GRASAS Y ACEITES 75 (1)
January-March 2024, e543
ISSN-L: 0017-3495
https://doi.org/10.3989/gya.0325231

Research progress on the genesis and removal methods of non-hydratable phospholipids from vegetable oils

F.G. Pan[a], J. Liu[a], J.X. Yang[a], J.R. Ren[a], Y.Y. Sun[a], P.Z. Li[a], E.Q. Yang[a], X.M. Chen[a] and B.Q. Liu[a,✉]

[a]Laboratory of Nutrition and Functional Food, College of Food Science and Engineering, Jilin University, Changchun 130062, PR China
✉Corresponding author: boqunliu@hotmail.com

Submitted: 29 March 2023; Accepted: 11 December 2023; Published: 10 April 2024

SUMMARY: Vegetable oil phospholipids can be divided into hydratable phospholipids (HP) and non-hydratable phospholipids (NHP). The general process of alkali refining or hydration degumming can remove most of the phospholipids, and the rest is mainly non-hydratable phospholipids. A non-hydratable phospholipid has obvious hydrophobicity, which cannot be completely removed even after 16 times of washing, so the non-hydratable phospholipid is the main research target of vegetable oil degumming. In order to better understand and study the non-hydratable phospholipids, the chemical composition and origin of non-hydratable phospholipids in vegetable oil are discussed. The advantages and disadvantages of these various detection and removal methods are analyzed in this paper.

KEYWORDS: *Vegetable oils; Non-hydratable phospholipids; Detection; Degumming; Research progress.*

RESUMEN: ***Avances en las investigaciones sobre la génesis y métodos de eliminación de fosfolípidos no hidratables de aceites vegetales.*** Los fosfolípidos de aceites vegetales se pueden dividir en fosfolípidos hidratables (HP) y fosfolípidos no hidratables (NHP). El proceso general de refinación alcalina o desgomado por hidratación puede eliminar la mayoría de los fosfolípidos, y el resto son principalmente fosfolípidos no hidratables. Un fosfolípido no hidratable tiene una hidrofobicidad obvia, que no se puede eliminar por completo incluso después de 16 lavados, por lo que el fosfolípido no hidratable es el principal objetivo de investigación del desgomado de aceites vegetales. Para comprender y estudiar mejor los fosfolípidos no hidratables, se discute la composición química y el origen de los fosfolípidos no hidratables en el aceite vegetal. En este artículo se analizan las ventajas y desventajas de estos diversos métodos de detección y eliminación.

PALABRAS CLAVE: *Aceites vegetales; Desgomado; Detección; Fosfolípidos no hidratables; Progreso de la investigación.*

Citation/Cómo citar este artículo: Pan FG, Liu J, Yang JX, Ren JR, Sun YY, Li PZ, Yang EQ, Chen XM, Liu BQ. 2024. Research progress on the genesis and removal methods of non-hydratable phospholipids from vegetable oils. *Grasas Aceites* **75** (1), e543. https://doi.org/10.3989/gya.0325231

1. INTRODUCTION

Vegetable oils, such as soybean oil, sunflower oil, olive oil, or peanut oil, can replace animal fat as a source of energy. Moderate intake of vegetable oils has many beneficial effects on health, including reducing the risk of cardiovascular disease and improving inflammatory diseases and the immune system (Hashempour *et al*., 2022). Vegetable oil mainly comes from all kinds of oil-bearing crops, and the crude oil is obtained by pressing or extracting, and then processed by degumming, alkaline refining, decolorization, deodorization and other refining processes to finally obtain finished, edible oil. Plant phospholipids mainly exist in the seeds of oil-bearing crops, an important class of lipid concomitants. Most of them exist in the colloid phase, binding with proteins, sugars, fatty acids, sterols, vitamins and other substances. In the process of oil production, phospholipids are extracted with the oil, and the effect of phospholipid removal directly determines the quality index of the refined oil.

Phospholipids are an amphiphilic molecule composed of a water-soluble phosphate group and two hydrophobic fatty acid groups. Phosphate groups usually bind to substances such as choline, ethanolamine, or glycerol to form different types of phospholipids, as shown in Figure 1. The phospholipids in vegetable oils can be divided into hydratable and non-hydratable phospholipids. Hydratable phospholipids are hydrophilic and can be removed by hydration, but in general, some phosphorus in oil exists in the form of non-hydratable phospholipids. A hydratable phospholipid has obvious hydrophobicity, which cannot be completely removed even after washing 16 times.

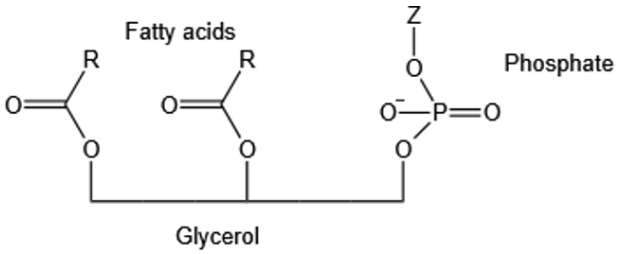

Figure 1. Schematic representation of lipid head group (Z) that acts as a substituent to connect with glycerophospholipid.
Lipid head group (Z) acts as a substituent to connect with glycerophospholipid.

In the refining process of vegetable oils, the content and nature of non-hydratable phospholipids affect the quality and stability of vegetable oils. Since non-hydratable phospholipids are difficult to remove, their presence increases the cost of oil treatment and leads to problems such as deepening the color of the oil and reducing storage stability (Jiang *et al.*, 2015). Vegetable oils with a high content of non-hydratable phospholipids are often accompanied by more metal ions, which will not only lead to vegetable oil acid and bad flavor, but also affect the post-sequence refining process (Zhao *et al.*, 2020). Therefore, the removal of non-hydratable phospholipids is the main research goal of vegetable oil degumming.

