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Review:

The Origin, Physicochemical Properties, and Removal Technology of Metallic Porphyrins from Crude Oils

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Abstract: *Crude oil is an indispensable energy feedstock for daily activities, although some amounts of metallic porphyrins components with undesired characteristics have been identified. These constituents are assumed to originate from the geochemical process of chlorophyll and heme derivatives. In addition, their chemical structures have been thoroughly characterized using spectroscopy techniques, while several analytical methods were adopted in the detection and concentration quantification in the crude oils. The metallic porphyrins have several demerits, including the deactivation of used catalysts, contamination of the treated petrochemical products, and corrosion of the industrial equipment. Also, the removal process is considered challenging due to the strong interaction with the asphaltene fraction of crude oil. This review article, therefore, provides brief information on the origin, physicochemical properties, and possible removal technology of metallic porphyrins from crude oil samples. Besides, a better understanding of chemistry contributes a useful insight towards the development and establishment of better futuristic processing technology.*

Keywords: *crude oil; metallic porphyrin; origin; property; removal*

■ INTRODUCTION

Despite the extensive research on renewable energy, crude oil remains an indispensable energy feedstock [1-4]. This is attributed to the limited amount of industrial processes implicated in serious demerits, including expensive upfront cost, geographic mal-distribution, natural intermittent supply, and others. In contrast, crude oil-based chemical materials are well established worldwide. Therefore, some industries prefer maintaining fossil-based technological systems against establishing new and high-cost technologies [5].

Crude oil is generally defined as a fuel liquid produced through long-time geological activities involving high temperature and pressure in oil reservoirs associated with sedimentary rocks and situated beneath earth's surface piles [6]. This natural resource comprises light and heavy hydrocarbon fractions with other impurities, including oxygenated-, nitrogenated-, and sulphated-compounds, alongside trace metals [7]. The respective compound composition varies appreciably across the reservoirs, and crude oil also contains paraffin (alkanes), naphthenes (cycloalkanes), as well as aromatic compounds [8]. In addition, some components have been separated through a fractionation distillation process for commercial applications, and further actions in the form of thermal cracking, catalytic reforming, isomerization, and hydrodealkylation processes are possibly required to attain the product market requirement [9]. Therefore, impurity elimination is pivotal to obtain products with high-purity [10].

The oxygenated-, nitrogenated- and sulphated-compounds present are easily removed through the absorption and hydrocracking processes [11]. However, trace metal removal is difficult in a simple process, due to the high solubility and the poisonous impact of catalysis techniques [12]. Furthermore, the amount present was reportedly dominated by metallic porphyrins [6], and special attention is attributed to these constituents over the past several years. This is due to the high poison potential and ability to deactivate catalysts used during petrochemical processes [11]. Hence, further information on the intrinsic chemical nature is required. This review article involves the assessment of data on the metallic porphyrin's origin, its chemical structure, and physicochemical properties. Also, the removal process from crude oils is briefly discussed to provide chemists and engineers working on crude oil processing with essential knowledge.

ORIGIN OF METALLIC PORPHYRINS

Treibs [13] firstly discovered metallic porphyrins as "molecular fossils" from crude oil samples in 1934, and further investigations have gained significant interest. This has been identified as the predominant trace metal, and Table 1 lists others present in Venezuelan crude oil, comprising vanadium and nickel at 440–617 and 70–94 mg L^{-1}, respectively, which is 600 times higher than the others [6]. Conversely, vanadium (160 mg L^{-1}) and nickel (80 mg L^{-1}) metals in the lithosphere are not as abundant as iron (50,000 mg L^{-1}) and calcium (40,000 mg L^{-1}). Therefore, some extensive studies were conducted to evaluate the reason for the much higher concentration of vanadyl-porphyrins or nickel-porphyrins in crude oil compared to others.

Furimsky [6] attributed the abundant quantity of vanadium and nickel to the intrinsic high reducibility of the mineral form. This property impacts greater stability on metallic species and ensures the formation of tighter bonds to the core porphyrin framework. This hypothesis suggests all metallic species are generated from the reduction of corresponding metallic oxides by hydrogen gas (Eq. (1)).

$$M_xO_y(s) + yH_2(g) \rightarrow xM(s) + yH_2O(g) \qquad (1)$$

The reduction reaction of V_2O_5 to V species is not spontaneous (ΔG_{300K} = +33.4 kJ mol^{-1}) while V_2O_5 to vanadyl (V=O) species is highly favorable (ΔG_{300K} = -8.3 kJ mol^{-1}). Similarly, the reduction of NiO to Ni species is also spontaneous (ΔG_{300K} = -4.0 kJ mol^{-1}), while FeO, CaO, or CuO are considered as unfavorable, due to the positive Gibbs energy produced, at +5.4, +227, and +24.2 kJ mol^{-1}, respectively [6]. Therefore, Furimsky stipulated the significance of much higher vanadyl and nickel metal concentrations in metallic porphyrins, compared to iron, calcium, and copper metals in crude oils.

