



# Utilization of paper sludge in preparation of high-purity calcium formate

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## Abstract

Paper sludge generated from recycling of printed paper is a negative value waste since cellulosic fibers in the sludge are too damaged to be used in paper making and, more important, the sludge has very high content of ash (up to ~ 35%) and ink residues. To be able to utilize cellulosic fibers in bio-conversion industries which depend on saccharification of the fibers into sugars, de-ashing of the sludge is necessary. The major component of the ash is fillers used in paper making, especially calcium carbonate. In the current work, high-purity calcium formate was prepared utilizing calcium carbonate in the paper sludge — as a zero-value precursor — via treatment with formic acid under controlled conditions. The synthesized calcium formate was characterized using Fourier transform infrared (FTIR), X-ray diffraction (XRD), X-ray fluorescence (XRF), thermogravimetric analysis (TGA), and scanning electron microscopy coupled with energy dispersive X-ray analysis (SEM–EDX). Calcium formate synthesized using paper sludge was compared to that prepared by reacting pure precipitated calcium carbonate and formic acid using the aforementioned tools of analyses. The results confirmed successful preparation of calcium formate with high-purity (99%) with orthorhombic crystal structure from paper sludge as pure as that prepared using pure commercially available precipitated calcium carbonate. The results and approach used in the current work could convert paper sludge to value-added products with high profit and at the same time reduce the huge amounts of land-filled sludge.

**Keywords** Paper sludge · Recycling · Calcium carbonate · Calcium formate · Orthorhombic crystals · Papermaking · Tissue paper

## 1 Introduction

Paper sludge is one of the main wastes resulting from paper industry, specifically paper sludge resulting from paper recycling processes for use in tissue paper products. The sludge contains large amounts of insoluble materials (up to 35% based on dry weight), which are usually fillers used in paper industry such as calcium carbonate, talc powder, kaolin, and alum (the double salt of aluminum sulfate) used in sizing of paper. Calcium carbonate constitutes the main

content of fillers in the sludge, since it is the most widely filler used due to its prevalence and lower cost than the other aforementioned fillers [1].

The sludge also contains cellulose pulp fibers, which are the basic material in the paper industry; but these fibers are not suitable for use in paper products due to their extreme shortness and poor mechanical properties [2, 3].

This sludge is a huge burden on the paper mills, as it is considered as “negative value” waste. The traditional disposal methods are mainly landfill and incineration. Landfill and incineration cause secondary pollution to the environment in addition to transportation cost and fees imposed by regulations. Therefore, developing environmentally friendly and economic utilization methods are the keys for sustainability of papermaking from recycled fibers.

Utilization of paper mill sludge, either as a whole or its different constituents, has been extensively studied in different ways and applications. For examples, paper mill sludge as a whole was used for production of hydrogen from steam gasification [4], biogas production [5], preparation of

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biochar [6], as a substrate for growth of bacteria for production of biodiesel [7, 8], a substrate for saccharification to get sugars for biofuel and other bio-based chemicals production [9–12], preparation of activated carbon [13, 14], removal of textile dyes [15], soil composting [16–18], removal of ammonia nitrogen from landfill leachate [19], manufacture of artificial bed soils [20, 21], medium density fiberboard manufacture [22], in paper coating [23], and additives in concrete [24].

Due to the high ash content in paper sludge, several studies have been published regarding utilization of the ash in different applications. For examples, use in construction materials such as lime-based geopolymer concrete [25], cement and ceramics [26], in preparation of metakaolinite-based cementitious binder [27], manufacture of building bricks [28], filler in papermaking [29, 30], preparation of ceramics [31], and adsorption of ionic dyes [32].

In order to use cellulose fibers in paper sludge in economically feasible products such as the production of biofuels and other chemicals, it is necessary to remove and benefit from those aforementioned non-cellulosic materials, in particular fillers such as calcium carbonate, so as not to negatively affect the properties and the quality of the products to be manufactured. Taking in account the huge amount of generated paper sludge, the high calcium carbonate content of paper sludge, and the price of the paper-grade calcium carbonate (<https://www.chemanalyst.com/Pricing-data/calcium-carbonate-1158>) (lowest price was ~ 132 US\$/ton in the second half of 2023) means that we have huge amount of money needs to be invested in a better way that lead to conversion of this sludge from waste with a negative value to a raw material without cost for manufacturing important materials with high economic profit and uses in different industries.

Calcium formate is an important chemical compound with multiple uses. The global calcium formate market was valued at USD 545 million in 2020 and is expected to reach USD 713 million by 2025, growing at 5.5% from 2020 to 2025 (<https://www.marketsandmarkets.com/Market-Reports/calcium-formate-market-191530782.html>). Calcium formate is used as a preservative additive in animal feed (known as E238 additive) because it is antibacterial, anti-mold, and has an acidic effect; it is also used as an additive to animal feed, as it increases appetite and reduces diarrhea [33, 34]. Calcium formate also finds use in concrete admixtures, where its addition leads to reducing the time of setting, especially at low temperatures, and increase the strength properties of concrete [35–37]. Calcium formate is used in gypsum boards as a fire-resistant material as well as increasing the mechanical strength properties of the boards [38, 39]. In power plants, calcium formate is used as a purification solution because it removes sulfur dioxide from fossil fuel exhaust [40]. In

addition, calcium formate is industrially used in leather tanning, in pickling of food, as a rust inhibitor for some metals, for improving performance and strength of adhesives, and in deicing and antifreeze additives.

So far, the methods of producing calcium formate depend on those published or patented; some of them have disadvantages as follows:

1. Cracking chloral with calcium hydroxide during the chloroform production process [41]. In this method, the produced calcium formate contains insoluble secondary compounds, which are difficult to eliminate.
2. Reaction of calcium hydroxide solution with formaldehyde in the presence or absence of hydrogen peroxide [42].
3. Reaction of formaldehyde solution with calcium hydroxide in the presence of boric acid or one of its salts as a catalyst [43]; the produced calcium formate contains residues of boric acid or its salts, as they dissolve in water like the formed calcium formate.
4. Reaction of carbon monoxide with a saturated solution of calcium hydroxide [44]; the reaction takes place at high temperatures ranging from 120 to 220 °C and under high pressure (~6 MPa).
5. Co-hydrolysis reaction in aqueous solutions of a mixture of sodium formate and calcium nitrate or chloride [45]; the method requires first preparing sodium formate salt, and also the reaction is reversible. This is in addition to the formation of residual crystals of sodium chloride or nitrate that result from the interaction with calcium formate.
6. Calcium formate was also prepared from calcium carbide residue via its reaction with carbon monoxide through carbonylation synthesis route [46]; the reaction requires a temperature of up to 200 °C and high pressure.
7. Reaction of dilute formic acid (11–12%) with calcium carbonate followed by addition of calcium hydroxide to pH 6–8 to neutralize the excess acid [47].