Furthermore, owing to the coexistence of hydrophobic and hydrophilic elements within phospholipids, the phosphate groups of phosphatides undergo esterification through the hydroxyl groups of diverse alcohols (e.g., ethanolamine, choline, inositol, and glycerol). Such diversity poses challenges in their isolation and analysis using conventional methodologies. Conventional phospholipid detection relies on chemical analysis techniques like thin-layer chromatography (TLC), high-performance liquid chromatography (HPLC), and mass spectrometry (MS) (Antonelli *et al.*, 2020). These approaches often entail intricate sample pretreatment and specialized equipment, making them time-consuming and costly. However, recent technological advancements have introduced novel methods for detecting phospholipids in vegetable oils. Spectroscopic techniques, such as near-infrared spectroscopy, offer non-destructive, real-time, and highly efficient means for rapid detection and quantitative analysis (Meng *et al.*, 2014). To delve deeper into understanding and studying non-hydratable phospholipids, the following section systematically elaborates on previous research in this domain.

2. GENESIS, MAIN MORPHOLOGY AND STRUCTURE OF NON-HYDRATABLE PHOSPHOLIPIDS

2.1. Genesis of non-hydratable phospholipids

According to the strength of the hydrophilic character, the phospholipids in plant crude oil are divided into hydratable phospholipids (HP) and non-hydratable phospholipids (NHP). The formation of non-hydratable phospholipids in vegetable oil is related to many factors, such as oil quality, storage, processing and transportation conditions, etc. Long

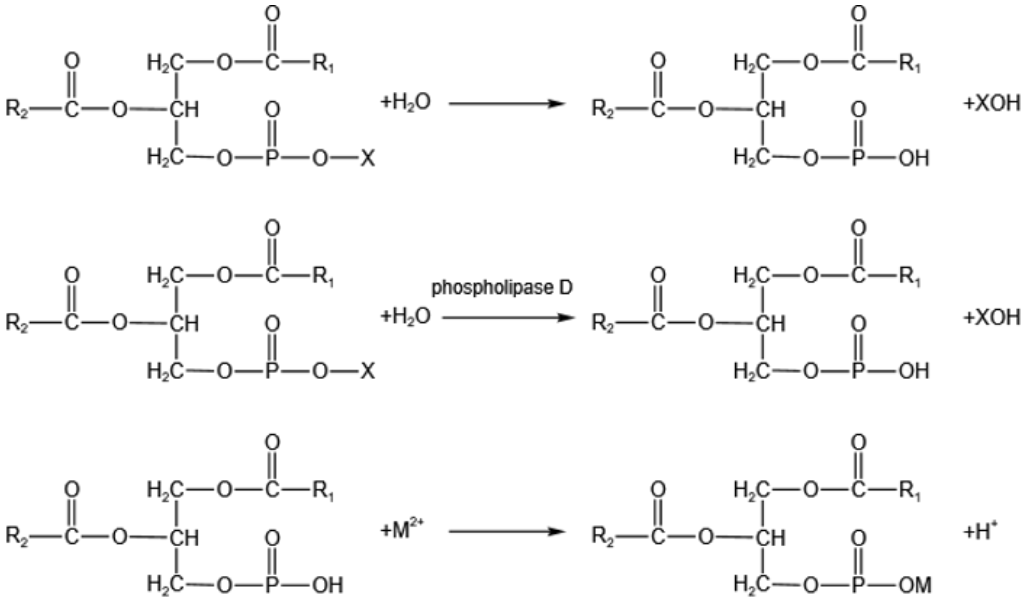

Figure 2. The major formation process of non-hydrated phospholipids
X represents choline, ethanolamine, inositol, etc.; M^{2+} represents divalent metal ions.

storage time, high water content and excessive phospholipase D activity all contribute to an increase in non-hydratable phospholipids in oil, which often leads to the hydrolysis of hydratable phospholipids into phosphatidic acid (Zhao *et al.*, 2020). Non-hydratable phospholipids form when they bind to divalent metal ions such as calcium and magnesium. The main formation process of non-hydratable phospholipids is shown in Figure 2.

2.2. Major morphology of non-hydratable phospholipids in vegetable oils

In vegetable oils, most NHP is mainly in the form of calcium-magnesium salts of phosphatidic acid and phosphatidic acid. Non-hydratable phospholipids (NHP) mainly include phosphatidic acid (PA), lysophosphatidic acid (LPA), lysophosphatidyl serine (PS), lysophosphatidyl ethanolamine (LPE) and calcium and magnesium salts of lysophosphatidic acid, etc. It was confirmed that phosphatidic acid is generated by phosphatidylcholine and phospholithyl ethanolamine subjected to phospholipase D, and can react with calcium to form non-hydratable phospholipids. The percentage of its composition obtained after detection and analysis is shown in Table 1 (Dijkstra, 2017). The common features are that they contain fewer polar groups, have obvious hydrophobicity, and are more difficult to bind with water in hydration degumming .

Table 1. Percent composition of non-hydratable phospholipids (%)

Constituent	America	Northeast China
Inorganic phosphate	15.8	24.0
Inositol monophosphate	2.1	0.7
Phasphoglyceric acid (PG)	18.7	5.2
Lysophosphatidic acid (LPA)	17.9	18.5
Phosphatidic acid (PA)	35.2	49.6
Phosphatidyl ethanolamine (PE)	9.3	1.8
Phosphatidyl serine (PS)	1.0	0.2

Hydratable phospholipids and non-hydratable phospholipids are mainly distinctive in the different functional groups linked to the hydroxyl group of the acid. The former contains more polar groups, such as choline, ethanolamine, serine, and inositol. Hydratable Phospholipids (HP) are mainly Phosphatidyl Choline (PC) and Phosphatidyl Ethanolamine (PE), so they are highly hydrophilic. They can precipitate in contact with water, but their hydration rate differs.

