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# SYNTHESIS OF METAL CARBOXYLATES FROM ALMOND SEED OIL (*TERMINALIA CATAPPA*)

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## ABSTRACT

The less exploited seed oil of almond was investigated for its potential utilization as a raw material for the synthesis of metal carboxylates. The oil was extracted from the almond seeds and a yield of 42% was obtained. The oil was characterized and used to synthesize the carboxylates of barium, calcium, cobalt, copper, iron, magnesium, nickel and zinc. The functional groups of fatty acid carboxylates produced were confirmed by FTIR. The characteristic colours of the carboxylates were white (barium, calcium, magnesium and zinc carboxylates), ash (Cobalt carboxylate), mint green (copper carboxylate), brown (iron carboxylate), and lemon green (nickel carboxylate). The pH of the solutions of the metal carboxylates varies from 6.6 to 10 with no free alkaline. The foam stability test revealed a length of 1.3 cm for barium carboxylate and 0.3 cm for magnesium carboxylate while other carboxylates did not foam.

**Keywords:**

## INTRODUCTION

Metal carboxylates have economic importance and wide application in various industries. They are useful as driers in paints, lubricating greases, corrosion inhibitors and thermal stabilizers in the production of poly(vinyl chloride), used for vulcanization reaction of rubbers among others (Aghzzaf et al., 2019; Folarin et al., 2012). Various vegetable oils have been utilized for the preparation of metal carboxylates (Maryudi et al, 2009).

Although almond trees (*Terminalia catappa*) are native to South-Central Asia (Ouzir et al., 2021; Pérez de los Cobos et al, 2021), they are found in Iran, the United States and are available in other parts of the world today. They are deciduous trees that are found to be drought–tolerant. Almond trees are freely available in Nigeria and are more widespread in the southern part of Nigeria where it is popularly called "fruit". The tree has been grown to serve as shades and for ornamental purposes (Akubude et al., 2020). Other species of almonds include *Prunus dulcis* Mill. DA Webb (Sakar et al, 2021), almond oil under accelerated storage conditions (Bernoussi et al., 2020).

**Figure 1: The almond tree and fruits.**

The almond kernel contains about 40-75% oil (Melhaoui et al., 2021; Roncero et al., 2016). The fatty acids constituents of almond oils are predominantly oleic and fatty acids, summing up to 90% of the oil composition (Melhaoui et al., 2021). The oil from the sweet almond has better shelf life than the bitter

In recent times, there has been an increase in the global production of almonds (FAO-Stat, 2020) with the United States of America being the global largest producer of almonds

(Melhaoui et al., 2021; Ouzir, 2021). Nigeria accounts for 14% of the global production of oil. (Akubude et al., 2016). Almond oil has been suggested as an industrial raw material for the production of food, biofuel, drilling mud, cosmetic and pharmaceutical industries (Akubude et al., 2016; Oseh et al., 2019).

There is a need to expand the supplies of the raw materials in the oleochemical industries by harnessing other sources of oils like almond oil for bio-based products. In this work, the metal carboxylates of almond oil were produced and characterized for possible application as industrial raw material.

## MATERIAL AND METHODS

### Seed collection and dehulling

The Nigerian almond seeds were obtained from Okene metropolis of Kogi State, Nigeria by handpicking the ripened fruits. The almond seeds were dehulled by cutting them into two halves and the seeds were removed and dried for 14 days. The size reduction of the seeds was achieved by using the locally available hand-operated grinder, in preparation for the oil extraction process.

### Extraction and refining of the seed oil

The extraction of 60 g of almond seed was done by Soxhlet extraction using n-hexane solvent, for 3 hours. The oil was recovered from n-hexane by simple distillation over the water bath. The Portion of the oil was refined by sequential processes of degumming, neutralization and bleaching in accordance to the methods described in the literature (Odetoye *et al*, 2014).