Treibs [13] proposed plausible evolution reactions required to form metallic porphyrins in crude oil. This includes the production from chlorophyll compounds in plants and heme compounds in animals [14], as shown in Fig. 1. Furthermore, the chlorophylls from plants are

Table 1. Trace metal composition in the Venezuelan crude oil sample [6]

Metals	Concentration (mg L^{-1})
Fe	4.0–7.5
Ca	11–57
Mg	1.0–10
V	440–617
Ni	70–94
Cu	2.0–17
Mo	3.0–22
Cd	1.0–5.0
Zn	1.0–12

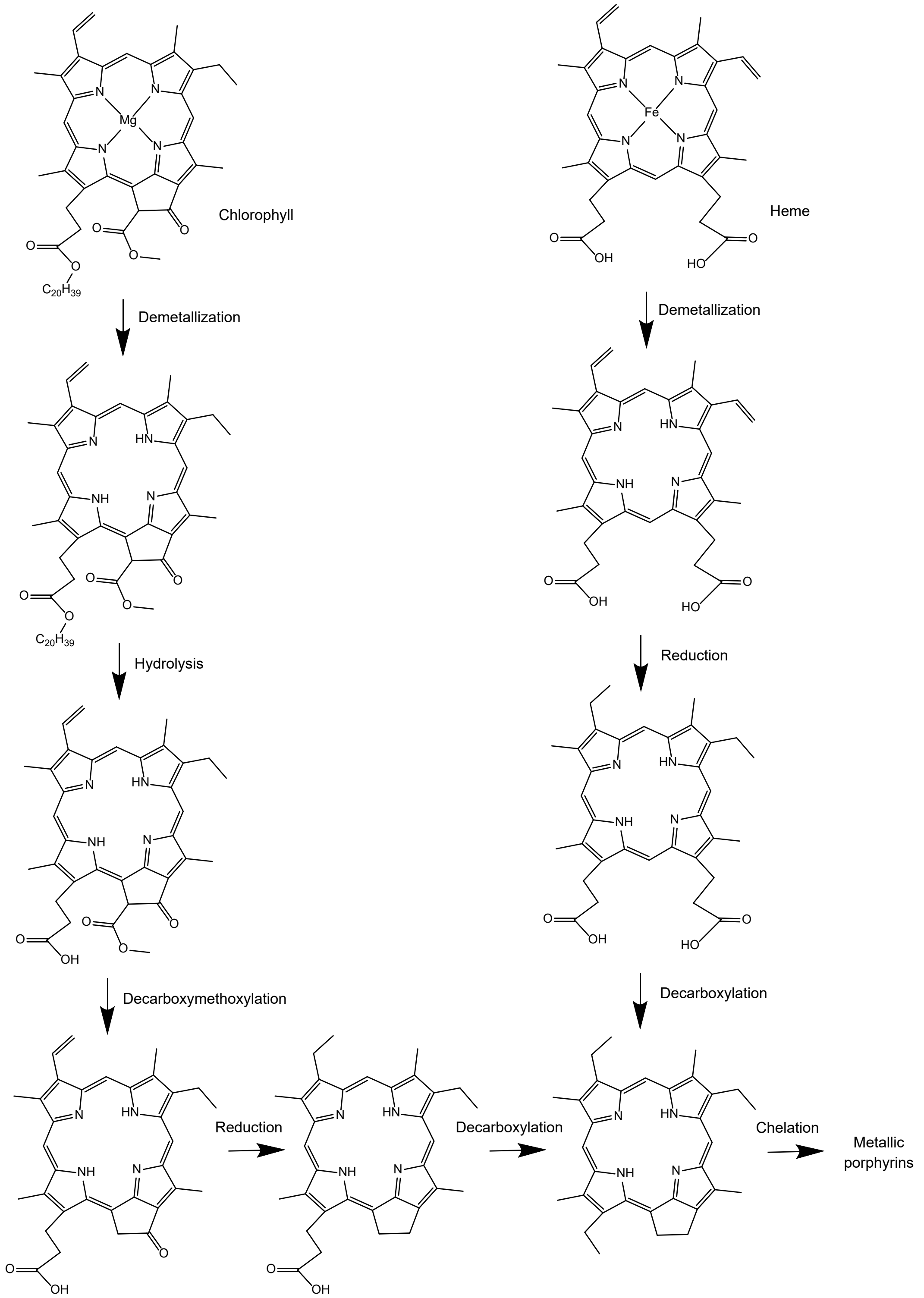

Fig 1. Schematic evolution reactions of chlorophyll and heme compounds to form metallic porphyrins