In order to reduce the cost of production of calcium formate, and at the same time to find alternative eco-friendly ways for dealing with the huge amount of paper sludge (as a raw material with zero cost), as well as establishing new industry for bio-based chemicals, the current work aimed at utilizing paper sludge for production of calcium formate with high purity via selective reaction of dilute formic acid with calcium carbonate filler exists without cost in the sludge in high amounts. To the best of our knowledge, this is the first time to utilize paper sludge in preparation of calcium formate with high purity using simple and scalable method.

## 2 Experimental

### 2.1 Materials

Paper sludge from recycling printing and writing paper after de-inking, as a negative-value material without cost, was kindly supplied by Interstat Company for Paper. It was pressed to ~35% solid content and kept in fridge at 4 °C until use.

Formic acid, precipitated calcium carbonate, formic acid, absolute ethanol, phenol, sulfuric acid (98%), toluene, phenol, sodium hydroxide, glacial acetic acid, and glucose were analytical grade purchased from Fisher Scientific UK Ltd (Loughborough, UK) and used as received. For chemical analyses, the sludge was dried at 40 °C for 48 h in an oven with air circulation.

### 2.2 Chemical analyses of paper sludge

Total sugars of paper sludge before and after formic acid treatment were determined using the standard phenol/sulfuric acid hydrolysis method [48], where optical absorbance at ~486 nm was measured using Jenway 7305 UV–visible spectrophotometer (Jenway, Staffordshire, England); the sludge was first hydrolyzed using 72% sulfuric acid (TAPPI standard T 222). The concentration of the hydrolyzed sugars was expressed as glucose.  $\alpha$ -cellulose content was determined using TAPPI standard method (TAPPI standard T 429). Extractives content was determined using ethanol/toluene mixture (TAPPI standard T 204). The ash content was determined by using muffle furnace (TAPPI standard T 413). The produced ash was further analyzed to know its exact composition by wavelength dispersive X-ray fluorescence (XRF) using Axios advanced sequential WDXRF spectrometer (Panalytical, Malvern, UK) and X-ray diffraction (XRD) using an D8 Advance Bruker X-ray diffractometer (Bruker, Billerica, USA) equipped with Cu K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ) at 40 kV and 40 mA. The diffractograms were recorded at ambient conditions in a  $2\theta$  range from 10° to 80° with scanning steps of 0.02° and an exposure of 4 s per step.

SEM and energy dispersive X-ray spectroscopy (EDX) were carried out using FEI Quanta 200 scanning electron microscope (FEI Company BV, Eindhoven, the Netherlands) with an acceleration voltage of 20 kV; the EDX spectra were displayed on TEAM ® software. Before scanning, paper sludge sample was coated with gold using a sputter coater system (Edwards Sputter Coater, Sussex, UK).

### 2.3 Preparation of calcium formate from paper sludge

Paper sludge was treated with 0.05 N formic acid at liquor ratio of 1:10 at 40 °C for 2 h with stirring. The

aforementioned conditions used in the treatment were reached after optimization several experiments to get the highest possible yield with good purity. The treated sludge was filtered under vacuum using filter paper (Whatman filter paper No. 1), and the liquor containing the prepared calcium formate was collected. The liquor was concentrated using rotary evaporator at 65 °C under vacuum to about third its volume. After cooling, the concentrated liquor was poured in absolute ethanol to precipitate calcium formate (volume of alcohol to liquor was 3:1). The product was further washed with absolute ethanol and finally oven-dried at 70 °C. For comparison, calcium formate was also prepared using precipitated calcium carbonate and 0.05 N formic acid in stoichiometric ratio. The produced calcium formate was precipitated by pouring in absolute ethanol, washed with absolute ethanol, and oven-dried at 70 °C.

### 2.4 Characterization of calcium formate

The crystallographic structure of calcium formate was studied by X-ray powder diffraction using Bruker D8 Advance X-ray diffractometer (Bruker, Billerica, USA) equipped with Cu K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ) at 40 kV and 40 mA. The diffractograms were recorded at ambient conditions in a  $2\theta$  range from 10° to 80° with scanning steps of 0.02° and an exposure of 4 s per step. The instrumental broadening was corrected using quartz standard sample. Thermogravimetric analysis (TGA) of the prepared calcium formate was carried out using Setaram Themys one + instrument (Setaram Instrumentation, Caluire, France). The analysis was carried out from 30 to 1000 °C under nitrogen atmosphere (purge rate 50 ml/min) and heating rate was 10 °C/min. FTIR spectra of calcium formate were recorded using a Bruker Alpha-P ATR FTIR Spectrometer (Bruker, Billerica, USA); the resolution of measurement was 4 cm<sup>-1</sup>. SEM and EDX analysis were carried out using FEI Quanta 200 scanning electron microscope (FEI Company BV, Eindhoven, the Netherlands) with an acceleration voltage of 20 kV; the EDX spectra were displayed on TEAM ® software. Wavelength dispersive X-ray fluorescence (XRF) was carried out using Axios advanced sequential WDXRF spectrometer (Panalytical, Malvern, UK).

## 3 Results and discussion

### 3.1 Chemical analyses of paper sludge

To get representative analytical results as much as possible, samples from paper sludge were collected at different days from the paper mill. Table 1 shows chemical composition of paper sludge. As shown in the table, paper sludge contains high ash content, low ethanol/toluene extractives

contents, also relatively low  $\alpha$ -cellulose content, and thus low total sugar content. It should be noted that the ash content is generally the oxide form of the inorganic compounds in the sludge, i.e., actual weight of inorganic materials is higher than the ash content.