### Characterization of Almond Oil Sample

The physical and chemical properties of the oil samples were determined using ASTM standard methods (1983) for acid value, iodine value and saponification value, density, specific gravity, viscosity. The spectra of the almond oil fatty acids were recorded on the Agilent Gas Chromatograph-Mass Spectrometer (Model 7890A GC system, 5675C inert MSD with triple-axis detector).

### Preparation of the metal carboxylates

Preparation of metal carboxylates of magnesium, cobalt, iron, zinc and calcium was done by metathesis using aqueous-alcoholic solution according to the method described by Ossai (2014) with little modification. In summary, for zinc carboxylate, 9.2 g of almond oil was dissolved in 10 ml of ethanol at a temperature of 70$^{o}$C followed by the addition of 5 ml of 5M NaOH solution. To this mixture, 20 ml of 1.86M ZnSO4 solution was slowly added with continuous stirring. Upon addition of the solution, the precipitation of the metal soap commenced. The metal carboxylate that was precipitated was then filtered off and washed with 30 ml hot water (80$^{o}$C) and air-dried at room temperature for 48 h. The colour of the metal soap was noted and the yield was calculated.

### Analysis of the metal carboxylates

The metal carboxylates produced were analyzed for alkalinity, foaming power, caustic content, stability, pH and infrared analysis.

## RESULTS AND DISCUSSION

### *The oil content of the Almond Seeds*

The seeds were subjected to 3 hrs extraction time. The average oil content of the almond seed was 42% based on the dry weight which simply means that the seeds are rich in oil.

### *Physicochemical properties of the Almond Oil*

The cloud and melting points determined for the crude oil are 34$^{o}$C and 33$^{o}$C respectively while 31$^{o}$C and 32$^{o}$C were recorded for the refined oil sample. The summary of the physical/chemical properties of the oil is as presented in Table 1.

**Table 1: The physical properties of almond oil.**

| | | |
|---|---|---|
| Density (g/cm$^3$) | 0.700 | 0.700 |
| Acid value (mg KOH/g oil) | 2.37 | 2.39 |
| Iodine value | 96 | 98 |
| Saponification Value (mg KOH/g oil) | 122 | 146 |
| Specific gravity | 0.900 | 0.900 |
| Free fatty acid | 1.68 | 1.70 |
| Melting point | 33$^{o}$C | 31$^{o}$C |
| Cloud point | 34$^{o}$C | 32$^{o}$C |
| Colour | Golden yellow | Pale yellow |
| Odour | Almond | Almond |

At room temperature (28±3$^{o}$C), the oil was liquid and golden yellow. The value obtained for the cloud point is within the range specified by the ASTM standard, which means almond oil has a good cloud point property. The density of the oil is 0.70 g/cm$^3$ which is slightly lower than 0.93g/cm$^3$ reported earlier (Matos et al, 2009) for tropical almond seed oil. The specific gravity of the oil is 0.90 similar to 0.92 reported earlier (Barku, et al, 2012) for tropical almond seed oil.

The Saponification value of the crude and refined oil were 145 and 148 mg KOH/g, this result is lower than 168.27 mg KOH/g reported by Barku, et al. for tropical almonds.

The saponification value is used in checking adulteration. The high saponification values recorded for the almond seed oil suggest a low level of impurities and therefore could be useful industrially for soap, shampoo and paint making.

The acid value and free fatty acid of both crude and refined oil are 2.37 and 2.40 mg KOH/g and 1.68 and 1.69 mg KOH/g respectively. This acid value is higher than 0.78 mg KOH/g and FFA is lower than 0.38 mg KOH/g reported by Barku but the acid value of the oil is lower than 15.37 mg KOH/g reported by Bello and Agge (2012) for groundnut oil. Free fatty acids were probably formed by the hydrolytic activity of lipolytic enzymes during the preparation of seeds for oil production. The acid value of the nut is lower when compared with cashew nut oil (5.82 mg KOH/g), palm oil (14.04 mg KOH/g). Results obtained from this work indicated that the acid value of the oil corresponds to low levels of free fatty acids present in the oil, which also suggested low levels of hydrolytic and lipolytic activities in the oils.

