RASĀYAN *J. Chem.*
Vol. 19 | No. 2 | 743-753| April-June | 2026
ISSN: 0974-1496 | e-ISSN: 0976-0083 | CODEN: RJCABP
http://www.rasayanjournal.com
http://www.rasayanjournal.co.in

REGENERABLE CALCIUM HYDROXYCITRATE ADSORBENT FOR EFFICIENT PHOSPHOLIPID REMOVAL IN CRUDE PALM OIL DEGUMMING

J. Ginting[1,✉] S. Nufus[1], E. D.Tarigan[2], Naomi E. M. Sinaga[3], Imelda D. Ambarita[3], Eko K. Sitepu[3], Nimpan Bangun[3], Juliati Br. Tarigan[3], and Helki I. Ginting[4]

[1]Department of Metrology and Instrumentation, Faculty of Vocational Education, Universitas Sumatera Utara, Medan 20155, Indonesia
[2]Department of Statistics, Faculty of Vocational Education, Universitas Sumatera Utara, Medan 20155, Indonesia
[3]Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Sumatera Utara, Medan 20155, Indonesia
[4]Department of Electrical Engineering, Faculty of Engineering, Universitas Sumatera Utara, Medan 20155, Indonesia
✉Corresponding author: junediginting@usu.ac.id

ABSTRACT

Degumming is a critical step in refining crude palm oil (CPO) to remove phospholipids (gums), which can negatively impact oil quality and processing efficiency. While conventional chemical and enzymatic degumming methods are widely used, they often suffer from drawbacks such as limited efficiency in removing non-hydratable phospholipids (NHPs), increased oil loss, environmental concerns, and high operational costs. Moreover, the potential of regenerable hybrid organic-inorganic adsorbents for efficient and selective phospholipid removal remains underexplored. Addressing this research gap, the present study investigates the efficacy of two calcium-based adsorbents—calcium silicate ($CaSiO_3$) and calcium hydroxycitrate acid ($Ca_3(HCA)_2$)—in reducing phospholipid content from CPO. The adsorbents were synthesised and characterised through EDTA titration, HPLC, and FT-IR spectroscopy. Adsorption experiments were conducted at 100 °C using varying adsorbent doses (2–8 g) with 2 g of CPO. Phosphorus content was quantified to estimate phospholipid removal efficiency. Results showed that $Ca_3(HCA)_2$ achieved superior gum removal, with up to 100% phospholipid reduction using 6 g of adsorbent, outperforming $CaSiO_3$. Regeneration of $Ca_3(HCA)_2$ was successfully achieved via acid-base treatment, allowing reuse in subsequent cycles. FT-IR analysis confirmed the adsorption of phospholipids without residual adsorbent contamination, indicating clean separation and high affinity of the adsorbents for gum components. The recovered phospholipid-rich fraction also demonstrated potential for downstream applications. This work highlights the promise of $Ca_3(HCA)_2$ as a highly effective and regenerable adsorbent, offering an environmentally friendly and cost-efficient alternative to conventional degumming. The findings support further exploration of hybrid adsorbent systems in sustainable edible oil refining technologies. The study provides an alternative approach to conventional degumming technologies and contributes to improving efficiency and sustainability in edible oil refining.

Keywords: Crude Palm Oil; Calcium Hydroxycitric Acid; Calcium Silicate; Phosphorus; Phospholipids; Sustainable Refining.

INTRODUCTION

Vegetable oils are among the most widely consumed food commodities globally, with palm oil accounting for a significant proportion of global edible oil production. However, crude palm oil (CPO) contains various impurities such as phospholipids, free fatty acids, pigments, and trace metals that must be removed before consumption. Among these impurities, phospholipids—commonly referred to as gums—pose major challenges in refining because they interfere with downstream processing and may contribute to the formation of undesirable contaminants during high-temperature treatment. Efficient degumming is therefore essential to improve oil quality, processing efficiency, and product safety.

Rasayan J. Chem., 19(2),743-753 (2026)
http://doi.org/10.31788/RJC.2026.1919487

Although palm oil is a nutritious edible oil, it contains various undesirable components such as free fatty acids (FFAs), gums, pigments, waxes, phosphates, toxic metal ions, and odour-causing compounds, making it unsuitable for direct consumption.[1,2] The industrial refining process is therefore essential and typically includes multiple stages: degumming, bleaching, and deodorisation, ultimately producing refined, bleached, and deodorised palm oil (RBDPO).

The development of more efficient and environmentally sustainable refining technologies aligns with Sustainable Development Goal 12 (Responsible Consumption and Production), which encourages resource-efficient industrial processes and the reduction of waste in food production systems. Improving degumming efficiency can reduce chemical consumption, minimise oil losses, and enhance the sustainability of edible oil refining processes.[2]

The degumming step is specifically aimed at removing impurities such as phospholipids (PLs), commonly referred to as gums. PLs are amphiphilic molecules, possessing both lipophilic fatty acid chains and hydrophilic glycerol phosphate groups. This dual nature enables them to act as emulsifiers, remaining soluble in oil and interfering with the bleaching process. At elevated temperatures, PLs may decompose and cause oil darkening or potentially react with chlorides to form 3-monochloropropane-1,2-diol esters (3-MCPDs)—recognised carcinogenic compounds.[2-6]