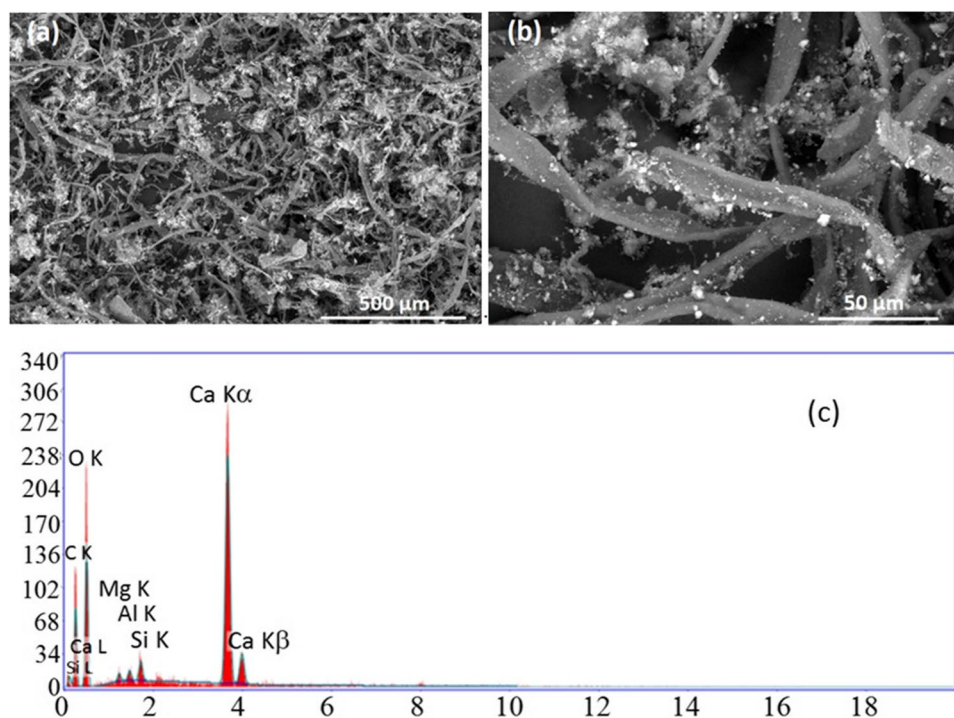
### 3.2 SEM and EDX analysis of paper sludge

In addition to chemical analyses of paper sludge shown above, microscopic investigation was carried using SEM (Fig. 1a, b). As the images show, there was noticeable amount of non-fibrous material due to the high ash content and other extractives. EDX analysis was used to investigate more the paper sludge (Fig. 1c). As the results show, paper sludge contains significant amounts of calcium compounds and smaller amounts of silica, aluminum, and magnesium-containing compounds, in addition to presence of carbon and oxygen which could be due to presence of cellulosic fibers, extractives, and also the aforementioned inorganic compounds.

**Table 1** Chemical composition of paper sludge

Ash content (wt. %)	Ethanol/toluene extractives (wt. %)	$\alpha$ -cellulose (wt. %)	Total sugars (as g glucose/g sample)
33.45 $\pm$ 4.34	7.13 $\pm$ 1.28	39.91 $\pm$ 1.29	0.26 $\pm$ 0.039

**Fig. 1** Scanning electron microscopy (SEM) image of paper sludge at different magnifications (a and b) and energy dispersive X-ray spectroscopy (EDX) spectrum of paper sludge (c)

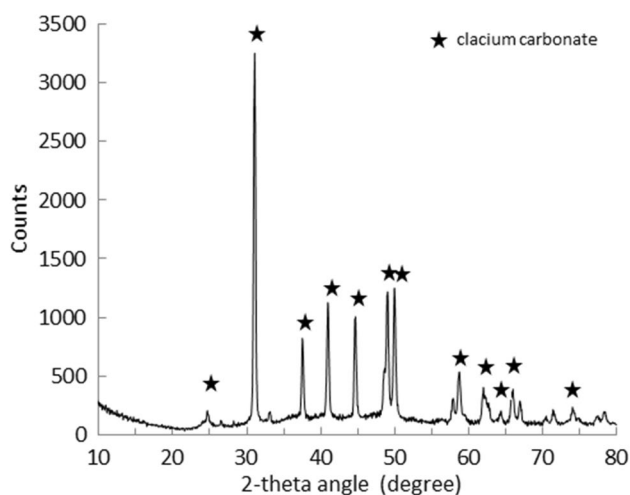


### 3.3 XRD of paper sludge

To get deeper information about the composition of paper sludge, XRD analysis was carried out. As shown in Fig. 2, the diffraction pattern of paper sludge showed complicated pattern due to presence of different materials in addition to the cellulosic fibers. Due to the high ash content and the much higher crystallinity of the ash compounds than cellulose, the diffraction peaks due to cellulose were very weak. The main diffraction peaks appeared in the pattern of paper sludge indicates presence of calcium carbonate filler with calcite crystal structure as a major component (JCPDS 47–1743 card) [49]. Other minor peaks could be attributed to the presence of kaolin (aluminum silicate) and magnesium silicate (talc powder), which are used as fillers in paper, and also the presence of residual alum (hydrated aluminum sulfate) used in paper making during the sizing process.

### 3.4 XRF analysis of paper sludge

The above results showed presence of considerable amount of ash in paper sludge (33.5%) which contains mainly calcium carbonate filler in addition to the presence of silica, aluminum, and magnesium-containing compounds. Therefore, paper sludge was further analyzed by XRF, and the results are shown in Table 2. As shown in the table, the main constituent in the sludge was CaO originated from calcium carbonate filler. The other significant amounts of oxides were those of silica and alumina, which could be originated from the use of kaolin (aluminum silicate) or



**Fig. 2** X-ray diffraction (XRD) patterns of paper sludge

**Table 2** XRF analysis of paper sludge

Element	Constituent	Wt. %
Ca	CaO	26.43
Si	SiO <sub>2</sub>	2.99
Al	Al <sub>2</sub> O <sub>3</sub>	2.03
Mg	MgO	0.46
Na	Na <sub>2</sub> O	0.42
Fe	Fe <sub>2</sub> O <sub>3</sub>	0.32
Cl	Cl	0.24
S	SO <sub>3</sub>	0.23
Ti	TiO <sub>2</sub>	0.08
Sr	SrO	0.076
K	K <sub>2</sub> O	0.04
P	P <sub>2</sub> O <sub>5</sub>	0.05
Mn	MnO	0.022
Cu	CuO	0.016
Zn	ZnO	0.011
Ni	NiO	0.007
Loss in ignition		66.58

alum as mentioned before. The other traces of oxides could be originated from other additives, inks, and the aforementioned fillers (calcium carbonate and kaoline). The loss due to ignition of the sample (66.58%) was in accordance with the determined ash content of sludge.

### 3.5 Treatment of paper sludge with dilute formic acid

Presence of high amounts of fillers and inorganic impurities can negatively affect the utilization of cellulose fibers in paper sludge for obtaining sugars in order to transform them

into bio-based chemicals. Therefore, decreasing this high amount of ash to an acceptable level is necessary to allow utilization of paper sludge in such applications. At the same time, it is also important to recycle the high amount of ash in order to make using of paper sludge economically feasible.