determined to engage in demetallization reactions and consequently release Mg^{2+} ions. These Mg^{2+}-free porphyrins then engage in hydrolysis, decarbomethoxylation, reduction, and decarboxylation reactions to produce the "free" ligand. The high reducibility of vanadyl and nickel facilitates the chelation required in the formation of stable metal complexes. Moreover, heme compounds are converted to Fe^{2+}-free porphyrins through a demetallization reaction and further treated with reduction and decarboxylation processes. The vanadyl and nickel species were finally complexed with the porphyrin ligand to form metallic porphyrins [14].

Castillo and Vargas [15] performed further studies by investigating the occlusion characteristics of metallic porphyrins during asphaltene aggregation. Consequently, either vanadyl- or nickel-porphyrin was predominant in the asphaltene fraction of crude oil [16]. Therefore, the combination phenomenon and the respective physicochemical properties were evaluated using UV-Vis spectroscopy. The asphaltene aggregation degree was examined at 350 nm, while the metallic porphyrin electronic properties were evaluated based on the Soret signal at 400–410 nm. Furthermore, the results obtained showed the trapping of more than 50% metallic porphyrins on the aggregate, which occurred during the colloidal asphaltene formation process, through strong acid-base interactions, hydrophobic inclusion, and π-π stacking intermolecular forces, based on UV-Vis data [17]. Tynan and Yen [18] reported free energy of about 60 kJ mol^{-1} generated through the combined interactions of asphaltene-vanadyl porphyrin aggregation, which is much stronger than hydrogen bonds (10–40 kJ mol^{-1}). This trapping process is considered irreversible, due to these strong connections formed, and further increases the difficulties of removing metallic porphyrins from asphaltene [15].

STRUCTURE OF METALLIC PORPHYRINS

The metallic porphyrins structure of vanadium and nickel have previously been studied to provide a better insight into the chemistry field. Initially, the structures were investigated through UV-Vis spectroscopy, by observing the conjugated moiety. Moreover, the electronic absorptions were predominantly investigated through the π-π* transition, as n-π* transition is unavailable, due to the discrepancy in the symmetry of the n orbital (on symmetry plane) and π* orbital (on anti-symmetry plane).

These metallic porphyrins produced high-intensity Soret signals at about 400 nm, and also around 500–600 nm, corresponding to α- and β- bands from peripheral substituents in the framework [19]. Fig. 2 shows the labelling of α-, β-, α*-, β*- and meso substituents, and the high signal intensity prompts researchers to use UV-Vis spectroscopy during quantification assessment. However, the concentrations calculated from the UV-Vis spectrum produced showed the absence of approximately half the total quantity, in contrast with the value measured through atomic absorption spectroscopy (AAS) [6]. These reports were observed in crude oil samples obtained from Europe, Russian, and others [20-21]. Therefore, metallic non-porphyrin species were assumed to be present, although none was ever discovered and verified to this day [22].

Through technological development over the years, further chemical analysis using mass spectrometry and X-ray spectroscopy have confirmed the non-existence of metallic non-porphyrins in crude oils [22]. Therefore, false calculation obtained with UV-Vis spectroscopy was attributed to the postulation stipulating the presence of only one species [6]. This possibility was neglected in previous assessments, owing to variations in electronic structures, and the instigating the consequent dissimilarity in spectra. Moreover, metallic porphyrins have also been identified in the form of alkyl-, oxygenated-, nitrogenated-, and sulfur-containing porphyrins [22].