2.3. The structure of non-hydratable phospholipids

NHPs are a class of compounds with a phosphate ester structure in a nonaqueous environment, and their structure consists of three main parts: glycerol backbone, phosphate group and fatty acid chain. The hydroxyl clusters on the second and third carbon atoms of the glycerol backbone are esterified to phosphorylated functional

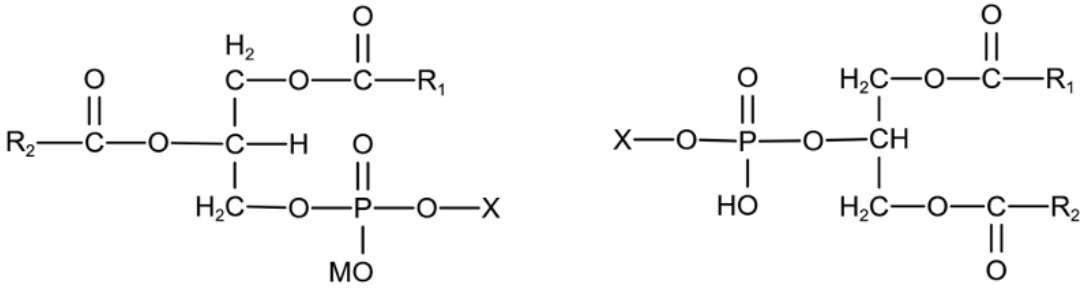

Figure 3. Non-hydratable phospholipid structures pass formula
X represents choline, ethanolamine, inositol, etc.; M represents the divalent metal ions.

groups, which can further esterify the hydroxyl groups of various alcohol groups including ethanolamine, inositol, choline and serine. The fatty acid tails of phospholipids are nonpolar and are mainly composed of two fatty acid chains linked to the glycerol backbone via ester bonds. The general formula of the non-hydratable phospholipid structure is shown in Figure 3.

3. COMPOSITION OF NHP IN DIFFERENT KINDS OF OILS

All kinds of oil processed as crude oil will contain a certain amount of NHP. This is especially relevant in the case of soybean, rapeseed and other major oils which are processed as crude oil. The composition of phospholipids in different kinds of vegetable oils is shown in Table 2.

As can be seen from Table 2, the proportion of HP and NHP in some vegetable oils is different, and is related to the longer storage time of crude oil and the conversion of some HP. Oil should be refined immediately after pressing, and soaked before steam heating or microwave treatment to inactivate phospholipase, prevent HP conversion, and lessen the burden of refining.

4. DETECTION OF NON-HYDRATABLE PHOSPHOLIPIDS

Stable and accurate PL quantification methods are needed to detect and analyze the process of oil degumming. Currently, techniques such as liquid chromatography, mass spectrometry, and spectrophotometry have been applied to the quantitative analysis of PL in edible oils. The Table 3 shows the

Table 2. Composition of phospholipids in different kinds of vegetable oils (%)

References	Plant oil species	Total phospholipids	HP			NHP		
			PC	PE	PA	LPA	PI	PG
Nash *et al*., 1984	Soybean oil	1-3	-	-	55	28	-	15.0
Hu *et al.*, 2011	Green bean crude oil	2-6	4	15	80	-	1	-
Diosady *et al.*, 1982	Rapeseed oil	1-1.5	40.2	23.0	7.0	-	11.6	18.0
Pérez *et al.*, 2019	Sunflower seed oil	0.5-1	31.6	5.67	31.75	-	31	-
Liu *et al.*, 2018	Maize germ oil	2.37	57.5-68.1	10.3-13.9	-	-	14.5-19.8	-
Ji *et al.*, 2012	Sesame oil	0.8-1.2	34.22	31.23	15.54	-	14.68	-
Zhao *et al.*, 2020	Peanut oil	0.3-0.7	59.3	11.0	2.0	-	27.7	-
Boukhchina *et al.*, 2004	Olive oil	2.3	5	9	12	-	11	63
Sengar *et al.*, 2013	Rice bran oil	1-4	20.4	17.8	-	-	5.8	-
Uitterhaegen *et al.*, 2016	French cilantro oil	0.3	25	17	33	-	17	-
Rao *et al.*, 2009	Curcas oil	1.45	60.5	15.5	-	-	24	-
Supansa *et al.*, 2017	Alga oil	5.1	-	-	-	-	-	-

HP: hydratable phospholipids, NHP: non-hydratable phospholipids, PC: Phosphatidyl Choline, PE: Phosphatidyl Ethanolamine, PA: phosphatidic acid, LPA: lysophosphatidic acid, PI: Phosphatidyl inositols, PG: Phasphoglyceric acid