In the current work, paper sludge was treated with dilute formic acid. Since formic acid is a weak acid, it can selectively react with the water insoluble calcium carbonate but not with other salts of strong acids, i.e., sulfates, chlorides, and nitrates. Dilute formic acid has also insignificant effect on cellulose and hemicelluloses in the sludge fibers. Reaction of formic acid with the ash generates also formation of carbon dioxide as shown in Eq. (1).



In fact, formation of pure carbon dioxide gas is another important product from the process and can add sustainability and economic profit. Carbon dioxide gas has several industrial uses such as a refrigerant, in fire extinguishers, carbonated beverages, and many others. In addition, the water formed could be easily re-used after separating the calcium formate product which increases the economic profit and sustainability as well.

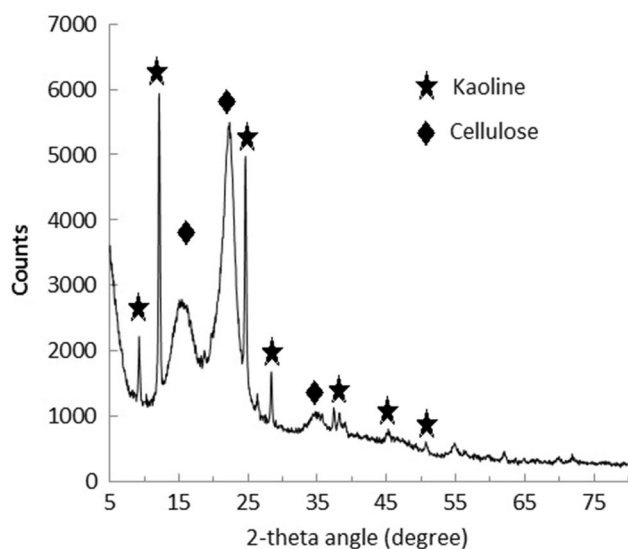
After treatment of the pulp with formic acid and washing, the ash content of paper sludge dropped to  $11.87 \pm 1.68\%$  and total sugars increased to  $0.54 \pm 0.066$  g glucose/g sample. As compared to original paper sludge, the acid-treated paper sludge had about 65% lower ash content. It should be noted that presence of kaolin, talc, or alum in the sludge will not be affected by the dilute formic acid treatment. Therefore, there is still ash in the pulp. Table 3 shows XRF analysis of the formic acid-treated sludge. Analysis of the ash of the formic acid-treated paper sludge by XRF showed significantly much lower CaO content than the original paper sludge (only 0.41% compared to 26.43% in case of the original paper sludge), which indicates successful extraction and transformation of the carbonate filler into calcium formate.

As a result of extracting majority of calcium carbonate from the paper sludge, XRD pattern of the formic acid-treated paper sludge showed significant change as shown in Fig. 3. The most important change is disappearance of calcium carbonate peaks and clear appearance of cellulose peaks of the fibers at  $2\theta$  values of about  $15^\circ$ ,  $22^\circ$ , and  $35^\circ$  due to diffraction from (110), (200), and (004) planes, respectively, of cellulose I triclinic crystal structure [50]. The other newly appeared major narrower peaks at  $9^\circ$ ,  $12^\circ$ ,  $25^\circ$ ,  $26^\circ$ ,  $28^\circ$ ,  $37.4^\circ$ ,  $38.2^\circ$ ,  $39.0^\circ$ ,  $45.2^\circ$ , and  $50.7^\circ$  could be attributed to presence of kaolin filler (aluminum silicate,  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ ) in form of kaolinite [51]; this is consistent with the XRF analysis which showed presence of relatively high percentage of Al and Si elements than others. The other minor peaks could be due to presence of

**Table 3** XRF analysis of ash of paper sludge after dilute formic acid pretreatment

Element	Constituent	Wt. %
Ca	CaO	0.41
Si	SiO <sub>2</sub>	5.99
Al	Al <sub>2</sub> O <sub>3</sub>	3.25
Fe	Fe <sub>2</sub> O <sub>3</sub>	0.87
Mg	MgO	0.40
S	SO <sub>3</sub>	0.25
Ti	TiO <sub>2</sub>	0.22
Cl	Cl	0.13
Cu	CuO	0.099
K	K <sub>2</sub> O	0.08
P	P <sub>2</sub> O <sub>5</sub>	0.06
Zn	ZnO	0.022
Co	Co <sub>3</sub> O <sub>4</sub>	0.016
Sr	SrO	0.011
Zr	ZrO <sub>2</sub>	0.028
Ni	NiO	0.01
Mn	MnO	0.009
Cr	Cr <sub>2</sub> O <sub>3</sub>	0.009
Pb	PbO	0.005
Rb	Rb <sub>2</sub> O	0.002
Loss due to ignition		88.13

trace amounts of other materials such as talc powder (magnesium silicate) or alum, which are used in papermaking and/or oxides used in coating or inks.

**Fig. 3** XRD diffraction of paper sludge after treatment with dilute formic acid and washing

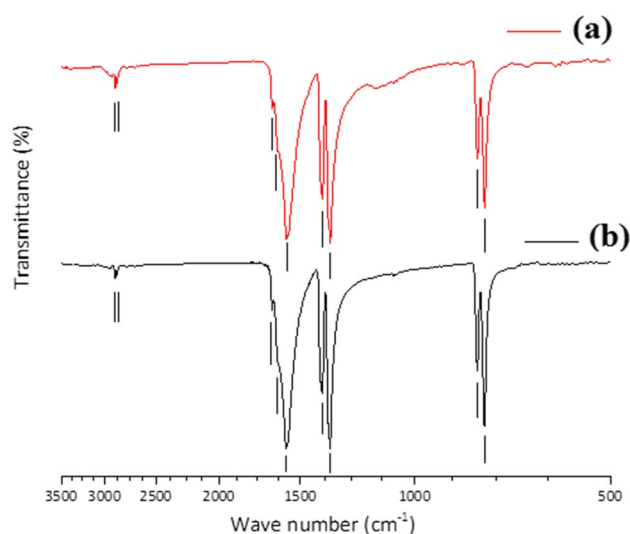
### 3.6 Characterization of calcium formate prepared from formic acid-treated paper sludge

The prepared calcium formate from paper sludge was characterized to ensure sufficient purity for different applications. In parallel, calcium formate prepared by reacting pure precipitated calcium carbonate with formic acid (so-called here synthetic calcium formate) was characterized too in order to prove the validity of the method used for preparing pure calcium formate from paper sludge.