Fig. 3 shows some examples of metallic porphyrin structures discovered, while Table 2 demonstrate the Soret-, α-, and β-bands of specific vanadyl forms. Berezin [23] introduced the concept of "Mutual Atomic Effect",

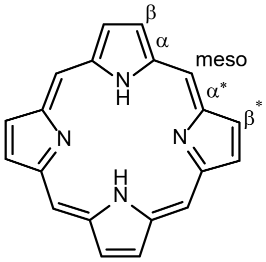

Fig 2. Peripheral substituents location on the porphyrin framework

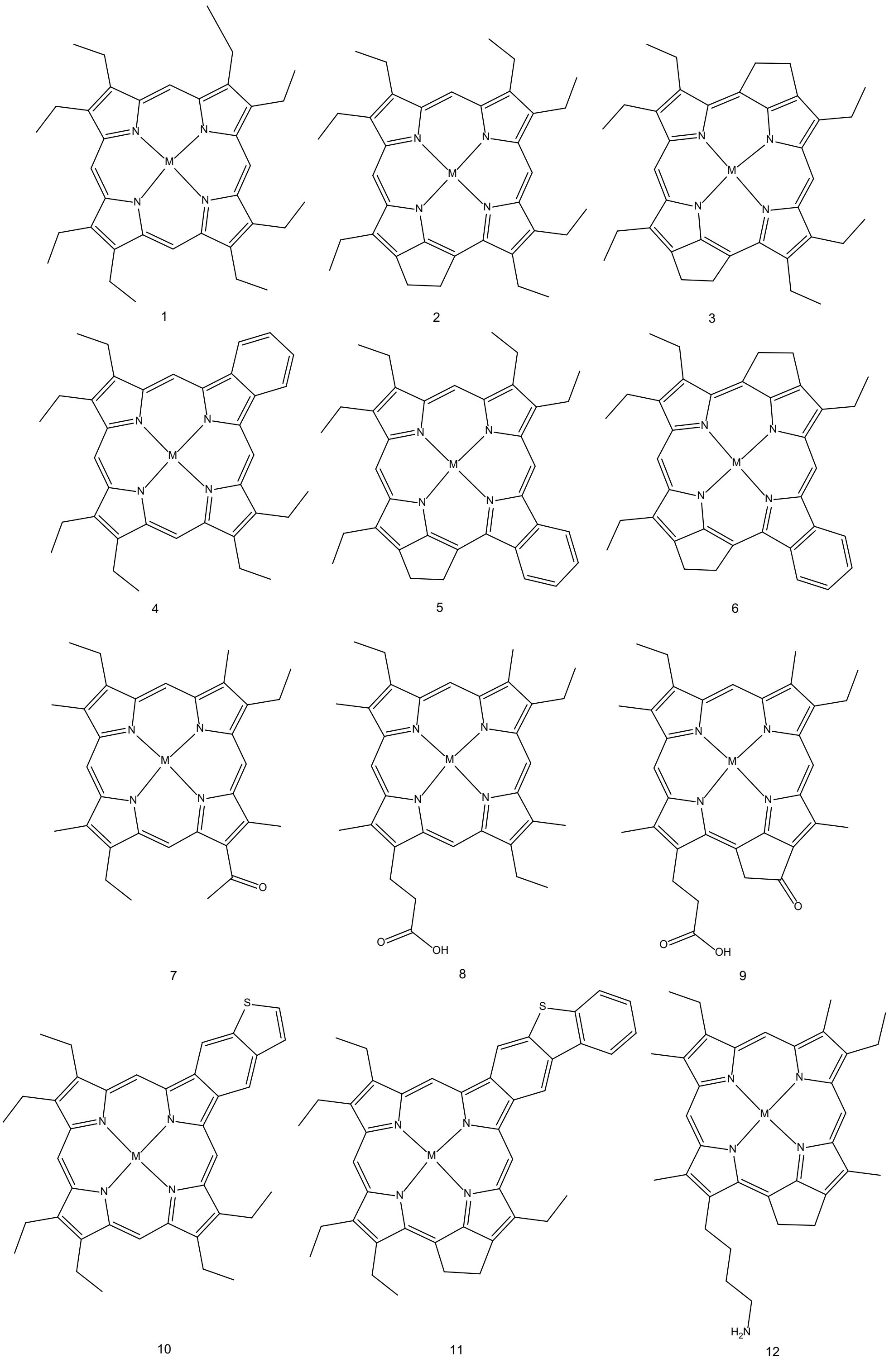

Fig 3. The example of the discovered metallic porphyrins (M = Ni or VO)

which describes the influence of different peripheral substitution on the electronic distribution and light absorption magnitude, as observed in Fig. 2. This phenomenon instigates a spectral shift and/or higher/lower extinction coefficient [23]. The dissimilarity in the Soret-, α- or β-band of each vanadyl-porphyrin caused

Table 2. Absorption signals of vanadyl-porphyrin derivatives on the UV-Vis spectrum [28]

Vanadyl-porphyrins	Wavelength (nm)		
	Soret band	α-band	β-band
Unmodified	399	559	524
ETIO	407	571	533
DPEP	411	573	533
Benzo-substituted	414	579	545
Octaethyl-substituted	407	571	533