Table 3. Advantages and disadvantages of each detection method for NHP

References	Test method	Detection limit	Advantages	Disadvantages
Yang *et al.*, 2008	Molybdenum blue colorimetry	0.42 mg/kg	RSD < 6%. Suitable for the accurate analysis of factory refined oil products.	There are more processes, more than 7 reagents required for detection, and need for high temperature carbonization, time-consuming.
Kou *et al.*, 2018	Fe_3O_4/TiO_2 composites Electrospray ionization mass spectrometry	0.01 μg/L	RSD=1.6-6.5%. Less sample consumption, fast analysis speed and simple operation. It can be used for direct and rapid detection of phospholipids in soybean oil.	Various parameters in the process, such as the elution ratio, are needed to be optimized.
van Rijn *et al.*, 2020	^{31}P nuclear magnetic resonance spectrometry	5 μmol/100g	Less interference factors, simple pretreatment, fast, high accuracy.	A large sample size is required, and the composition and proportion of the extraction agent are relatively strict.
Antonelli *et al.*, 2020	Liquid chromatography-High-resolution mass spectrometry	9-36 ng/g	The sensitivity is high and applied to oil detection with low phospholipid content.	The pretreatment process is complex, large sample consumption, but also requires a large number of chemical solvents, resulting in resource waste and environmental pollution.
Beneito-Cambra *et al.*, 2020	Environmental mass spectrometry analysis	0.53-1.14 μg/mL	With a small amount or even no sample manipulation, the analysis was rapid and accurate.	Incomplete or inadequate sample status may cause instrument problems with a residual effect.
Meng *et al.*, 2014	FTIR spectroscopy combined with partial least-square regression	0.0001 mg/kg	Simplified calibration, sample preparation and analysis, and facilitated automation.	The oil type has a significant influence and produces a significant deviation.
Aleksandra *et al.*, 2003	MG spectrophotography	5.00×10^{-7} –8.00×10^{-6} mol/L	RSD < 1%. With a high sensitivity and recovery rate.	Not suitable for the determination of oils with low phospholipids.

detection limit for these methods, along with their advantages and disadvantages.

Due to the high sensitivity and selectivity of detecting phospholipids, more and more researchers have established qualitative and relative quantitative methods of non-hydratable phospholipids in vegetable oils, which are applied to vegetable oil categories of different characterizations. These methods to reveal the changes in composition can lead to the removal of non-hydratable phospholipids and the quality improvement of refined oil products.

5. REMOVAL TECHNIQUES FOR NON-HYDRATABLE PHOSPHOLIPIDS

Degumming is an important step in refining, where PLs are removed from crude vegetable oils. NHP is a world-class problem in the oil industry. Water, acid, enzyme and membrane degumming methods have been used in vegetable oil degumming in recent years.

5.1. Traditional degumming method

The traditional methods are mainly hydration and the simple acid method.

5.1.1. Hydration degumming

In the industry, the method of removing PL is mainly hydration. That is, a certain amount of hot water is added to crude oil so that the phospholipids in crude oil expand and are then separated after condensation to be removed, The process is generally carried out at 40-45 ºC, which is relatively energy-efficient, has a short production cycle, and reduces the acid value. The crude oil phospholipid content and temperature determine the amount of water added during degumming. For example, at high temperatures, the amount of water added is about 3-5 times that of the crude oil PL content (Dijkstra, 2017). In addition, metal ions in tap water may combine with HP in oils to form NHP, which affects the degumming effect.

The degumming process parameters and the final degumming results differ for different oil samples. The results show that the phospholipid removal rates for soybean oil, rapeseed oil, rice bran oil, sunflower oil and olive oil are 98.3, 67.1, 89.8, 80.6 and 48% respectively. The phospholipid removal rate of mixed algal oil was only 19.4% (Supansa *et al.*, 2017). Hydration degumming can only remove hydratable phospholipids with strong hydrophilic properties, while NHP with weak polarity and hydrophobicity is difficult to remove. After degumming, the phospholipid content is still 80-200 mg/kg, which cannot guarantee low phosphorus content (Aleksandra *et al.*, 2003). Moreover, due to the high content of NHP, it is not always the best for all kinds of oil.

5.1.2. Acid degumming

The acid degumming method entails adding a certain amount of phosphoric acid or citric acid in order to dissociate NHP by adjusting the pH, and then cool the phospholipids to form crystals. The phosphorus content can be reduced to less than 30 mg/kg.

Phosphoric acid was used to refine palm oil to remove phospholipids, and the optimal dose of phosphoric acid was determined to be 0.05 wt% by adopting the wet degumming process (Harrison *et al.,* 2022). The researchers used a 1:1 mixture of citric acid and phosphoric acid to degum sunflower oil, and the degumming effect was better and the amount of phospholipid remaining was 0.05 mg/kg (Pan *et al.*, 2000).

Some studies have shown that phosphoric acid is used for degumming vegetable oils with high phospholipid contents, such as soybean and algal oil. As a result, the phosphorus content of crude algal oil was reduced from 530 ppm to 93 ppm in the optimal acid degumming process, with a phospholipid removal rate of 82.5%, which is much higher than that of 19.4% for water degumming (Supansa *et al.*, 2017).

At present, acid degumming has been widely used in oil processing. The technology is simple, but closely correlated with the crude oil quality, and is suitable for low phosphorus oil such as palm oil. Some vegetable oils with high non-hydratable phosphorus contents are still not up to the requirements.

5.2. New degumming method

The main disadvantages of the above conventional degumming processes are considerable oil loss, significant wastewater, and high energy consumption, which cannot guarantee the low phosphorus levels required for physical refining. These techniques are not suitable for oils containing high levels of non-hydratable phospholipids.

5.2.1. Enzymatic degumming

In recent years, research on the application of phospholipase in vegetable oil degumming has become more and more in-depth. Enzymatic degumming uses the biological enzymatic method to convert NHP into HP, and then the hydration method to maximize the phospholipids' removal and recovery. There are four types of phospholipases used for vegetable oil degumming. Phospholipase A_1 (PLA_1) and phospholipase A_2 (PLA_2) remove fatty acids from positions 1 and 2, respectively, and phospholipids are hydrolyzed to free fatty acids and soluble phospholipids. Phospholipase B (PLB) eliminates fatty acids from glyceryl. Phospholipase C (PLC) hydrolyzes the bond between acylglycerol and the phosphate group to release Diacylglycerol (DAG) (Jiang *et al.*, 2015). The site of action of phospholipase D is after the phosphate group. The action sites of four different phospholipases are shown in Figure 4.