Phospholipids in crude oil are generally classified into two types based on their water solubility: hydratable phospholipids (HPs) and non-hydratable phospholipids (NHPs). The conventional degumming method uses water to hydrate and remove HPs. While effective, this method requires significant volumes of high-quality water and is limited in its ability to remove NHPs.[7] To address this, researchers have explored the use of acids such as phosphoric acid or citric acid to convert NHPs into hydratable forms. For instance, degumming with 0.05% phosphoric acid has been reported to reduce PLs to below 30 mg P/kg oil; however, it may also promote the formation of FFAs, leading to additional oil loss during processing.[8-11]

The degumming process involving a combination of acid and base offers certain advantages. The basic component neutralises free fatty acids (FFAs), converting them into soap, while sodium ions bind to phospholipids to convert them into hydratable forms.[12] The introduction of ethylenediaminetetraacetic acid (EDTA), a well-known chelating agent, further stabilises phospholipids and facilitates their separation.[13] Although chemical degumming methods enable smoother processing, they often lead to environmental concerns and significant oil loss, resulting in higher operational costs.[14]

To address these challenges, alternative degumming technologies such as enzymatic and membrane-based methods have been developed. Enzymatic degumming offers improved environmental performance and oil quality; however, it typically requires a series of specific enzymes due to their selective action on different phospholipid bonds, which increases overall process complexity and cost.[15-17] On the other hand, membrane separation techniques offer non-thermal, size-selective degumming. Membranes such as polyvinylidene fluoride (PVDF), polyethersulfone (PES), polysulfone (PSf), and ceramic membranes have demonstrated effective phospholipid separation.[18-20] However, their application is often limited by the complexity and cost of membrane system installations.

More recently, activated carbon nanoparticles have been explored as adsorbents for degumming Ceiba pentandra oil, achieving up to 95% reduction in phosphorous content through surface interactions and high porosity.[21] Importantly, recovery of adsorbed phospholipids is of interest, as gum derived from palm oil has shown potential as an additive to improve vehicle fuel performance.[22]

In this study, two types of adsorbents were investigated: calcium silicate ($CaSiO_3$), an inorganic compound, and calcium hydroxycitric acid ($Ca_3(HCA)_2$), a hybrid organic-inorganic material. Calcium ions (Ca^{2+}) are known to play a role in adsorbing carotenoids from CPO.[23,24] While the combination of calcium ions with sulfonated long-chain hydrocarbons enhances carotenoid adsorption, desorption becomes difficult. In contrast, calcium silicate shows lower adsorption capacity but improved desorption ability. Both adsorbents contain Ca–O–X linkages, where X can be either SiO_3^{2-} or HCA^{3-}. The silicon atom in $CaSiO_3$ contains partially vacant d-orbitals, enabling interactions with Lewis base sites in crude palm oil. Additionally, the molecular ring structure of calcium silicate forms pores through ion pairing (Ca^{2+} and SiO_3^{2-}), promoting interactions with phospholipids.

Meanwhile, $Ca_3(HCA)_2$ contains the HCA^{3-} anion, an organic moiety with a medium-length carbon chain that interacts with hydrocarbon chains in CPO. Its ionic bond with Ca^{2+} forms a polar structure that induces dipole interactions, while two hydroxyl (–OH) groups on a non-polar backbone allow it to act as a surfactant. The molecule likely has a polymeric structure with randomly sized rings formed by calcium and hydroxycitric acid, enhancing phospholipid (PL) adsorption through synergistic polarity and organic interactions. Like calcium silicate, it forms –(Ca–O–Si)– ring moieties via Ca^{2+} and SiO_4^{4-} interactions, facilitating dipole–dipole interactions with PLs. Both adsorbents are neutral and interact with oil components through affinity-based, not chemical, mechanisms.

Despite advances in degumming methods, key limitations remain in effectively removing NHPs without excessive oil loss or environmental impact. Conventional chemical and enzymatic methods face challenges related to operational cost, oil retention, and component selectivity. While some adsorbent-based approaches show promise, they often lack regeneration capability or selectivity in phospholipid recovery. Additionally, the synergistic potential of hybrid organic-inorganic adsorbents such as calcium silicate and calcium hydroxycitric acid has not been thoroughly evaluated. Therefore, a research gap exists in developing efficient, regenerable, and selective adsorbents for sustainable degumming of crude palm oil. This study aims to address this gap by evaluating the adsorption performance of $CaSiO_3$ and $Ca_3(HCA)_2$ in reducing phospholipid content from crude palm oil. The objective is to evaluate their effectiveness in degumming CPO and to assess their potential as sustainable alternatives for edible oil refining.

EXPERIMENTAL

Research Methodology Overview

This study employed an experimental approach to evaluate the degumming performance of calcium-based adsorbents in crude palm oil. The methodology consisted of three main stages: (1) synthesis and characterisation of calcium hydroxycitrate and calcium silicate adsorbents, (2) adsorption experiments to evaluate phospholipid removal efficiency at different adsorbent dosages, and (3) regeneration and reuse of the adsorbent, followed by analytical characterisation of the recovered fractions. Phospholipid removal efficiency was quantified by measuring phosphorus content using spectrophotometric analysis.

Material and Methods

Crude palm oil (CPO) from the local area was donated by PTKI, Medan. $CaCl_2{\cdot}H_2O$, Na_2H_2EDTA, $Na_2SiO_3{\cdot}9H_2O$, triethanolamine, and hydroxynaphthol blue were purchased from Merck, Germany. KMgHCA, with an HCA content of approximately 64–68%, was used as the precursor, and $Ca_3(HCA)_2{\cdot}2H_2O$, provided by Glykon Company, USA, was used as the standard. Demineralised or deionised water was used throughout the study.