*Dichloromethane was used as the solvent

the inevitable miss-calculations observed with UV-Vis spectroscopy. In addition, Foster and Cantu [24-25] also reported on the variations in extinction coefficients amongst one another. This was detected with the values for etioporphyrin (ETIO) determined to be four times higher than deoxophylloertythroetioporphyrin (DPEP) derivatives [20]. Moreover, other possible factors implicated in the underestimated calculation comprise the multiple π-π stacking interactions in asphaltene-metallic porphyrin aggregations. The presence of polycyclic aromatic hydrocarbons potentially influenced poor measurement precision, and consequently interfered with signal intensity, as observed using UV-Vis spectroscopy [26].

Yakubov et al. [27] reported on the UV-Vis spectra modifications observed with porphyrins, after the demetallization reaction. Subsequently, the free porphyrins provided four Q-signals in the visible regions after the removal of central metal ions (either Ni^{2+} or VO^{2+}). These were usually noted as I, II, III, and IV signals [10], and the order is numbered from the longer to shorter wavelength, at 620, 565, 535, and 500 nm, respectively. Also, the signals attributed for the conformation and nature of peripheral substitutions possibly existed in six different conformations, including saddle, ruffle, dome, wave on the x-axis, wave on the y-axis, and propeller forms, as shown in Fig. 4 [22].

The limitations of metallic porphyrins characterization through UV-Vis instigated the use of mass spectrometry and Fourier-transform ion cyclotron resonance mass spectrometry. This technique elucidated the correct structure [19,28-30], and about 370 variants were consequently reported. In addition, the vanadyl-porphyrin alone were classified into 6 categories, including

1. $C_nH_{2n-y}N_4VO$ ($35 < n < 60$; $39 < y < 46$)
2. $C_nH_{2n-y}N_4VO_2$ ($26 < n < 47$; $29 < y < 39$)
3. $C_nH_{2n-y}N_4VO_3$ ($26 < n < 34$; $29 < y < 39$)
4. $C_nH_{2n-y}N_4VO_4$ ($27 < n < 37$; $31 < y < 37$)
5. $C_nH_{2n-y}N_4VSO$ ($34 < n < 56$; $37 < y < 47$)
6. $C_nH_{2n-y}N_5VO$ ($28 < n < 43$; $26 < y < 36$)

Fig. 3 shows the structures of alkyl-, sulfur-containing and oxygenated-porphyrins, where M denotes either VO^{2+} or Ni^{2+}. Particularly, M at VO^{2+} yields compound **1**–**6**, which are collectively classified as alkyl porphyrins class 1 ($C_nH_{2n-y}N_4VO$ with $35 < n < 60$ and $39 < y < 46$). In addition, compounds **1**, **2**, and **3** were infamous as ETIO, DPEP, and Di-DPEP (dicyclic-deoxophylloerythroetioporphyrins), while **4**, **5**, and **6** comprise rhodo-ETIO (rhodo-etioporphyrins), rhodo-DPEP (rhodo-deoxophylloerythroetioporphyrins), and rhodo-Di-DPEP (rhodo-dicylic-deoxophylloerythroetio porphyrins), respectively. Moreover, **7**, **8**, and **9** are oxygenated-porphyrin derivatives, with **7** belonging to class 2 ($C_nH_{2n-y}N_4VO_2$ having $26 < n < 47$ and $29 < y < 39$), resulting from the one extra oxygen atom present in the form of a ketone group. Conversely, compound **8** is categorized in class 3 ($C_nH_{2n-y}N_4VO_3$ with $26 < n < 34$ and $29 < y < 39$), due to the two extra oxygen atoms in the form of carboxylic acid. The compound **9** is grouped in class 4 ($C_nH_{2n-y}N_4VO_4$ with $27 < n < 37$ and $31 < y < 37$) because of the additional three oxygen atoms, while

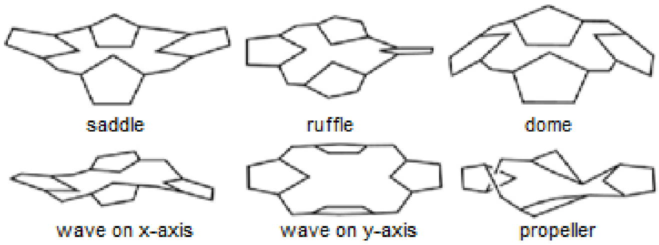

Fig 4. Conformation of metallic porphyrins

10 and **11** represent sulfur-containing porphyrins ($C_nH_{2n-y}N_4VSO$ with $34 < n < 56$ and $37 < y < 47$), and **12** denotes a nitrogen-containing class ($C_nH_{2n-y}N_5VO$ with $28 < n < 43$ and $26 < y < 36$).

