.42%. These results showed that the reaction of limestone with propionic acid remained incomplete at 0.1:1 and 0.12:1 ratios and reached equilibrium at 0.14:1 ratio. Therefore, 0.14:1 was found to be sufficient for the synthesis of calcium propionate.

3.2.4. Effect of reaction time

The effect of the reaction time on the calcium propionate yield prepared from limestone is shown in Figure 4. The product was synthesized by performing the reaction for 1, 1.5, 2, and 2.5 hours, keeping all other parameters constant. The figure presents a notable increase in the percentage yield of calcium propionate with the increase in reaction time leading to a maximum of 87.01% in 2.5 hours. Therefore, 2.5 hours were found to be the optimum reaction time for the present study.

3.2.5. Effect of reaction temperature

The percentage yield of calcium propionate as a function of the reaction temperature (60, 80, 90, and 100 °C) keeping the other reaction parameters constant is shown in Figure 5. The results showed that the percentage yield had a tendency to increase with increasing reaction temperature. A considerable increase can be observed with the increase in temperature from 60 to 80 ° C, i.e., 70.01 to 85.03% followed by a trivial change in the quantity of the product obtained, i.e., 87.04 and 89.02% with the further increase in temperature from 90 to 100 °C. Therefore, carrying out the synthesis at temperatures above 80 °C seems to be insignificant. In fact, the number of activated molecules of the solute increases with the increase in temperature, resulting in an increase in the effective collisions, thus increasing the yield of the product. Furthermore, the volatilization of propionic acid increases with temperature. However, these phenomena take place to a certain extent and further rise in temperature leads to a decrease in the yield of the product [13]. Therefore, it was found that 80 °C was the appropriate temperature for the preparation of calcium propionate from limestone.

3.3. Characterization

3.3.1. Infrared spectroscopy

The IR spectrum of the prepared calcium propionate was recorded in the frequency range of 4000-600 cm^{-1} and is illustrated in Figure 6. The spectrum demonstrates a weak broad absorption band at 3258 cm^{-1} corresponding to the stretching vibrations of hydroxyl groups of surface adsorbed water molecules. The absorption band at 2974 cm^{-1} is associated with the stretching vibrations of the alkyl groups. The distinct absorption band in the region 1610-1550 cm^{-1} is typical for asymmetric stretching modes of the CO_2^- group of carboxylic acid salts. The multiple bands merged in the region 1470-1420 cm^{-1} are also specific for CO_2^- group symmetric stretching modes of the calcium salts [14,17,18]. Researchers have reported that the carboxyl group–metal linkage makes some spectral changes compared to the acid regardless of the acid selected, whether a monocarboxylic acid, hydroxy acid, amino acid, *etc*. It is obvious from these results that the band around 1700 cm^{-1} due to the stretching modes of the carbonyl group C=O of carboxylic acid disappeared, which confirms the formation of calcium propionate [19].

The sharp absorption band at 1297 cm^{-1} and another weaker band at 1081 cm^{-1} are observed due to the C–O stretching vibrations, since the region 1300-1000 cm^{-1} is attributed to these vibrations [20]. Furthermore, absorption bands of relatively less intensity in the frequency range 950-800 cm^{-1} are assigned to the deformation of stretching vibrations of carboxylate ions [19]. Another weaker and broad band at 671 cm^{-1} is related to the bending vibrations of the C–O bond [14].

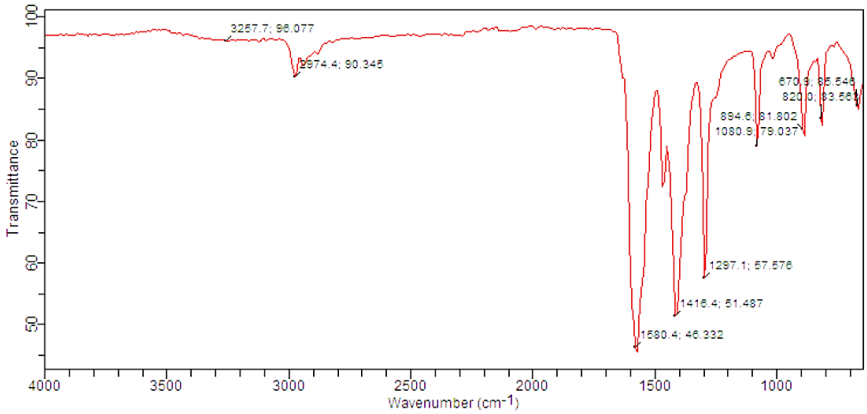

Figure 6. Infrared spectrum of calcium propionate.