Preparations of Calcium Hydroxycitric Acid ($Ca_3(HCA)_2$)

The preparation method follows the procedure reported in US Patent No. 11,066,423 B2.[25] Potassium magnesium hydroxycitric acid (KMgHCA) (320 g, approximately 1.096 moles) was dissolved in 400 mL of hot demineralised water and placed in a 1 L beaker. A solution of $CaCl_2{\cdot}2H_2O$ (290.988 g, 1.644 moles) in 400 mL of demineralised water was then added slowly to the KMgHCA solution under vigorous stirring, resulting in the formation of a white solid precipitate of $Ca_3(HCA)_2$. The precipitate was isolated and washed three times with 200 mL portions of hot demineralised water. The dried solid product weighed 310.1 g. Calcium content was determined by EDTA titration, and HCA content was quantified using high-performance liquid chromatography (HPLC) analysis.

Determination of Calcium Content using EDTA Titration

A 302 mg sample of calcium hydroxycitric acid was dissolved in 5 mL of 3 N HCl in a beaker. The solution was then diluted with 120 mL of demineralised water. While stirring continuously, 0.5 mL of triethanolamine, 300 mg of hydroxynaphthol blue, and 22 mL of 0.0494 M EDTA solution were added from a burette. Next, 5 M NaOH was added until a colour change occurred. The solution was then titrated with an additional 32.18 mL of EDTA solution until a clear blue endpoint was reached. The calcium content was determined to be 21.09%.

Analysis of HCA Content using HPLC

Calcium hydroxycitric acid was analysed by HPLC using a Chromolith High Resolution RP-18 column (100 × 4.6 mm, encapped). The mobile phase consisted of 10 mM $(NH_4)_2HPO_4$ adjusted to pH 2.7. The flow rate was set to 1 µL/10 min, with an injection volume of 20 µL. The run time was 5 minutes, and the column temperature was maintained at 30°C. Detection was performed using a UV detector at 210 nm. The system operated at a gas pressure of 32 bar.

Procedure

Ten milligrams of calcium hydroxycitrate, $Ca_3(HCA)_2$, were placed in a 10 mL volumetric flask and dissolved with 10 mM $(NH_4)_2HPO_4$ solution (pH 2.7) to prepare the standard solution. From this solution, 2 mL and 4 mL aliquots were pipetted into separate 10 mL volumetric flasks and diluted with the same 10 mM $(NH_4)_2HPO_4$ solution (pH 2.7). The concentration of HCA was calculated based on the conversion factor that 1 mg of $Ca_3(HCA)_2$ is equivalent to 0.785 mg of HCA. A sample containing 8 mg of $Ca_3(HCA)_2$ was weighed, dissolved in 10 mL of 10 mM $(NH_4)_2HPO_4$ (pH 2.7), and prepared for HPLC analysis. The chromatogram areas obtained for the three solutions were 1073.705, 1875.359, and 2435.800, respectively.

Preparation of Calcium Silicates

A 5 L beaker equipped with a mechanical propeller and an oil bath was used. A solution of 1000 mL of 0.5 M $CaCl_2 \cdot 2H_2O$ and 100 mL glycerol was placed in the beaker. Under vigorous stirring at 80°C, 1000 mL of 0.5 M $Na_2SiO_3 \cdot 9H_2O$ solution was added dropwise over 1 hour. The resulting white suspension was stirred continuously for 12 hours at 80°C. After cooling to room temperature, the suspension was filtered, and the white precipitate was washed three times with 500 mL portions of demineralised water. The powder was then dried at 250°C until constant weight was achieved. The final yield was 73.56 g. Characterisation of the product was performed by X-ray diffraction (XRD).

Degumming CPO Performance of the Adsorbents

Adsorbent $Ca_3(HCA)_2$

In an Erlenmeyer flask with a side arm connected to a vacuum system, 2 g of crude palm oil (CPO) and 2.0 g of the adsorbent were placed and heated at 100 °C for 3 hours. The resulting dry powder was transferred to a 50 cm burette column, and 30 mL of n-hexane was added. Under a nitrogen atmosphere at atmospheric pressure, the effluent was collected and distilled to obtain the oil fraction. The weight of the residual oil fraction was calculated by the difference between the initial CPO weight and the oil recovered in the effluent. Adsorption experiments were repeated with adsorbent amounts of 4.0 g, 6.0 g, and 8.0 g, each using 2 g of CPO. The oil retained in the adsorbent was collected and analysed for phosphorus content after adsorbent regeneration. Similar procedures were applied using calcium silicate ($CaSiO_3$) as the adsorbent. The amount of adsorbed phospholipids (PLs) was determined based on the phosphorus content.

Regeneration of the used $Ca_3(HCA)_2$ Adsorbent

The used adsorbent containing residual CPO was treated with 5–15 mL of 0.1 N HCl until the solution reached pH 5. Then, 25 mL of n-hexane was added, resulting in two distinct layers. The aqueous layer was neutralised by adding NaOH solution, which precipitated solid $Ca_3(HCA)_2$. The recovered $Ca_3(HCA)_2$ was reused as the adsorbent. The upper organic layer was dried under vacuum to obtain a semi-solid mixture of phospholipids and free fatty acids, which were weighed and analysed for phosphorus content.