#### 3.6.1 FTIR spectroscopy

FTIR spectra of calcium formate prepared from paper sludge and synthetic calcium formate are shown in Fig. 4. As the spectra show, identical bands were obtained for calcium formate from paper sludge and synthetic calcium formate without any interfering bands for impurities. The obtained spectra are typical to that of polycrystalline orthorhombic  $\alpha$ -calcium formate [52–55]. The bands and their assignments are as follows [52, 53]: Bands at 2870–2892  $\text{cm}^{-1}$  due to C–H stretching vibrations; bands at 1578–1658 and 1389  $\text{cm}^{-1}$  due to asymmetric and symmetric stretching vibrations of the carboxylate group; bands at 1351  $\text{cm}^{-1}$  due to bending vibration of O–C–H group, bands at 1079 and 1066 due to out-of-plane bending of C–H group, and bands at 782–802  $\text{cm}^{-1}$  due to bending vibration of the O–C–O group combined with O–C–H bending vibration.

These results clearly show that dilute formic acid treatment of the sludge pulp is very selective in reaction with calcium formate without affecting the other constituents of paper sludge, especially cellulose and hemicelluloses.

**Fig. 4** FTIR spectra of **a** calcium formate prepared from paper sludge and **b** calcium formate prepared from pure precipitated calcium carbonate and formic acid

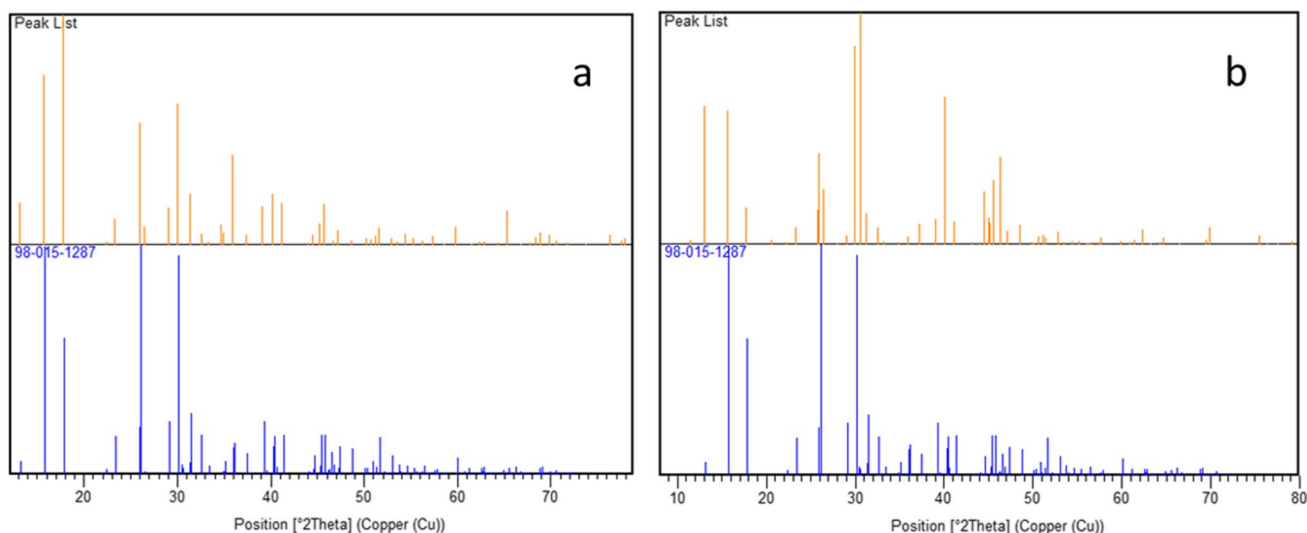
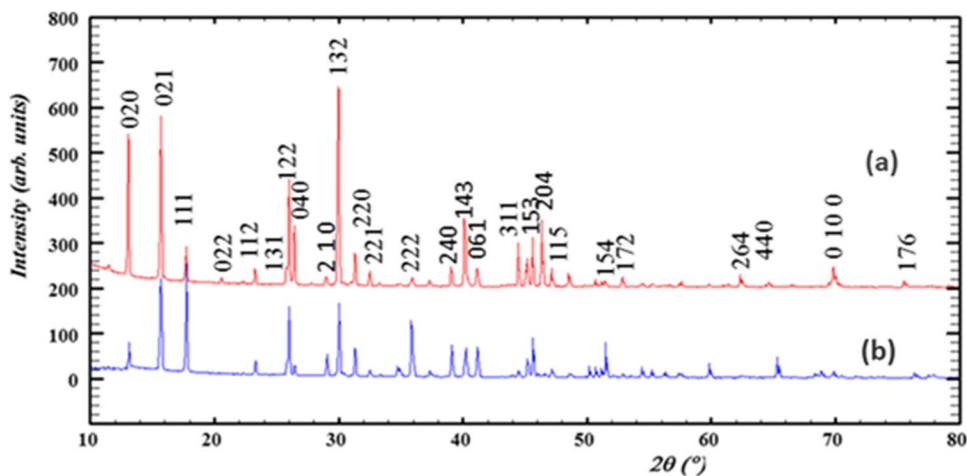
### 3.6.2 XRD pattern

X-ray analysis was used for proving formation of calcium formate crystals and their purity via their X-ray diffraction pattern. The crystal structure of calcium formate prepared from paper sludge and synthetic calcium formate was studied in details. Figure 5 represents the X-ray diffraction patterns of calcium formate samples. The diffraction patterns were analyzed using the Highscore Plus software and found to be matched to the calcium diformate ICSD card no. 98–015–1287 (as shown in Fig. 6). Only changes in the maximum intensity of the diffraction peaks as well as their relative intensity were found for the two samples when compared to the standard card. For the standard card, the major calcium formate peak (100% peak) was at  $2\theta$  26.123° for the plane (122), while the synthetic calcium formate the major peak

was at  $2\theta$  17.79° related to the plane (111), and the calcium formate from paper sludge the major peak was at  $2\theta$  30.04° corresponding to the plane (132).