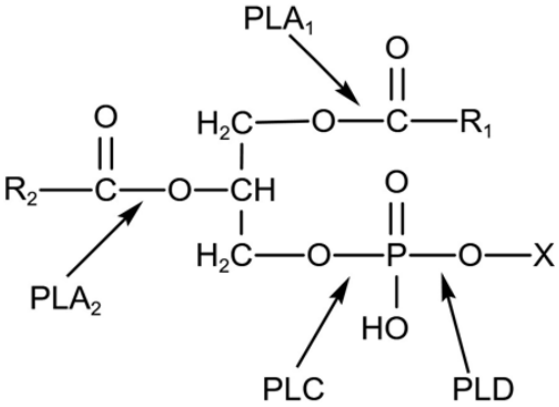

Figure 4. Different phospholipase action sites.
X represents choline, ethanolamine, inositol, hydrogen, etc.

Applying PLA_1 and PLC to eight crude oils, the researchers found that the PLA_1 degumming process significantly reduced residual phosphorus to less than 10 mg/kg and that PLC degumming improved the oil yield of most oil samples (Jiang *et al.*, 2015). The enzyme mixture Purifine® 3G was applied to crude soybean oil to reduce the residual phosphorus content to 8.9 mg/kg (dos Passos *et al.*, 2022). To

improve the stability and reusability of phospholipase, magnetic immobilized PLA was used for degumming soybean oil. The results showed that even after 5 cycles of degumming, magnetic immobilized PLA_2 retained more than 80% of its initial activity (Qu *et al.,* 2016). Immobilized phospholipases show excellent potential for enzymatic degumming.

Enzymatic degumming has many advantages over traditional methods, including higher degumming efficiency, lower chemical requirements, higher product yield, and less environmental pollution. Despite the obvious advantages of this approach, it has drawbacks, particularly the cost of the enzyme. Moreover, the quality of different crude oils is different, so a specific enzymatic degumming process should be selected (Jiang *et al.*, 2015). For example, for oil samples with low NHP content and high initial phosphorus content, PLC degumming with acid pretreatment can meet the requirements of physical refining and improve the yield simultaneously. For oil samples with high NHP content and low initial phosphorus content, acid-pretreated PLA_1 degumming is the best choice.

5.2.2. Membrane filtration degumming process

Membrane degumming is a non-thermal process that selectively separates phospholipids based on the size or properties of the membrane and is an emerging method for efficient degumming at low energy costs. Different types of membranes are applied to the crude vegetable oil membrane degumming process, such as polyethersulfone (PES) membranes, polysulfone (PSf) membranes, polyvinylidene fluoride (PVDF) membranes and ceramic membranes have shown good permeation flow with good degumming effect.

The PVDF membrane is more stable to hexane reagent than PES and PSf membranes (de Souza Araki *et al.,* 2010). The filtration of rice bran gross oil (CRBO) using 50 kDa PVDF membranes mixed with hexane solvent achieved 95.5% phospholipid removal (Sehn *et al.,* 2016). It was shown that membrane degumming combined with hydration degumming and acid degumming could improve the phospholipid removal rate of crude oil. By combining conventional acid degumming with PES membrane separation, the phospholipid content of jatropha oil can be reduced to less than 20 ppm (Liu *et al.,* 2012).

In addition to the above polymeric membranes, ceramic membranes have a highly repulsive reaction to phosphorus. In a recent study using ceramic membranes to degum CRBO, phosphorus was reduced by 95%, along with a 42-62% reduction in color. The average phospholipid retention was 95±2% using 5 kDa ceramic membranes (Abdellah *et al.,* 2020). It has been shown that a three-stage hybrid membrane process of ultrafiltration, nanofiltration and permeation vaporization treats crude canola oil with almost complete rejection of phospholipids (> 99.9%) (Abdorrezaee *et al.,* 2021).

The membrane filtration de-adhesive process replaces the traditional energy-intensive process. It has the advantages of low energy consumption, safety, no chemicals, good retention of nutrients, reduced wastewater production, simple operation and so on. Despite these advantages, the poor stability and low osmotic flux of some organic membranes during membrane filtration and degumming lead to problems such as scaling and clogging, requiring high operation and maintenance costs, making the process economically unfeasible and unlikely to be applied on a large scale.

5.2.3. Other degumming processes

In addition to the above degumming processes, some novel degumming technologies are less widely used, such as Ultrasonic Assisted Enzymatic Degumming (UAED), saturated steam degumming, cavitation reactor-assisted ethanolamine degumming and electrolyte degumming. The comparison of new degumming processes for different kinds of vegetable oils is shown in Table 4 below.

The ultrasonic treatment of crude vegetable oil can separate the phospholipids completely, which has the enhanced benefit of reducing the reaction time and processing cost. When water, acid and enzyme degumming are combined with ultrasonic degumming, phosphorus content significantly reduces, which can eliminate alkali refining neutralization, improve degumming efficiency, and reduce the use of chemical degumming reagents, temperature and processing time. Cavitation reactor-assisted degumming is used to purify crude soybean oil. The degumming treatment based on cavitation can produce high-quality oil, and reduce reaction time and energy consumption, but this process has high requirements for equipment. Compared to other methods,