The metallic porphyrin derivatives have been thoroughly investigated through theoretical and experimental researches. The Density Functional Theory (DFT) computational method has been applied to evaluate the electronic structure of vanadyl-porphyrins present in the crude oil. Furthermore, tests using the varied porphyrin substituent showed the influence of alkyl chains on the solubility of metallic variants in an oily environment. The results also predicted the development of higher reactivity following an increase in the substituent quantity. This output consequently becomes more poisonous after applying catalysts in hydrodemetallization and hydrodesulfurization processes [16].

Garcia-Montoto et al. [9] predicted the three steps of the poisoning mechanism. First is the coke formation from metallic porphyrins on the catalyst surface, which is a rapid reaction with first-order reaction halftime of about a hundred hours. Second, the metallic porphyrins slowly cover the entire surface to ensure gradual activity deactivation. Third, the yields tend to create pore plugging, then facilitate access restriction to the catalyst active site, and consequently prompt a drastic termination of activity [9].

In addition, the product also demonstrated some other disadvantages, in the crude oil. These include influencing the physicochemical properties of petrochemicals, contaminating the desired output, and corroding metallic equipment during the process [6]. Therefore, porphyrin detection and quantification are crucial to select a suitable removal technique.

■ DETECTION AND QUANTIFICATION OF METALLIC PORPHYRINS IN CRUDE OILS

Prior to the detection and quantification processes, several analytical methods have contemporarily been developed to isolate the metallic porphyrins in crude oil samples [31]. This approach is pivotal due to the existence of trace concentration (less than 1.0 g L^{-1}) in the investigated entity [6]. The matrix crude oil samples tend to vary across sources, and further enhances the difficulty towards establishing a direct and standard detection as well as quantification [26]. Besides, there are a total of three well-known analytical isolation techniques, including Saturate, Aromatic, Resin and Asphaltene (SARA), Soxhlet extraction, and vacuum sublimation method, as shown in Fig. 5 [16].

Particularly, SARA has been identified as the most used approach, resulting from the good ability to separate asphaltene fractions from others, including the saturated, aromatic, and resin fractions [32-34]. This technique is initiated by dissolving the crude oil in dichloromethane solvent, followed by the addition of alumina material, and drying through flowing nitrogen gas [35]. The residue is packed as the stationary phase of the chromatography column and subsequently eluted stepwise using *n*-hexane:cyclohexane 1:1 v/v, *n*-hexane:toluene 7:3 v/v, carbon tetrachloride:chloroform 7:3 v/v, and acetonitrile:methanol 1:1 v/v to respectively obtain the saturated (A1), aromatic (A2), resin (A3), and asphaltene (A4) fractions of crude oil. Preconcentration of metallic porphyrins using the SARA method has been reported for Venezuela crude oil, Russia Tatarstan crude oil, Kuwait crude oil, Athabasca oil sand, Utah oil sand, China Qingchuan gilsonite oil, Texas shale oil, heavy Eurasian oil, and light East Asian oil [16,36-37].

Marquez et al. [16] adopted the SARA technique while isolating metallic porphyrins from Venezuela crude oil (Table 3) to give concentrated vanadium and nickel-porphyrins in resin and asphaltene fractions. Compared to other methods, SARA technology gives satisfying preconcentration of metallic porphyrins which are commonly found only in resin and asphaltene fractions. Zheng et al. [36] also reported a successful preconcentration of metallic porphyrins at 120–550, 50–800, 240–640, 21–170, 366–3888, and 257–270 mg kg^{-1} from Russia Tatarstan crude oil, Kuwait crude oil, Athabasca oil sand, Utah oil sand, China Qingchuan gilsonite oil, and Texas shale oil samples, respectively, which is remarkable. However, the SARA technique is time-consuming and expensive due to a complicated chromatographic solvent composition for each fraction.