The same behavior of the different crystal facets was obtained before [56]; this behavior may be related to the anisotropic supply of the initial solution which is most likely to blame for the observed patterns, which is one of the degraded examples of the ideal shape. These facets have lower growth rates due to their relatively higher lattice-plane-space ratios. This increases the probability of finding these facets in growing crystals. The crystal structure of the obtained patterns was refined based on  $Pbc a$  orthorhombic space group no. 61 using Rietveld method implemented in FullProf program [57]. In this refinement, all of Ca, C, O, and H atoms occupy Wyckoff atomic positions at the different  $x$ ,  $y$ , and  $z$  fractional atomic coordinates. In the first

**Fig. 5** Collected XRD patterns with the major planes indexed of **a** paper sludge calcium formate, and **b** synthetic calcium formate



**Fig. 6** X-ray diffraction patterns of **a** calcium formate prepared from paper sludge and **b** synthetic calcium formate compared to ICSD card no. 98–015–1287 of calcium formate

**Table 4** Refined unit cell dimensions, unit cell volume, microstrain, and crystallite size

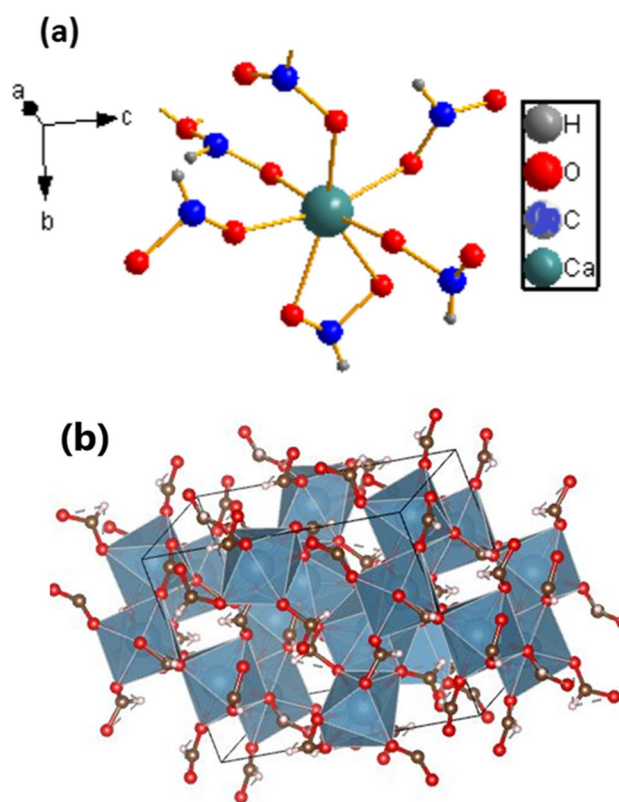
Property	Synthetic calcium formate	Calcium formate from paper sludge
System group	<i>P b c a</i> (61)	<i>P b c a</i> (61)
Formula sum	Ca <sub>8</sub> C <sub>16</sub> O <sub>32</sub> H <sub>16</sub>	Ca <sub>8</sub> C <sub>16</sub> O <sub>32</sub> H <sub>16</sub>
Formula weight (g/mol)	1040.91	1040.91
System	Orthorhombic	Orthorhombic
Space group	“ <i>P b c a</i> ”	“ <i>P b c a</i> ”
<i>a</i> (Å)	6.3023	6.3033
<i>b</i> (Å)	13.4467	13.4549
<i>c</i> (Å)	10.2183	10.2165
Volume (Å <sup>3</sup> )	865.95	866.46
Axes ratio	<i>alb</i> =0.4687; <i>b/c</i> =1.3159; <i>ca</i> =1.6214	<i>alb</i> =0.4685; <i>b/c</i> =1.3170; <i>ca</i> =1.6208
Microstrain	0.094	0.198
Crystallite size (nm)	285	291
Calculated Density (g/cm <sup>3</sup> )	1.99591	1.99473
Chi <sup>2</sup>	2.57	2.647

step of the refinement, the global parameters were refined; in the second step, the structural parameters were refined, and finally, all the parameters of global and structures were refined. The refined unit cell dimensions, volumes, crystallite size, and micro-strain for both calcium formate samples are listed in Table 4. It is clear from the table that the unit cell volume of the calcium formate from paper sludge is slightly greater than that of synthetic calcium formate; this increase in the lattice parameters may be due to the increase in the crystallite size as shown in the same table. The crystallite size of the synthetic calcium formate was 285 nm, while that of calcium formate from paper sludge was 291 nm. The bond lengths and bond angles for both calcium formate samples agree well with the previously published results [57, 58]. The refined fractional atomic coordinates, selected bond lengths, and bond angles for the two calcium formate samples are tabulated in Supplementary Information Table S1 and S2, which demonstrated that the Ca<sup>2+</sup>-O lengths of the chelate formate groups are longer than the other Ca<sup>2+</sup>-O distances.

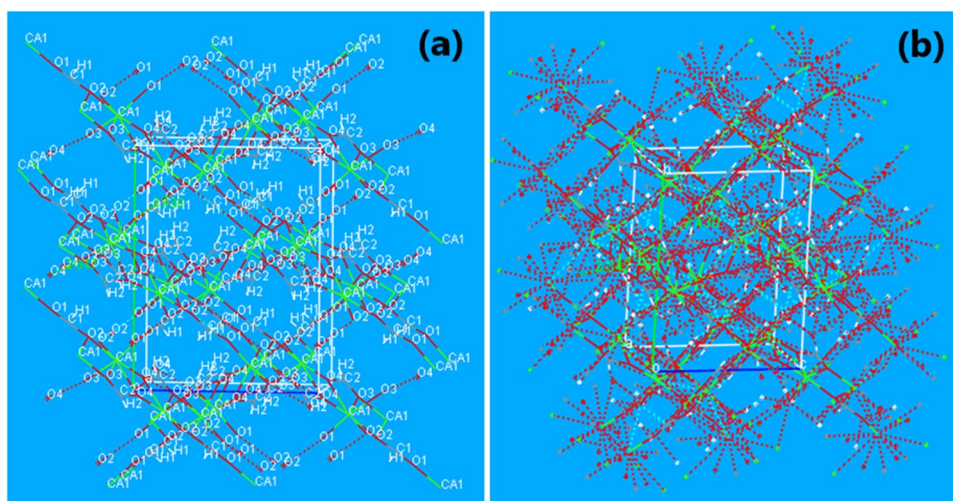
Regarding crystallographic structure of  $\alpha$ -Ca(HCOO)<sub>2</sub>, one crystallographically non-equivalent Ca atom was coordinated by seven O atoms from two different formate groups to create a deformed pentagonal bipyramid as a coordination polyhedron (Fig. 7a), with two more formate groups, positioned up and beneath. Only one of the six formate groups engaged in the coordination was bidentate and served as a chelate ligand, while the other five groups were monodentately connected to the calcium atom. Ca-centered polyhedra formed layers that resembled dioctahedral by sharing edges with nearby deformed bipyramids as shown in Fig. 7b.

Figure 8a shows the packing diagram of calcium formate prepared from paper sludge as a representative example

which gives some highlight on the intermolecular contacts through the hydrogen bonding. These intermolecular interactions play a crucial role in maintaining the stability of the molecules in their space group's crystallographic positions.