Measurement of Phospholipids

Pretreatment of CPO Fraction Samples

The method for measuring phospholipids follows the procedure reported by Chen *et al.*[26]. Crude palm oil (CPO) and its residual fractions were treated by adding 0.5–1 mL of concentrated sulfuric acid (H_2SO_4, 98%) in a crucible, then heated and cooled to room temperature. The resulting char was mixed with 1.5–7 g of KOH and heated in a furnace at 700°C for 1.5 hours. After cooling to room temperature, 30 mL of

hot deionised water was added to the crucible to extract the sample. The resulting solution was filtered into a 100 mL volumetric flask, acidified to approximately pH 5.5 with dilute hydrochloric acid, and diluted to 100 mL with deionised water. A 10 mL aliquot of this solution was mixed with 8 mL of 0.015% hydrazine sulfate and 2 mL of 2.5% ammonium molybdate. After heating in a boiling water bath and cooling to room temperature, the solution was diluted to 50 mL with deionised water. The absorbance of these samples was measured and compared to that of the standard solution.

Measurement of the Standard Curve

A stock solution of 0.04387 g/L KH_2PO_4, equivalent to approximately 10 ppm phosphorus (P), was prepared and diluted to create standards of 0.00, 0.01, 0.02, 0.04, 0.06, and 0.08 mg/L phosphorus. To each solution, 8 mL of 0.015% hydrazine sulfate and 2 mL of 2.5% ammonium molybdate were added. The mixtures were heated in a vigorously boiling water bath for 10 minutes. After cooling to room temperature, the solutions were diluted to 50 mL with deionised water. Absorbance was measured at 713 nm, which corresponds to the maximum wavelength (λmax) for this assay. The phospholipid content in crude palm oil (CPO) and its fractions was estimated by multiplying the phosphorus content by a factor of 24.24, as reported by Goh.[27] The calculation is expressed by Equation (1):

$$PLs = \frac{P}{m} \times V3 \times \frac{V1}{V2} \times 24.24 \quad (1)$$

Where:

PLs	=	phospholipid content (mg/kg)
P	=	phosphorus content (mg/L)
m	=	mass of oil sample (g)
V3	=	final dilution volume (50 mL)
V2	=	aliquot volume taken for analysis (10 mL)
V1	=	volume of extract solution (100 mL)

This can be simplified to Equation (2):

$$\text{PLs} = \frac{P}{m} \times 12.120 \quad (2)$$

RESULTS AND DISCUSSION

This section presents the experimental findings obtained from the characterisation of the synthesised adsorbents and their performance in the degumming of crude palm oil. The results are organised according to the experimental procedures described in the methodology, including adsorbent characterisation, degumming efficiency, adsorbent regeneration, and FT-IR analysis. The data provide quantitative evidence of the adsorption capability of the investigated materials and their effectiveness in reducing phospholipid content in CPO.

Characterization of $Ca_3(HCA)_2$ the Adsorbent

The calcium content of the synthesised adsorbent $Ca_3(HCA)_2$ was determined using complexometric titration with EDTA. Each millilitre of 0.05 M EDTA corresponds to 2.004 mg of calcium. The calcium percentage was calculated using the following formula:

$$\%Ca = \frac{V_{EDTA} \times M_{EDTA} \times 2.004 \times 100\%}{0.05 \times W} \quad (3)$$

Substituting the experimental values:

$$\%Ca = \frac{32.18\,mL \times 0.0494\,mol/L \times 2.004\,mg \times 100\%}{0.05\,mol/L \times 302\,mg} = 21.09\% \quad (4)$$

This result is consistent with the literature value of 21.1% reported for $Ca_3(HCA)_2 \cdot 2H_2O$.[24] HPLC analysis yielded chromatogram peak areas of 1073.705, 1875.359, and 2435.800, corresponding to 2 mg and 4 mg of HCA standard and 8 mg of preparative $Ca_3(HCA)_2$, respectively, all at a retention time of 2.87 minutes. The calibration curve of peak area versus $Ca_3(HCA)_2$ mass (Fig.-1) gave a linear function

of $Y = 214.6X + 793.4$ ($R^2 = 0.917$). The high linearity indicates that the preparative $Ca_3(HCA)_2$ exhibits comparable HCA content and chromatographic behaviour to the standard.

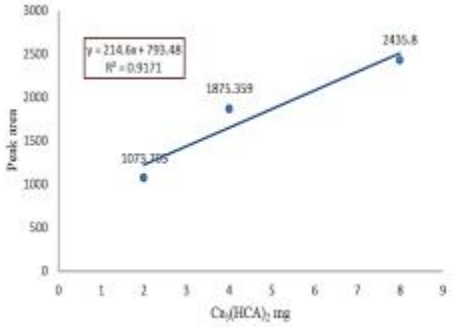

Fig.-1: Linearity of $Ca_3(HCA)_2$ Mass versus HPLC Peak Area

Degumming CPO Performance of the Adsorbents

The degumming performance of the two adsorbents for crude palm oil (CPO) was evaluated using column chromatography.The difference between the initial weight of CPO oil (Wi, in grams) and the weight of the oil collected after column treatment (Wef, in grams) was used to determine the amount of oil adsorbed (Wads), where:

$$Wads = Wi - Wef$$

After elution with 30 mL of n-hexane, the phosphorus content in the initial CPO (Pi), the effluent (Pef), and the adsorbed fraction (Pads) was quantified using the calibration equation derived from the standard curve (Fig.-2):

$$y = 3.675x + 0.033$$

where y is the absorbance and x is the phosphorus concentration in mg/L.