The iodine value of both crude and refined oil is 96 and 98 g$I_2$/100g this value is lower than 121.19 g $I_2$/100 g reported by Barku, et al. It indicates the degree of unsaturation in the fatty acid of triglyceride. This value could be used to quantify the amount of double bond present in the oil which reflects the susceptibility of oil to oxidation. High iodine value indicates high unsaturation of fats and oils and low iodine value of oils are more saturated with fewer double-bonds. The values obtained here suggested that the oil is highly unsaturated and may be susceptible to rancidity. Also, higher iodine values are evidence that the oils could be used in the manufacture of cosmetics, oil paints and vanish as well as nutritional purposes. The iodine value obtained is within the standard value.

**The fatty acid composition of the almond oil**

Figure 2 shows the gas chromatogram of the almond seed oil. The major components were n-hexadecanoic acid (45.58 %), oleic acid (45.58 %) and 8.85 linoleate % (see supplementary data for the details).

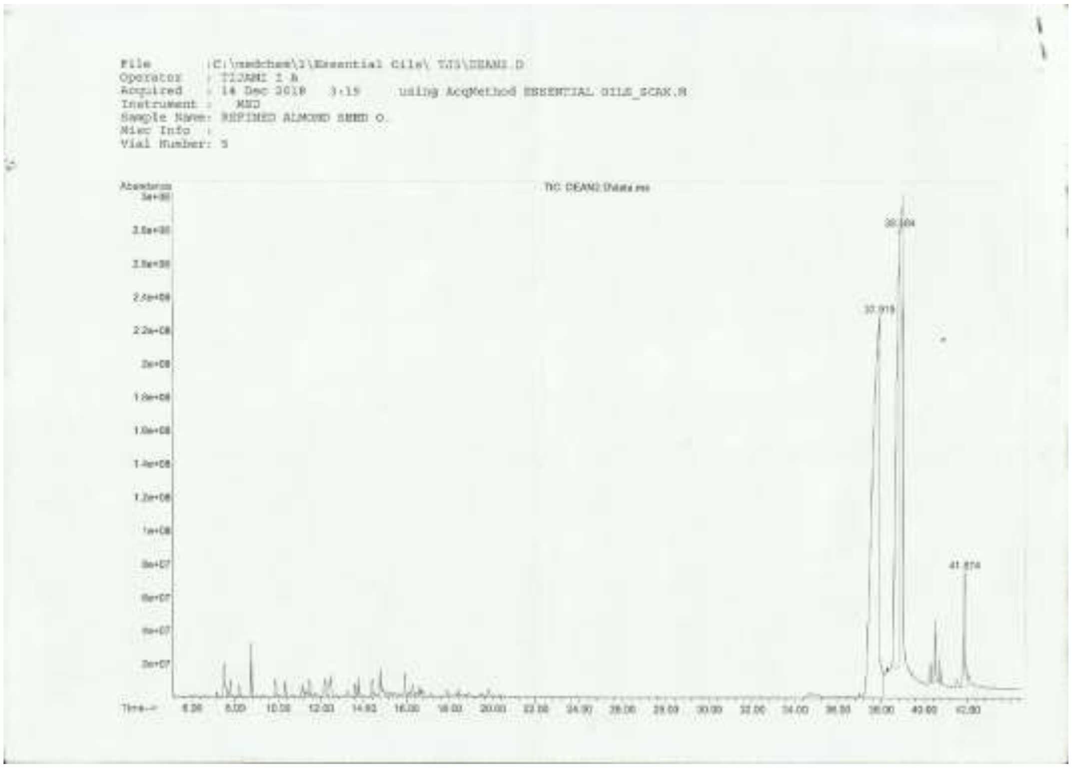

Figure 2: GC chromatogram of refined almond oil

**Properties of the metal carboxylates**

Figure 3 shows the picture of the metal carboxylates synthesized from almond seed oil.