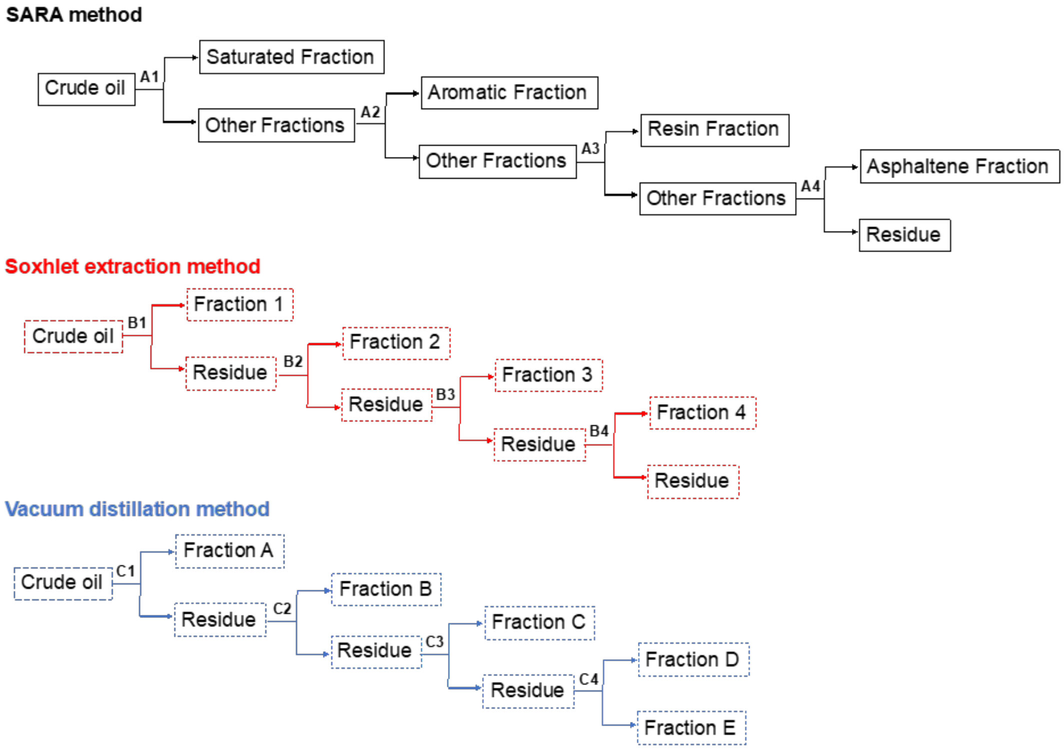

Fig. 5. Isolation of metallic porphyrins from crude oil using SARA, Soxhlet extraction, and vacuum distillation methods

Table 3. The physicochemical properties of the obtained fractions of crude oils for metallic porphyrins from Venezuelan crude oil [16]

Fraction	Color	Yield (%)	Vanadium content (mg kg^{-1})	Nickel content (mg kg^{-1})
SARA method				
Saturated fraction	Pale yellow	21	0	0
Aromatic fraction	Yellow	6	0	0
Resin fraction	Black	36	900	80
Asphaltene fraction	Red wine	15	1,100	100
Soxhlet extraction method				
Fraction 1	Red wine	8	120	2
Fraction 2	Orange	29	75	2
Fraction 3	Brown dark	49	950	26
Fraction 4	Colorless	11	1,060	39
Vacuum sublimation method				
Fraction A	Light yellow	12	5	34
Fraction B	Orange	15	104	14
Fraction C	Dark red	19	226	7
Fraction D	Red	23	178	6
Fraction E	Black	29	514	50

Conversely, Soxhlet extraction method is distinguished as a low-cost and faster isolation method. This process is initiated by mixing the crude oil and alumina material in dichloromethane as the solvent, followed by covering the residue in a Soxhlet extractor with cellulose filter paper. The extraction process required four consecutively used solvents, including acetonitrile, methanol, *n*-heptane, and benzene to obtain fractions 1, 2, 3, and 4, respectively. Table 3 shows the existence of metallic porphyrins in all yields from Venezuela crude oil, especially fraction 4, which however contained a lesser amount in contrast with the asphaltene fraction generated through SARA [16]. Additionally, the Soxhlet extraction method employs carcinogenic benzene as the solvent which has been banned for a green and safety process [38]. Kumolo et al. [39] identified the metallic porphyrins in Duri crude oil using the Soxhlet extraction method and it was found that both vanadium and nickel-porphyrins were found in *n*-heptane and aromatic solvents demonstrating low efficiency of the Soxhlet extraction method.