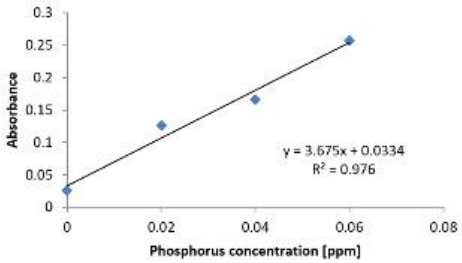

Fig.-2: Standard Curve for Phosphorus Quantification

The phospholipid content in the initial oil (PLs i), effluent (PLs ef), and adsorbed fraction (PLs ads) was calculated and expressed in mg/kg. Table-1 summarizes the yield (Wef), phosphorus content (Pef), phospholipid concentration (PLs ef), and absorbance values for each type of adsorbent. Subscripts (1) and (2) denote $Ca_3(HCA)_2$ and $CaSiO_3$, respectively.

Table-1: Degumming Performance of $Ca_3(HCA)_2$ and $CaSiO_3$ Adsorbents in Crude Palm Oil

Types of adsorbents: (1) $Ca_3(HCA)_2$ and (2) $CaSiO_3$				
Adsorbent (g)	2	4	6	8
W ef (1) g	1.958	1.952	1.951	1.952
W ef (2) g	1.954	1.950	1.950	1.952
Abs ef (1)	0.0664	0.0437	0.0367	-
Abs ef (2)	0.0697	0.0583	0.0524	0.0517
[P]ef (1) mg/L	0.0091	0.0029	0.001	-
[P]ef (2) mg/L	0.0110	0.0069	0.053	0.051
PLs ef (1) mg/kg	56.233	20.133	0.030	-
PLs ef (2) mg/kg	68.243	42.737	33.372	31.455

Phospholipid concentrations (PLs) were obtained after a 5-fold dilution to 500 mL total volume. The total phosphorus mass (mg) was calculated using the following equation:

$$\text{Mass P (mg)} = \text{P (mg/L)} \times V_3 \times (V_1/V_2) \times (1\ \text{L} / 1000\ \text{mL}) \quad (5)$$

Where:
V_3 = 50 mL (volume of ashed solution)
V_1 = 100 mL (volume before dilution)
V_2 = 10 mL (aliquot used for measurement)
Phosphorus content per unit mass of oil was then calculated as:
P (mg/kg) = (Mass P / mass of oil (g)) × 1000
For simplicity, the equation can be expressed as:
P (mg/kg) = (P (mg/L) / m (g)) × 500
PLs (mg/kg) = P (mg/kg) × 24.24
Thus:

$$\text{PLs (mg/kg)} = (\text{P (mg/L)} / \text{m (g)}) \times 12.120 \quad (6)$$

Ashing tests showed phosphorus absorbance values of 0.1467 (for 5 g oil) and 0.0783 (for 2 g oil), corresponding to phosphorus concentrations of 0.0309 mg/L and 0.0123 mg/L, respectively. Using equation (6), the calculated PLs content was 74.90 and 74.54 mg/kg, consistent with previously reported values.[27] The degumming performance of the adsorbents on CPO is illustrated in Fig.-3, which shows the residual phospholipid content in the oil effluent after treatment. As seen in the figure, the adsorbent $Ca_3(HCA)_2$ demonstrates a notably higher efficiency in removing gum (phospholipids) from the oil, particularly when using 6 g of the adsorbent. This indicates that $Ca_3(HCA)_2$ has a strong adsorption capacity for phospholipids compared to other adsorbents evaluated.

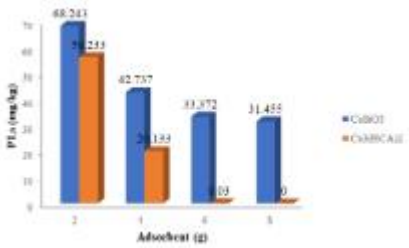

Fig.-3: Adsorption Performance of the Adsorbents in Removing Gum from Crude Palm Oil

Regeneration of the used $Ca_3(HCA)_2$ Adsorbent

The used $Ca_3(HCA)_2$ adsorbent, which contained residual CPO, was regenerated through acid treatment. The spent adsorbent was treated with 15 mL of 0.1 N HCl and 25 mL of n-hexane, resulting in the formation of two distinct layers. The bottom aqueous layer was separated and neutralised with a sodium hydroxide (NaOH) solution, which led to the precipitation of solid $Ca_3(HCA)_2$. This regenerated solid was recovered and reused as an adsorbent. The upper organic layer was collected, evaporated under vacuum, and the resulting semi-solid residue was weighed and analysed for phosphorus content to estimate the phospholipid (PLs) concentration. The results are summarised in Table-2.

Table-2: Phospholipid Content in the Recovered Fraction after Regeneration of $Ca_3(HCA)_2$ Adsorbent

Adsorbent (g)	2	4	6	8
W ads	0.040	0.045	0.046	0.046
Abs	0.0448	0.0661	0.0781	0.0783
P mg/L	0.0032	0.0090	0.0123	0.0123
PLs mg/kg	974.25	2,439	3,239	3,239

Using 6 g of $Ca_3(HCA)_2$ to treat 2 g of CPO resulted in the complete removal of phospholipids from the oil. However, the recovered semi-solid contained approximately 3,239 mg/kg of PLs, suggesting that the residue may also include other components such as free fatty acids. The acidic form of the adsorbent is more likely to remain in the aqueous phase, which simplifies its recovery and enables efficient regeneration and reuse in subsequent adsorption cycles.