**Fig. 7** Crystal structure of  $\alpha$ -Ca(HCOO)<sub>2</sub> (a) and polyhedra formed layers (b)

**Fig. 8** Packing diagram of calcium formate from paper sludge showing the intermolecular contacts (a) and the packing diagram showing infinite chains with the formula  $[\dots \text{Ca}\dots \text{O}-\text{CH}-\text{O}\dots]_{\infty}$  (b)



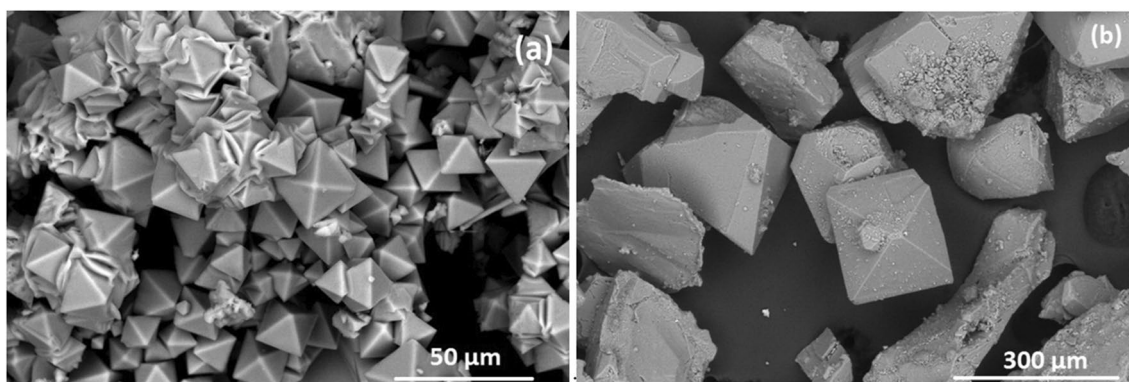
Infinite chains with the formula  $[\dots \text{Ca}\dots \text{O}-\text{CH}-\text{O}\dots]_{\infty}$  exist and are cross-linked by  $\text{Ca}^{2+}$  ions as shown in Fig. 8b. The chains are convoluted, and there are four ways that the C-H vectors might point.

### 3.6.3 SEM and EDX investigation

SEM/EDX analysis is an important tool for identifying the microscopic crystal structure and investigating chemical composition and purity of compounds. The crystals of calcium formate prepared using paper sludge or using precipitated calcium carbonate were investigated using SEM/EDX. Figure 9 shows SEM images of the prepared calcium formate from paper sludge and pure calcium carbonate, and Fig. 10 shows EDX spectra of the aforementioned samples. SEM images showed that bipyrimidal polyhedral shape crystals of calcium formate obtained from paper sludge had much smaller size than those obtained in case of using pure calcium carbonate where a lot of irregular fragments were shown in addition to bipyramidal crystals were observed.

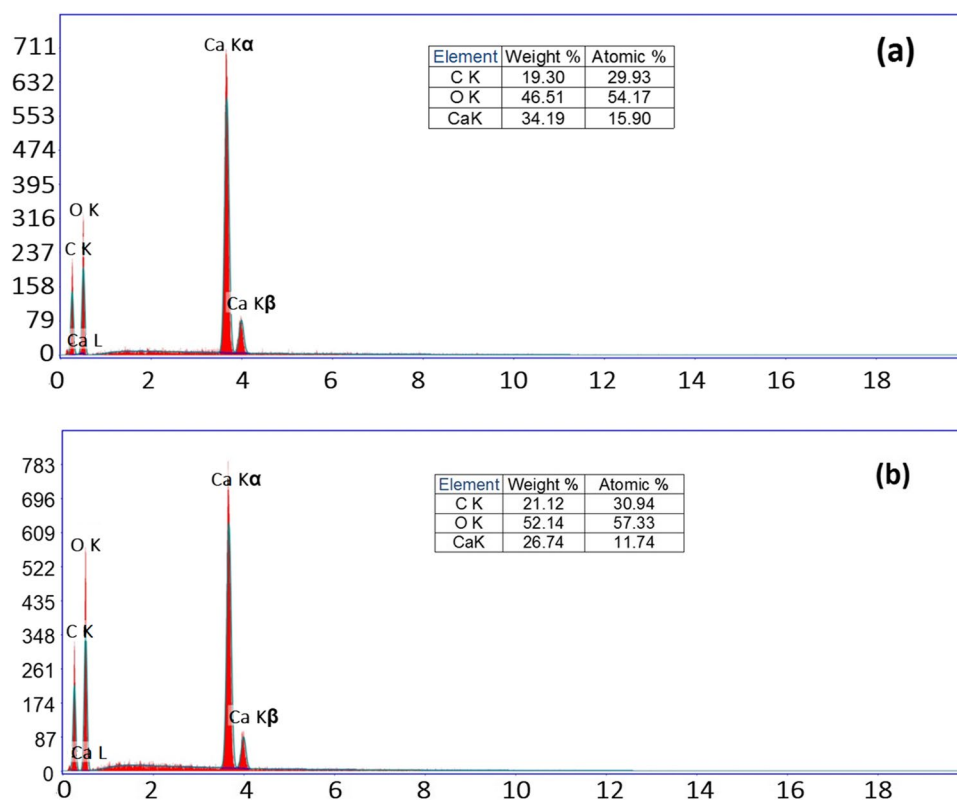
This means that crystallization of calcium formate from the liquor in case of using paper sludge induces smaller size crystal formation than in case of using pure calcium carbonate. In case of using pure calcium carbonate as a precursor, the crystals of calcium formate grew in much larger size and interfered separate crystal formation. Therefore, the shape of the crystals was not as definite as in case of calcium formate crystals formed in case of using paper sludge. The shape of the crystals of calcium formate is in accordance with the XRD results mentioned above.

It is interesting to see from the EDX spectra that calcium formate obtained from paper sludge was as pure as that obtained from precipitated calcium carbonate (Fig. 10); only signals for Ca and O atoms were detected in both spectra, and also very close atomic and weight % for Ca, O, and C to the theoretical values was noticed. Theoretical atomic % of C, O, and Ca in calcium formate are 28.57%, 57.14%, and 14.29%, respectively, while theoretical weight % of C, O, and Ca in calcium formate are 18.44%, 49.19, and 30.82%, respectively.