**Figure 3: The physical appearance of the metal carboxylates.**

The colours and the mass of metal carboxylates obtained are shown in Table 2.

**Table 2: The colour and mass of metal carboxylates synthesized.**

| Metal carboxylate | Colour | Weight (g) |
|---|---|---|
| Ba- carboxylate | White | 2.6 |
| Ca- carboxylate | White | 6.5 |
| Co- carboxylate | Ash | 5.6 |
| Cu- carboxylate | Mint green | 4.0 |
| Fe- carboxylate | Brown | 5.4 |
| Mg- carboxylate | White | 5.5 |
| Ni- carboxylate | Lemon green | 9.2 |
| Zn- carboxylate | White | 5.0 |

Ba, Ca, Mg and Zn metal carboxylates are always white, Co metal carboxylate is ash, Cu and Ni are always greenish and Fe metal carboxylates are also always brown. The mass of Ni-carboxylate is highest (9.2g), followed by Ca-carboxylate (6.5g), Co-carboxylate, Cu-carboxylate (5.47g), Mg-carboxylate (5.47g), Zn-carboxylate (5g) and Ba-carboxylate (2.6g) being the lowest.

**Table 3: The pH values, foam stabilities and free caustic alkalinity of the metal carboxylates.**

| Metal soap | pH | 1st length of foam stability | 2nd length of foam stability | Free caustic alkalinity |
|---|---|---|---|---|
| Ba-carboxylate | 10.0 | 1.3 cm | 1.3 cm | None |
| Ca-carboxylate | 8.7 | Non-foaming | Non-foaming | None |
| Co-carboxylate | 8.5 | Non-foaming | Non-foaming | None |
| Cu-carboxylate | 8.2 | Non-foaming | Non-foaming | None |
| Fe-carboxylate | 6.6 | Non-foaming | Non-foaming | None |
| Mg-carboxylate | 7.7 | 0.3cm | 0.00 | None |
| Ni-carboxylate | 7.5 | Non-foaming | Non-foaming | None |
| Zn-carboxylate | 8.0 | Non-foaming | Non-foaming | None |

**The pH, foam power and stability, and free caustic alkalinity of the metal carboxylates**

Also, Table 3 shows the values obtained for pH values, foam stabilities and free caustic alkalinity as obtained for the metal carboxylates synthesized. From the Table, the pH value of Ba-carboxylate is the highest (10.0), followed by Ca-carboxylate (8.7), Co-carboxylate (8.5), Cu-carboxylate (8.2), Zn-carboxylate (8.0), Mg-carboxylate (7.7), Ni-carboxylate (7.5), and the lowest is Fe-carboxylate (6.6).

The metal carboxylates lack foaming power except for Ba-carboxylate with 1.3 cm foam stability and Mg-carboxylate with 0.36 cm - 0.00 cm foam stability. The lack of pink colouration in each solution of the metal carboxylate indicated the absence of free caustic alkalinity.

## RESULTS OF INFRARED ANALYSIS

Figure 3 below shows the functions present in the cobalt carboxylates synthesized as the representative datum.