FT-IR Spectroscopy Analysis

FT-IR spectra were obtained for the $Ca_3(HCA)_2$ adsorbent (blue), crude palm oil (CPO, red), and the isolated gum fraction recovered from the $Ca_3(HCA)_2$ adsorbent (black). The results are presented in Fig.-4.

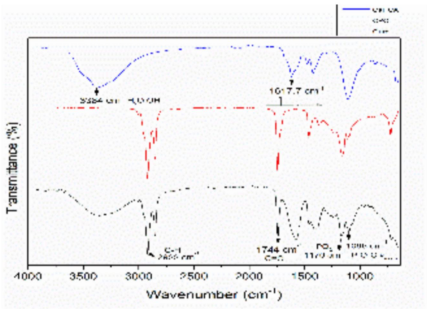

Fig.-4: FT-IR Spectra of $Ca_3(HCA)_2$ Adsorbent, CPO Oil, and Isolated Phospholipids

The absorption band observed at 1617.7 cm^{-1}corresponds to the stretching vibration of carboxylate groups coordinated with metal ions (–COO^-M), specifically calcium (Ca), indicating the presence of calcium salts. In the crude palm oil (CPO) spectra, characteristic peaks are evident at 1744 cm^{-1}, assigned to ester carbonyl (–COOR) stretching, and at 1170 cm^{-1}, corresponding to phosphate (–OPO–) stretching vibrations. In the spectra of the isolated gum fraction, prominent bands appear in the broad region between 3750 and 3150 cm^{-1}, typically attributed to O–H stretching vibrations, which are characteristic of hydroxyl groups in phospholipids (PLs). Additional peaks at 1744 cm^{-1} and 1170 cm^{-1} confirm the presence of ester and phosphate functional groups, consistent with earlier reports.[28] The broad O–H band suggests that the gum fraction likely contains PL-associated compounds such as choline, ethanolamine, or inositol moieties.[27] The high concentration of isolated phospholipids resulted in well-defined FT-IR spectra, enabling clear identification of key functional groups. Notably, there was no spectral evidence indicating the presence of any adsorbent residues. This absence supports the hypothesis that the adsorption process did not leave detectable traces of the material on the gum fraction. Based on this, a plausible transformation mechanism involving the adsorbent, specifically calcium dihydroxy citric acid [$Ca_3(HCA)_2$], during the adsorption process is proposed, as illustrated in Fig.-5.

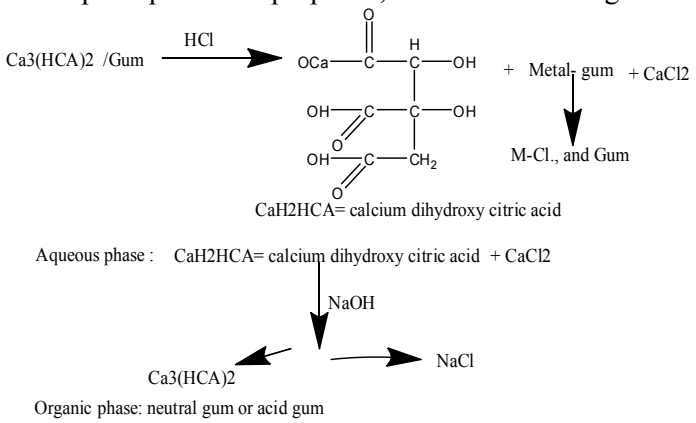

Fig.-5: Plausible Transformation Adsorbent Ca3 (HCA)2 in the Adsorption Process

The findings of this study reaffirm the critical role of degumming in phosphorus removal, which is essential to prevent catalyst poisoning in subsequent refining steps. Our results demonstrate that both acid and water degumming significantly reduce phosphorus content, consistent with the previous findings, which optimised chemical refining parameters for kenaf seed oil.[3] Similarly, the effective removal of phospholipids in palm oil has been observed to correlate with a reduction in the formation of harmful byproducts, underscoring the necessity of optimised degumming for enhancing overall oil quality.[6] These findings are further supported by earlier studies,[7,8,] which emphasised that water degumming alone is insufficient for oils rich in non-hydratable phosphatides (NHPs). Acid treatment is required to convert NHPs into their hydratable forms, thereby facilitating more efficient removal. Our data corroborate this

perspective, demonstrating significantly higher phosphorus reduction when acid degumming is applied, particularly in oils with elevated NHP content.

In addition, our study revealed a notable decrease in 3-monochloropropane-1,2-diol esters (3-MCPDE) and glycidyl esters (GE) with optimised degumming parameters. This outcome is consistent with previous findings ([2,5]which reported that modifications to the degumming and bleaching stages can significantly mitigate the formation of these processing contaminants. Our findings contribute to this growing body of evidence, highlighting that lowering residual phosphorus and other precursor components upstream reduces the potential for GE and 3-MCPDE formation during deodorization. Complementary to this, another study demonstrated that post-bleaching washing of palm oil further reduces GE levels,[4] reinforcing the cumulative benefit of sequential refining steps when paired with effective degumming practices.