Table 4. Comparison of the new degumming processes currently studied

Oil	Degumming method	Reference	Degumming condition	Phosphorus content (ppm)		Removal (%)
				Crude	Degummed	
Soybean oil	Degumming with saturated water vapor	Sun *et al.*, 2011	T=110 ºC, t=50 min, speed agitation=90r/min, 2% saturated water vapor	1148	17.9	98.4
	Ultrasonic assisted enzymatic degumming	More *et al.*, 2018a	Working volume=100 ml, Enzyme load=2.0 ml/L, pH=5, 5% water, Ultrasonic power=100 W		73.13	93.63
	Cavitation reactor-assisted degumming	More *et al.*, 2018b	Volume=250 ml, T= 60 ºC, t=100 min, P=4 bar		72.90	93.65
	Electrolyte degumming	Nasirullah, 2005	1.5% Potassium chloride: 0.5% SCS=95:5		0.574	99.95
Rapeseed oil	MEA degumming	Zufarov *et al.*, 2009	0.5 wt% MEA, T=20-30 ºC	445	3.5	99.2
	Acid+ultrasonic degumming	Gaber *et al.*, 2020	T=40 ºC, 2 MHz, t=30 min		11	97.53
Coriander oil	Electrolyte degumming	Zhang *et al.*, 2022	3% SCS	508	47.2	90.7
Curcas oil	Acid+ultrasonic degumming	Liu *et al.*, 2012	65 ºC, 4% phosphoric acid, speed agitation =1600 rpm	1200	20	98.3
Rice Bran oil	Membrane filtration degumming	Sehn *et al.*, 2016	50kDa PVDF membrane	640.5	29	95.5
	Electrolyte degumming	Nasirullah, 2005	1.5% Potassium chloride:0.5% SCS= 95:5		0.38	99.94
Sunflower oil	MEA degumming	Zufarov *et al.*, 2009	0.5 wt% MEA, T=20-30 ºC	163	2.2	98.6

SCS: sodium chloride solution, MEA: monoethanolamine.

saturated steam degumming does not add any chemical reagent and has no residual problem, which can provide a theoretical basis for industrial production. The ethanolamine degumming can be carried out at an ambient temperature, and does not need additional energy, uses simple technology, has low production cost, and avoids energy and equipment-intensive problems. The degumming agent is cheap, highly efficient and easy to obtain. By contrast, the electrolyte degumming uses potassium chloride and sodium chloride aqueous solution to improve the degumming performance, with water, total phenol, phytosterol content and taste well retained. The recycled gelatin can be used in commercial applications, which has good potential.

5.3. Model of dynamics

To meet the phosphorus content specifications of the vegetable oil refining process and better optimize the process parameters, many researchers have proposed kinetic models. These models enable the estimation of crucial parameters, such as time, temperature, and acid concentration, based on the initial phospholipid content, thereby optimizing the efficiency of the degumming process. For the refining process already in operation, the data on the degumming process can be dynamically monitored by using the kinetic model to optimize the parameters in real time, so as to improve the effect of the degumming and reduce the production cost. Hydrodynamic models, especially computational fluid dynamic (CFD) models, play an important role in predicting the concentration and polarization thickness of corn oil in the drying process using tubular ceramic films (Wibisono *et al.,* 2015). By simulating the flow of fluid in the tubular ceramic film, this model can accurately calculate the concentration distribution of corn oil in the pipeline, thus predicting the concentration polarization thickness of corn oil throughout the treatment. To solve the problem of longer computation time, a method combined with an artificial neural network is proposed to enable the model to predict the corn oil concentration polarization thickness more quickly and optimize the production process. The study showed that the kinetic models developed for the de-

gumming and bleaching stages determined the doses of 0.015 wt% and 0.047 wt% for citric acid and bleaching clay, respectively. The phosphorus content in degummed palm oil was reduced from 35 ppm to product specifications and the reversible first order kinetic model was optimal (Serrano-Bermúdez *et al.*, 2021). Furtherdelving into kinetic studies concerning the refining stages, notably degumming and bleaching in vegetable oil, facilitates a comprehensive grasp of the reaction mechanisms. These studies not only enhance our predictive capabilities regarding these processes but also enable a profound comprehension of the underlying principles governing non-hydratable phospholipid (NHP) removal from vegetable oil. Moreover, they furnish a robust theoretical framework, pivotal in augmenting the efficacy of dephosphorylation techniques.

6. CONCLUSIONS

Non-hydratable phospholipids (NHP) play a crucial role in both the taste and revitalization of oils, making their elimination a primary focus in the realm of vegetable oil refinement. Comprised of a mixture of phosphatidylcholine (PC), phosphatidylethanolamine (PE), phosphatidylinositol (PI), and other components, NHP remain a crucial target for purification. In the quest for purifying these non-hydratable phospholipids, delving into the specific impact of distinct phospholipid components on oil quality warrants further investigation. Attention to the variations in species, origin, and processing techniques of plant oil, coupled with a meticulous exploration of pertinent factors, serves as the bedrock for understanding the nuances within this domain.

By scrutinizing the origins, physical attributes, and chemical properties of non-hydratable phospholipids, a more precise segregation of these compounds from other impurities becomes achievable. This in-depth comprehension paves the way for designing the NHP removal process in vegetable oil more effectively. In summary, the systematic investigation and isolation of non-hydratable phospholipids in vegetable oils hold promise for significant advancements in the oil industry. Through a comprehensive understanding of NHP components and their effects on oil quality, the refinement process can be optimized, producing oils that meet the rigorous benchmarks of safety and health, thereby fortifying their integration into industrial production.

7. ACKNOWLEDGMENTS

The authors acknowledge the financial support provided by the Jilin Province Science and Technology Development Project (NO.20220202074NC).

8. DATA AVAILABILITY

All the data presented in the paper are included in the manuscript and references.

9. DECLARATION OF COMPETING INTEREST

The authors of this article declare that they have no financial, professional or personal conflicts of interest that could have inappropriately influenced this work.