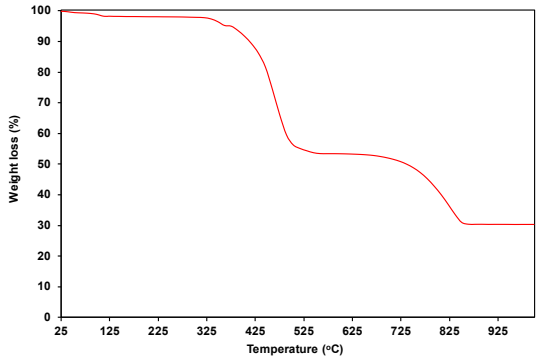

Figure 7. Thermogravimetric analysis of calcium propionate.

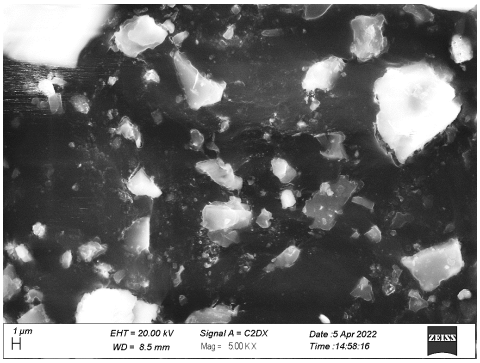

Figure 8. SEM micrograph of calcium propionate at 5000× magnification.

3.3.2. Thermal analysis

Figure 7 illustrates the calcium propionate TGA curve, where in the first stage a gradual weight loss occurred followed by an abrupt decrease in mass resulting in a total weight loss of 46.33% till 545 ° C due to the decomposition of calcium propionate into $CaCO_3$. During this phase, an organic compound pentanone ($C_5H_{10}O$) is emitted from calcium propionate according to the following equation, since the observed mass loss is very close to the ideal value of 46.24% for this thermal decomposition reaction [21].

$$(CH_3CH_2COO)_2Ca \rightarrow CaCO_3 + C_5H_{10}O \quad (1)$$

It shows that 53.67% of the initial mass remained at 545 °C, which is equivalent to the theoretical mass of 53.7% attributed to calcium carbonate [6]. At the second stage, the weight again decreased, which continued until 900 °C, *i.e.,* 23.37% as the residue was further decomposed to calcium oxide, which is equivalent to the theoretical weight loss of $CaCO_3$ when it decomposes to CaO and CO_2 i.e. 23.62 % according to the following stoichiometric equation [21]:

$$CaCO_3 \rightarrow CaO + CO_2 \quad (2)$$

Therefore, based on the TGA results, it can be inferred that calcium propionate of >99.8% purity has been synthesized.

3.3.3. Scanning electron microscopy

The surface morphology of the prepared calcium propionate was studied by scanning electron microscopy. The micrograph recorded at 5000× magnification is shown in Figure 8. The figure shows calcium propionate particles aggregated to form clusters ranging from a few to several microns in size. This cluster formation can be attributed to the high surface energy

attained by the fine particles during their synthesis. As a result of this, the particles usually combine through weak van der Waals forces to lower their energy [22].

In the recent past, researchers have employed eggshells to produce calcium propionate, turning the waste material into a valuable product [13], but the availability of raw material seems to be limited. However, the present study reveals that high purity calcium propionate can be obtained by a novel process using indigenous resources since limestone is locally available as huge deposits in Pakistan. In addition, the process involves a single-step reaction and operates under mild conditions which make it feasible for large-scale production.

4. Conclusions

Calcium propionate has been successfully prepared using indigenous limestone as a raw material in the process comprising of its reaction with propionic acid. Parameter optimization studies identified the optimal conditions to be 200 mesh particle size, 15% propionic acid concentration, 0.14:1 solid-liquid ratio, 2.5 hours reaction time, and 80 °C temperature. The product obtained by keeping the optimal conditions was characterized for its purity and surface morphology. Infrared spectroscopy confirmed the presence of propionate, whereas thermogravimetric analysis proved the purity of calcium propionate. Scanning electron microscopy showed that the fine particles of calcium propionate aggregated to form clusters ranging from a few to several micrometers in size. Therefore, based on these results, it can be inferred that a product having ≥ 99.8% purity with 85% yield can be obtained by this process.

Disclosure statement

Conflict of interest: The authors declare that they have no conflict of interest.
Ethical approval: All ethical guidelines have been adhered.
Sample availability: Samples of the compounds are available from the author.

CRediT authorship contribution statement

Conceptualization: Ansar Mahmood; Methodology: Ansar Mahmood; Investigation: Ansar Mahmood; Data Curation: Rashid Mahmood, Asma Sheikh; Writing - Review and Editing: Samreen Zahra; Supervision: Samreen Zahra; Project Administration: Samreen Zahra.

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