Although this present study focused on conventional acid and water degumming, literature highlights the advantages of enzymatic methods. Several studies have reported that phospholipase-assisted degumming significantly improved phosphorus removal with minimal oil loss.[16-18] These enzymatic methods also allow for a gentler refining process that helps retain sensitive bioactives. In this regard, the potential of enzymatic degumming represents a promising future direction. Incorporating enzyme technology could further improve the efficiency and sustainability of the process while maintaining oil quality.

A critical concern in refining is the retention of valuable phytonutrients. In our study, more aggressive degumming methods improved impurity removal but led to greater loss of carotenoids and tocopherols. This observation is in line with the results of the previous study, reporting that certain degumming methods, while effective in dephosphorization, compromise the concentration of bioactive components.[15] Similarly, other research highlighted the delicate balance between refining effectiveness and phytonutrient preservation in palm-pressed mesocarp fibre oil.[12] In response to this, some researchers have explored the use of adsorbents, such as M-polystyrene sulfonate, to selectively extract carotenoids from crude palm oil.[23,24] Our findings, though not employing these adsorbents, similarly indicate that alternative or selective degumming strategies may help preserve valuable minor components.

Emerging technologies such as ultrafiltration and nanoparticle-assisted degumming have demonstrated promising results. Studies have shown that membrane-based methods can effectively remove phosphorus while eliminating the need for chemical additives.[19,20] While our study did not directly utilise membrane filtration, the findings suggest compatibility and potential synergy between conventional and physical methods. Moreover, the use of activated carbon nanoparticles in hydro-degumming shows enhanced impurity removal.[21] These novel approaches highlight the increasing interest in hybrid or advanced degumming systems that combine high performance with environmental sustainability. The method used for phosphorus quantification in our study correlates well with the approaches of several experts,[26,28] who validated more sensitive and accurate protocols for monitoring phospholipid content in vegetable oils. This analytical alignment enhances the robustness of our results and ensures comparability across studies.

CONCLUSION

This study demonstrated the effectiveness of calcium-based adsorbents in the degumming of crude palm oil. Among the two materials evaluated, calcium hydroxycitrate ($Ca_3(HCA)_2$) exhibited superior adsorption performance, achieving complete phospholipid removal when 6 g of adsorbent was applied to 2 g of crude palm oil. Calcium silicate ($CaSiO_3$) also showed phospholipid adsorption capability, but with lower efficiency. Spectroscopic analysis confirmed the successful adsorption of phospholipids without contamination of the oil fraction. In addition, $Ca_3(HCA)_2$ could be regenerated through a simple acid-base treatment and reused, demonstrating its potential as a cost-effective and sustainable adsorbent. These findings indicate that $Ca_3(HCA)_2$ is a promising material for improving degumming efficiency in edible oil refining processes. Furthermore, the use of regenerable adsorbents contributes to more resource-efficient refining technologies, supporting sustainable industrial practices aligned with Sustainable Development Goal-12 on responsible consumption and production.

ACKNOWLEDGMENTS

We wish to thank Glykon Company for their support by providing the calcium hydroxycitric acid standard and KMgHCA materials.

CONFLICT OF INTERESTS

The authors declare that there is no conflict of interest.

AUTHOR CONTRIBUTIONS

The present work is related to *SDG-12: Responsible Consumption and Production*. All the authors contributed significantly to this manuscript, participated in reviewing/editing and approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:

Junedi Ginting http://orcid.org/0009-0002-0201-0571
Syukratun Nufus http://orcid.org/0000-0003-0638-7966
Enita Dewi Tarigan https://orcid.org/0000-0002-5635-5287
Naomi E. M. Sinaga https://orcid.org/0009-0002-3064-9292
Imelda D. Ambarita https://orcid.org/0009-0001-1899-6403
Eko K. Sitepu https://orcid.org/0000-0003-3565-9027
Nimpan Bangun https://orcid.org/0009-0003-5125-7041
Juliati Br. Tarigan https://orcid.org/0000-0001-5705-506X
Helki I. Ginting https://orcid.org/0009-0003-7155-0528

Cite this article as: J. Ginting *et al.*, *Rasayan J. Chem.*, 19(2), 743-753(2026), https://doi.org/10.31788/RJC.2026.1929487.