10. REFERENCES

Abdellah MH, Scholes CA, Liu L, Kentish SE. 2020. Efficient degumming of crude canola oil using ultrafiltration membranes and bio-derived solvents. *Innovative Food Sci. Emer. Technol.* **59**, 1–9. https://doi.org/10.1016/j.ifset.2019.102274

Abdorrezaee Z, Raisi A. 2021. A hybrid ultrafiltration/nanofiltration/pervaporation membrane process for intensifying the refining of crude canola oil and solvent recovery. *Chem. Engineer. Processing-Process Intensificat.* **169**, 1–15. https://doi.org/10.1016/j.cep.2021.108598

Aleksandra SC, Edward S. 2003. Spectrophotometric determination of total phosphorus in rape seeds and oils at various stages of technological process: calculation of phospholipids and non-hydratable phospholipids contents in rapeseed oil. *Food Chem.* **81**, 613–619. https://doi.org/10.1016/S0308-8146(02)00562-9

Antonelli M, Benedetti B, Cavaliere C, Cerrato A, Montone CM, Piovesana S, Lagana A, Capriotti AL. 2020. Phospholipidome of extra virgin olive oil: Development of a solid phase extraction protocol followed by liquid chromatography–high resolution mass spectrometry for its software-assisted identification. *Food Chem.* **310**, 1–9. https://doi.org/10.1016/j.foodchem.2019.125860

Beneito-Cambra M, Moreno-González D, García-Reyes JF, Bouza M, Gilbert-López B, Molina-Díaz A. 2020. Direct analysis of olive oil and other vegetable oils by mass spectrometry:

A review. *Trends Anal. Chem.* **132**, 1–18. https://doi.org/10.1016/j.trac.2020.116046

Boukhchina S, Sebai K, Cherif A, Kallel H, Mayer PM. 2004. Identification of glycerophospholipids in rapeseed, olive, almond, and sunflower oils by LC–MS and LC–MS–MS. *Canadian J. Chem.* **82**, 1210–1215. https://doi.org/10.1139/v04-094

de Souza Araki M, de Morais Coutinho C, Gonçalves LAG, Viotto LA. 2010. Solvent permeability in commercial ultrafiltration poly meric membranes and evaluation of the structural and chemical stability towards hexane. *Sep. Purif. Technol.* **71**, 13–21. https://doi.org/10.1016/j.seppur.2009.10.005

Dijkstra AJ. 2017. About water degumming and the hydration of non-hydratable phosphatides. *Eur. J. Lipid Sci. Technol*. **119**, 1600496. https://doi.org/10.1002/ejlt.201600496

Diosady LL, Sleggs P, Kaji T. 1982. Chemical degumming of canola oils. *Am. Oil Chem. Soc.* **59**, 313–316. https://doi.org/10.1007/BF02662234

dos Passos RM, da Silva RM, de Almeida Pontes PV, Morgano MA, Meirelles AJA, Stevens CV, Ferreira MC, Sampaio KA. 2022. Phospholipase cocktail: A new degumming technique for crude soybean oil. *Food Sci. Technol.* **159**, 1–9. https://doi.org/10.1016/j.lwt.2022.113197

Gaber MAFM, Juliano P, Mansour MP, Shrestha P, Taylor C, Smith R, Trujillo FJ. 2020. Improvement of the Canola Oil Degumming Process by Applying a Megasonic Treatment. *Indus. Crops Prod.* **158**, 1–10. https://doi.org/10.1016/j.indcrop.2020.112992

Harrison LNL, Yi ST, Mieow KC, Soek ST. 2022. Phosphorus Removal and Phytonutrients Retention in the Refining of Solvent Extracted Palm-Pressed Mesocarp Fiber Oil. *J. Oleo Sci*. **71**, 177–185. https://doi.org/10.5650/jos.ess21256

Hashempour BF, Farshi P, Alizadeh AM, Azadmard DS, Torbati M. 2022. Nutritional Aspects of Vegetable Oils: Refined or Unrefined? *Eur. J. Lipid Sci. Technol.* **124**, 2100149. https://doi.org/10.1002/ejlt.202100149

Hu J, Zhang B. 2011. Resarch on the refining process of green soybean oil in northeast China. *J. Wuhan Instit. Technol.* **30**, 1–3.

Ji H, Liu Y, Wang X, Peng M. 2012. Analysis of phospholipid components and fatty acid composition in sesame oil. *Agric. Machin.* **15**, 34–37.

Jiang X, Chang M, Jin Q, Wang X. 2015. Application of phospholipase A_1 and phospholipase C in the degumming process of different kinds of crude oils. *Process Biochem.* **50**, 432–437. https://doi.org/10.1016/j.procbio.2014.12.011

Kou W, Zhang H, Lu H, Zhu L, Liu A, Huang K, Chen H. 2018. Determination of Phospholipids in Soybean by Titanium Dioxide Nanowires Array Enrichment Combined with Internal Extractive Electrospray Ionization Mass Spectrometry. *Chinese J. Anal. Chem.* **46**, 1913–1922.