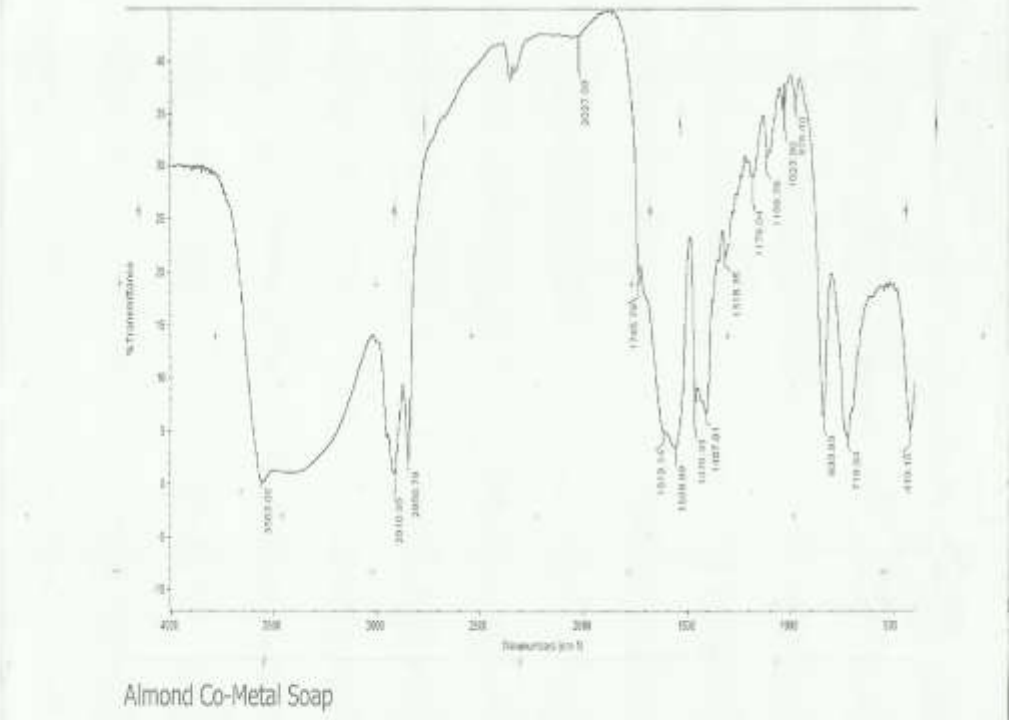

**Figure 3: IR spectrum of the Cobalt carboxylate.**

Figures **3** (representative spectrum, see supplementary data for other metal soaps' spectra) is the infrared spectrum of the cobalt metal soap in region 4000 to 500 $cm^{-1}$. From the spectrum, the asymmetry vibration of $CH_2$ stretch is observed at 2926 $cm^{-1}$, while the symmetry vibration of $CH_2$ stretch is at 2850 $cm^{-1}$. The C=O stretch of triglyceride linkage is observed at 1742 $cm^{-1}$. The characteristic carbonyl stretching band of ester linkage (C=O) is observed at 1669 $cm^{-1}$. When compared to the spectrum of the almond oil (Figure 4 on supplementary data), the absorption at 1710 $cm^{-1}$ due to C=O of free fatty acids has disappeared in the metal soaps. The C-H absorption of bending vibration of $CH_2$ and $CH_3$ bands was observed at 1470 $cm^{-1}$. The bands of $CH_2$ bending vibrations were also observed at 1381 and 1109 $cm^{-1}$. The absorptions due to C-O ester bonds are observed at 992, 830 and 1097 $cm^{-1}$ while the $CH_2$ rocking vibration is seen at 722 $cm^{-1}$. The FTIR spectra confirmed the functional groups of fatty acid carboxylates of metal soaps produced.

## CONCLUSION

Almond seeds are rich in oil that can be harnessed for the production of diversified industrial products among which are the metal soaps explored in this work. The oil extracted was used to prepare carboxylates of barium, calcium, cobalt, copper, iron, magnesium, nickel and zinc by metathesis in aqueous alcohol, the products can be employed as grease, paint additives, metal corrosion inhibitor and stabilizers for PVC. The FTIR spectra confirmed the functional groups of fatty acid carboxylates of metal soaps produced. The metal carboxylates were safe to handle (pH 6.6 - 10.0), insoluble in water, non-foaming, and tougher than the common household soaps.

***Supplementary data***

See supplementary data for the GC chromatogram/ information of the almond oil and the FTIR spectra of the metal carboxylates synthesized.

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