**Fig. 9** SEM images of calcium formate: **a** prepared from paper sludge and **b** prepared from pure calcium carbonate

**Fig. 10** EDX spectra of calcium formate: **a** prepared from paper sludge and **b** prepared from pure calcium carbonate



### 3.6.4 XRF analysis

The purity of prepared calcium formate from paper sludge or by using precipitated calcium carbonate was further

investigated using XRF analysis; the results are presented in Table 5. It was interesting to see that loss in weight of both of calcium formate samples due to ignition at 1000 °C was very similar and also very close to the theoretical

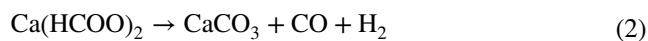
**Table 5** XRF analysis of calcium formate prepared from paper sludge and from pure precipitated calcium carbonate

Element	Compound formula	Calcium formate from paper sludge	Calcium formate from precipitated calcium carbonate
		Concentration (%)	Concentration (%)
Loss due to ignition (%)		56.48	56.68
Ca	CaO	42.89	42.20
Na	Na <sub>2</sub> O	-	0.069
Mg	MgO	0.035	0.333
Al	Al <sub>2</sub> O <sub>3</sub>	0.16	0.123
Si	SiO <sub>2</sub>	0.214	0.313
P	P <sub>2</sub> O <sub>5</sub>	0.046	0.082
S	SO <sub>3</sub>	0.029	0.063
K	K <sub>2</sub> O	-	0.01
Fe	Fe <sub>2</sub> O <sub>3</sub>	0.057	0.049
Mn	MnO	0.019	-
Sr	SrO	0.027	0.025
Cl	Cl	0.033	0.049
Pb	PbO	0.008	-
Ni	NiO	-	0.009

weight loss (56.90%) calculated from conversion of calcium formate to calcium oxide (molecular weight of calcium formate and calcium oxide are 130.113 and 56.077, respectively). Calcium oxide content of both samples was very close too and also very close to the theoretical calcium oxide content of calcium formate (43.09%). The slightly lower calcium oxide content of both calcium formate samples (42.20% and 42.89%) than the theoretical value is expected due to presence of residual elements in the samples. Based on the XRF analysis shown in the table, the purity of calcium formate is about 99% in case of using precipitated calcium carbonate or paper sludge; the sum of non-calcium oxide residues was  $\leq 1\%$ . This is in accordance with the EDX results shown above where only peaks for Ca, C, and O atoms were observed.

### 3.6.5 Thermogravimetric analysis (TGA)

TGA was used to study thermal stability and degradation behavior of calcium formate prepared from paper sludge and their comparison to that prepared from precipitated calcium carbonate. The analysis can also give significant indication about the purity of the prepared materials since each substance has its characteristic thermal stability and degradation behavior. Figure 11 shows TG and DTG curves of both of calcium formate samples. As the figures show, calcium formate samples from paper sludge or using precipitated calcium carbonate has two-stage thermal degradation profile. In the first stage, calcium formate is decomposed into calcium carbonate and formaldehyde, which is further decompose into carbon monoxide and hydrogen, as shown in Eq. 2 [58]. In the second stage of degradation, calcium carbonate decomposes into calcium oxide and carbon dioxide as shown in Eq. 3 [59].

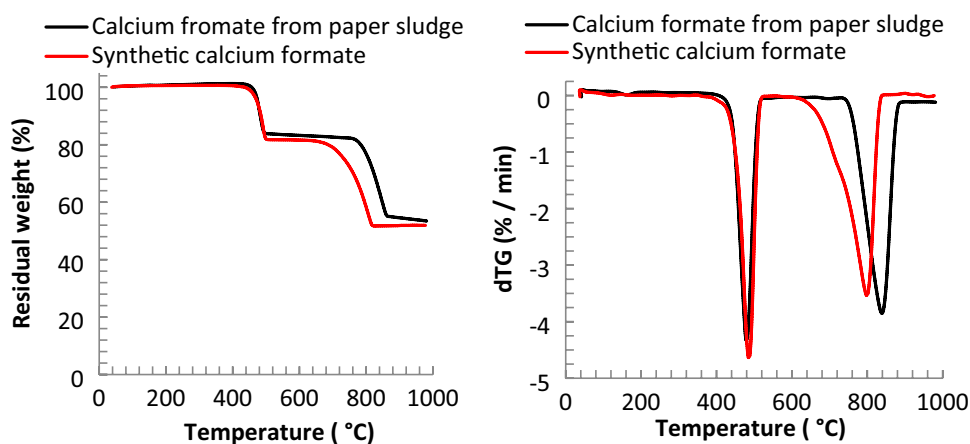


Calcium formate samples from paper sludge or using precipitated calcium carbonate had close initial weight loss temperature at about 394 and 398 °C, respectively. The first-stage maximum weight loss temperature was at about 480 and 486 °C for calcium formate from paper sludge and precipitated calcium carbonate, respectively. The second degradation stage started at 728 and 619 °C for calcium formate from paper sludge and precipitated calcium carbonate, respectively, while the second-stage maximum weight loss temperature was at about 839 and 799 °C for calcium formate from paper sludge and precipitated calcium carbonate, respectively. At the end test, the residual weight was 46.53 and 48.07% for calcium formate from paper sludge and using precipitated calcium carbonate, respectively. The different thermal degradation behavior of calcium formate samples during the second stage of thermal degradation could be due to the difference in residual elements present in the samples as shown in the XRF analysis. These different residual elements may catalyze thermal degradation of calcium formate in different rates.

## 4 Conclusions

Paper sludge, a negative value raw material containing high content of calcium carbonate filler, was used for preparing calcium formate with high purity ( $\geq 99\%$ ) via treatment with dilute formic acid, which can selectively react with calcium carbonate in the sludge without significantly affecting the other existing components (fibers and other residues). Under the conditions used in the current work, treatment with formic acid did not affect the other

**Fig. 11** TGA and DTGA curves of calcium formate prepared from paper sludge and precipitated calcium carbonate



constituents of paper sludge, and  $> 98\%$  of calcium carbonate in the paper sludge could be utilized. Comparing results of analyses of calcium carbonate prepared from paper sludge to that prepared from precipitated calcium carbonate and formic acid confirmed the suitability of the method used for preparation of calcium formate with high purity. Formation of pure carbon dioxide gas as a by-product with several industrial uses improves more the economic profit and sustainability of the process. The approach used in the current work opens the way for utilization calcium carbonate filler found in high amounts in paper sludge for preparing other important organic calcium compounds via treatment the sludge with the corresponding organic acids which is currently under investigation.

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**Data availability** All data generated or analyzed during this study are included in this published article (and its Supplementary Information files).

## Declarations

**Ethical approval** Not applicable.

**Competing interests** The authors declare no competing interests.

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