Liu H, Liu T, Fan H, Gou M, Li G, Ren H, Wang D, Cheng Z. 2018. Corn Lecithin for Injection from Deoiled Corn Germ: Extraction, Composition, and Emulsifying Properties. *Eur. J. Lipid Sci. Technol.* **120**, 1–11. https://doi.org/10.1002/ejlt.201700288

Liu KT, Gao S, Chung TW, Huang C, Lin YS. 2012. Effect of process conditions on the removal of phospholipids from Jatropha curcas oil during the degumming process. *Chem. Engin. Res. Design* **90**, 1381–1386. https://doi.org/10.1016/j.cherd.2012.01.002

Meng X, Pan Q, Ding Y-Jiang L. 2014. Rapid determination of phospholipid content of vegetable oils by FTIR spectroscopy combined with partial least-square regression. *Food Chem.* **147**, 272–278. https://doi.org/10.1016/j.foodchem.2013.09.143

More NS, Gogate PR. 2018a. Ultrasound assisted enzymatic degumming of crude soybean oil. *Ultrason. Sonochem.* **42**, 805–813. https://doi.org/10.1016/j.ultsonch.2017.12.031

More NS, Gogate PR. 2018b. Intensified degumming of crude soybean oil using cavitational reactors. *J. Food Eng.* **218**, 33-43. https://doi.org/10.1016/j.jfoodeng.2017.08.029

Nash AM, Frankel EN, Kwolek WF. 1984. Degumming soybean oil from fresh and damaged beans with surface-active compounds. *J. Am. Oil Chem. Soc.* **61**, 921–923. https://doi.org/10.1007/BF02542167

Nasirullah. 2005. Physical refining: Electrolytic degumming of nonhydratable gums from selected vegetable oils. *J. Food Lipids*. **12**, 103–111. https://doi.org/10.1111/j.1745-4522.2005.00009.x

Pan LG, Campana A, Toms MC, n MCA. 2000. A kinetic study of phospholipid extraction by degumming process in sunflower seed oil. *J. Am.*

Oil Chem. Soc. **77**, 1273–1277. https://doi.org/10.1007/s11746-000-0200-8

Pérez EE, Baümler ER, Crapiste GH, Carelli AA. 2019. Effect of Sunflower Collets Moisture on Extraction Yield and Oil Quality. *Eur. J. Lipid Sci. Technol.* **121**, 1–7. https://doi.org/10.1002/ejlt.201800234

Qu Y, Sun L, Li X, Zhou S, Zhang Q, Sun L, Yu D, Jiang L, Tian B. 2016. Enzymatic degumming of soybean oil with magnetic immobilized phospholipase A_2. *Food Sci. Technol.* **73**, 290–295. https://doi.org/10.1016/j.lwt.2016.06.026

Rao KS, Chakrabarti PP, Rao BVSK, Prasad RBN. 2009. Phospholipid Composition of Jatropha curcus Seed Lipids. *J. Am. Oil. Chem. Soc.* **86**, 197–200. https://doi.org/10.1007/s11746-008-1325-8

Sehn GAR, Gonçalves LAG, Ming CC. 2016. Ultrafiltration-based degumming of crude rice bran oil using a polymer membrane. *Grasas Aceites.* **67**, 1–8. http://dx.doi.org/10.3989/gya.0498151

Sengar G, Kaushal P, Sharma H, Kaur M. 2013. Degumming of rice bran oil. *Rev. Chem. Eng.* **30**, 183–198. https://doi.org/10.1515/revce-2013-0030

Serrano-Bermúdez LM, Monroy-Pena CA, Moreno D, Abril A, Niño ADI, Riascos CAM, Buitrago Hurtado G, Narváez Rincón PC. 2021. Kinetic models for degumming and bleaching of phospholipids from crude palm oil using citric acid and Super Flo B80® and Tonsil®. *Food Bioprod. Proc.* **129**, 75–83. https://doi.org/10.1016/j.fbp.2021.07.005

Sun B, Guan Y, Li H, Jiang L, Yu D. 2011. Non-hydratable phospholipids in soybean oil were removed by water vapor method. *Food Sci.* **32**, 49–52.

Supansa P, Pakamas C, Sininart C. 2017. Assessment of water degumming and acid degumming of mixed algal oil. *J. Envir. Chem. Eng.* **5**, 5115–5123. https://doi.org/10.1016/j.jece.2017.09.045

Uitterhaegen E, Sampaio KA, Delbeke EIP, De Greyt W, Cerny M, Evon P, Merah O, Talou T, Stevens CV. 2016. Characterization of French Coriander Oil as Source of Petroselinic Acid. *Molecules.* **21**, 1–13. https://doi.org/10.3390/molecules21091202

van Rijn JHJ, Lankhorst PP, Groen PBM, Muntendam R, de Souza AC. 2020. Robust and Reliable Quantification of Phospholipids in Edible Oils Using ^{31}P NMR Spectroscopy. *J. Am. Oil Chem. Soc.* **97**, 253–262. https://doi.org/10.1002/aocs.12296

Wibisono Y, Widodo S. 2015. Concentration boundary layer in membrane degumming: A CFD model and neural network approach. *Procedia Envir. Sci.* **28**, 224–233. https://doi.org/10.1016/j.proenv.2015.07.029

Yang M, Zhou X, Jin Y. 2008. Non-hydratable phospholipids and their quantitative detection. *Chinese J. Health Inspect.* **1**, 71–72.

Zhang L, Akhymetkan S, Chen J, Dong Y, Gao Y, Yu X. 2022. Convenient method for the simultaneous production of high-quality fragrant rapeseed oil and recovery of phospholipids via electrolyte degumming. *Food Sci. Technol.* **155**, 1–8. https://doi.org/10.1016/j.lwt.2021.112947

Zhao Q, Li P, Wang M, Zhang W, Zhao W, Yang R. 2020. Fate of phospholipids during aqueous extraction processing of peanut and effect of demulsification treatments on oil-phosphorus-content. *Food Chem.* **331**, 1–9. https://doi.org/10.1016/j.foodchem.2020.127367

Zufarov O, Schmidt Š, Sekretár S, Cvengroš J. 2009. Ethanolamines used for degumming of rapeseed and sunflower oils as diesel fuels. *Eur. J. Lipid Sci. Technol.* **111**, 985–992. https://doi.org/10.1002/ejlt.200900025