REFERENCES

1. A. K. M. Omar, T. L. T. Norsalwani, M. S. Asmah, Z. Y. Badrulhisham, A. M. Easa, F. M. Omar, M. S. Hossain, M. H. Zuknik and N. A. N. Norulaini, *Journal of CO2 Utilisation*, **25**, 205(2018), https://doi.org/10.1016/j.jcou.2018.03.021
2. K. S. Hew, A. J. Asis, T. B. Tan, M. M. Yusoff, O. M. Lai, I. A. Nehdi and C. P. Tan, *Food Chemistry*, **307**, 125545(2020), https://doi.org/10.1016/j.foodchem.2019.125545
3. S. C. Chew, C. P. Tan and K. L. Nyam, *Separation and Purification Technology*, **188**, 379(2017), https://doi.org/10.1016/j.seppur.2017.07.049
4. W. C. Silva, J. K. Santiago, M. F. Capristo, R. A. Ferrari, E. Vicente, K. A. Sampaio and A. P. Arisseto, *Food Additives & Contaminants: Part A*, **36**, 244(2019), https://doi.org/10.1080/19440049.2019.1566785
5. B. I. Sim, Y. P Khor, O. M. Lai, C. B. Yeoh, Y. Wang, Y. Liu, I. A. Nehdi and C. P. Tan, *Food Chemistry*, **328**, 127147(2020), https://doi.org/10.1016/j.foodchem.2020.127147
6. M. Zulkurnain, O. M. Lai, R. A. Latip, I. A. Nehdi, T. C. Ling and C. P Tan, *Food Chemistry*, **135(2)**, 799(2012), https://doi.org/10.1016/j.foodchem.2012.04.144
7. T. N. Indira, J. Hemavathy, S. Khatoon, A. G. G. Krishna and S. Bhattacharya, *Journal of Food Engineering*, **43(2)**, 83(2000), https://doi.org/10.1016/S0260-8774(99)00135-1
8. A. J. Dijkstra, *European Journal of Lipid Science and Technology*, **119(9)**, 1600496(2017), https://doi.org/10.1002/ejlt.201600496
9. S. Y. Chen, N. Teerananont, T. Sonthisawate, P. Sreesiri, C. Puemchalad, T. Mochizuki, Y. Abe, M. Toba and Y. Yoshimura, *European Journal of Lipid Science and Technology*, **117(7)**, 1079(2015), https://doi.org/10.1002/ejlt.201400293
10. E. Costa, M. F. Almeida, M. C. Alvim-Ferraz and J. M. Dias, *Renewable Energy*, **124**, 27(2018), https://doi.org/10.1016/j.renene.2017.08.089
11. S. Paisan, P. Chetpattananondh and S. Chongkhong, *Journal of Environmental Chemical Engineering*, **5(5)**, 5115(2017), https://doi.org/10.1016/j.jece.2017.09.045
12. L. N. L. Harrison, Y. S. Tee, M. K. Chan and S. S. Teh, *Journal of Oleo Science*, **71(2)**, 177(2022), https://doi.org/10.5650/jos.ess21256

13. V. Kulkarni, S. Jain, F. Khatri and T. Vijayakumar, *International Journal of ChemTech* Research, **6(8)**, 3969(2014), https://www.sphinxsai.com/2014/ICSET/1/(3969-3978)%20014.pdf
14. A. Choukri, M. A. Kinany, V. Gibon, A. Tirtiaux and S. Jamil, *Journal of the American Oil Chemists' Society*, **78(11)**. 1157(2001). http://dx.doi.org/10.1007/s11746-001-0405-x
15. Z. Li, W. Wang, X. Liu, S. Qi, D. Lan and Y. Wang, *Process Biochemistry*, **133**, 190(2023), https://doi.org/10.1016/j.procbio.2023.08.019
16. X. Jiang, M. Chang, Q. Jin and X. Wang, *Process Biochemistry*, **50(3)**, 432(2015), https://doi.org/10.1016/j.procbio.2014.12.011
17. R. M. dos Passos, R. M. da Silva, P. V. de Almeida Pontes, M. A. Morgano, A. J. A. Meirelles, C. V. Stevens, M. C. Ferreira and K. A. Sampaio, *LWT,* **159**, 113197(2022), https://doi.org/10.1016/j.lwt.2022.113197
18. Z. B. Mohammadi, Z. H. Esfahani, M. A. Sahari and K. K. Darani, *Iranian Journal of Chemistry and Chemical Engineering*. **40(5)**, 109(2021), https://doi.org/10.30492/ijcce.2020.40607
19. A. M. de Souza, C. C. de Morais, L. A. G. Gonçalves and L. A. Viotto, *Separation and Purification Technology*, **71(1)**, 13(2010), https://doi.org/10.1016/j.seppur.2009.10.005
20. G. A. R. Sehn, L. A. G, Gonçalves, C. C. Ming, *Grasas Aceites,* **67**, 1(2016), https://doi.org/10.3989/gya.0498151
21. S. Syahrudin, S, L. Yuliati, D. Widhiyanuriyawan and I. N. G. Wardana, *Alexandria Engineering Journal*, **61(6)**, 4729(2022), https://doi.org/10.1016/j.aej.2021.10.025
22. M, Supeno, B. Aritonang, A. H. Ritonga, R. Gurusinga, K. Harefa and R. Tambun, *Rasayan Journal of Chemistry*, **15(04)**. 2394(2022), http://doi.org/10.31788/RJC.2022.1547090
23. N. Bangun, S. B. Sembiring, N. K. Putri and J. A. Karo Karo, *Procedia Chemistry*, **16**, 349(2015), https://doi.org/10.1016/j.proche.2015.12.063
24. J. A. Karo Karo, S. B. Sembiring, N. Bangun and Tj. Herawan, *Indian Journal of Science and Technology*, **7(12)**, 1925(2014), https://dx.doi.org/10.17485/ijst/2014/v7i12.10
25. D. E. Clouatre, N. Bangun and D. L. Clouatre, US Patent No 11,066,423 B2 (2021), https://patents.google.com/patent/WO2018049216A1/en
26. B. Chen, X. Xiao, R. Li, W. Zhao, K. Yang, G. Chen and X. Ma, *European Journal of Lipid Science and Technology*, **116**, 548(2014), https://doi.org/10.1002/ejlt.201300378
27. S. H. Goh, H. T. Kohr and P. T. Gee, *Journal of the American Oil Chemist Society*, **59(7)**, 296(1982), https://doi.org/10.1007/BF02662230
28. J. M. Nzai and A. Proctor, *Journal of the American Oil Chemist Society*, **75(10)**, 1281(1998), https://doi.org/10.1007/s11746-998-0173-x

[RJC-9487/2026]