The vacuum distillation method required heating the desired sample under vacuum conditions to ensure crude oil fraction sublimation. Therefore, yields from the asphaltene fraction in SARA served as the feedstock, after drying with flowing nitrogen gas and placing in the vacuum distillation apparatus. Nikolaychuk et al. [40] reported that vacuum distillation required a high temperature (350–1300 K) depending on the origin of crude oil. Usage of high temperature on the vacuum distillation method was reported for the undesired thermal cracking of crude oil, which is unfavorable [41]. For the Venezuela crude oil samples, the vacuum condition was set at 1.3×10^{-5} atm, a heating temperature from 353 to 513 K, which was gradually increased, and the products were obtained at respective levels (Table 3). The obtained fractions from the vacuum distillation method include fraction A (collected at 363–393 K), fraction B (collected at 403–433 K), fraction C (collected at 443–473 K), fraction D (collected at 483–523 K), and fraction E (residue). Table 3 identified this technique as the least useful ascribed to poor preconcentration ability as well as narrow suitability for only volatile compounds [16]. Therefore, the vacuum distillation technique is the most expensive due to the usage of vacuum technology.

Numerous analytical approaches have been adopted during metallic porphyrin detection and quantification [26]. These include gel permeation chromatography, Ultraviolet-Visible (UV-Vis) spectroscopy, inductively coupled plasma-mass spectrometry (ICP-MS), and electron paramagnetic resonance. However, UV-Vis spectroscopy is known to be the simplest with extensive application [31], as observed with the concentration of vanadyl-porphyrins, estimated using the Eq. (2) as follow;

$$\text{Conc. of vanadyl-porphirins (mg kg}^{-1}) = \frac{1.87\ \text{h V}}{\text{m l}} \tag{2}$$

where h denotes the height of α-band at 570–580 nm, V represents the sample volume (dilution factor), m is the crude oil sample mass, and l signifies the cuvette thickness [27].

Reliability of up to 15% was determined during vanadyl-porphyrin direct quantification using UV-Vis spectroscopy [42]. This analysis technique has low applicability due to the presence of various metallic porphyrins in the sample. Furthermore, the consequent aggregation with the asphaltene fractions lowers the collective absorbance in contrast with the free form [31].

Conversely, gel permeation chromatography reportedly provides metallic porphyrin measurements with better validity [43]. Garcia-Montoto et al. [9] reported a successful quantification using this technique, alongside the addition of HR4 styrene-divinylbenzene as well as 0.5% v/v isopropanol in benzene as the stationary and mobile phase, respectively. Subsequently, the metallic porphyrin yields were separated based on molecule size and concentration before the standard calibration curve is calculated [9]. The preparation and purification processes were technically difficult because of the inability to directly inject crude oil into the apparatus [44]. Moreover, a different porphyrin ligand structure demonstrates varied retention time, which subsequently increases the analysis complexity. Furthermore, some metallic porphyrins tend to be adsorbed on the stationary phase and consequently poison the column used [45].

Electron paramagnetic resonance is potentially adopted in vanadyl-porphyrins. This is due to the presence of one unpaired electron in the 3d orbital of V^{4+} ions [46], which easily resonates in the static magnetic field. In addition, the measurement technique is assumed valid enough because quantification is centered on vanadium atoms and not the porphyrin frameworks as observed with UV-Vis spectroscopy. The precision with this method is remarkable at up to 99.9% [47].

Tynan and Yen [18] reported on the tendency to effectively use electron paramagnetic resonance in the detection of both non-aggregated and aggregated vanadyl-porphyrins. However, the only limitation was impacted by the inability to distinguish the different porphyrin framework types attached to vanadium atoms.

The total intrinsic metallic content was determined through ICP-MS analysis [26]. This required first ashing the crude oil sample for 12 h at 823 K. Therefore, the output was digested using a mixture of concentrated nitric acid (75% wt/v): hydrogen peroxide (30% v/v): concentrated hydrochloric acid (36% wt/v) 4:1:1 v/v/v for 24 h. Subsequently, the solution derived was diluted with distilled water before subjecting to the ICP-MS measurement for the quantification of ^{51}V and ^{60}Ni. This assessment procedure was analyzed for precision and the results showed similarity with the electron paramagnetic resonance method because measurements were based on the metal elements.

■ REMOVAL OF METALLIC PORPHYRINS FROM CRUDE OILS

Currently, there are numbers of separation techniques established to ensure metallic porphyrin removal from crude oils [31]. These include solvent extraction, chelation with chemical agents, supercritical water extraction, and hydrodemetallization processes [12]. Solvent extraction is a well-known technique for metallic porphyrins removal from crude oil because of its convenient operation condition. Particularly, the solvent extraction technique is aimed at releasing the metal ions from the metallic porphyrins complex, and polar solvents in the form of *N*,*N*-dimethylformamide, acetonitrile, *iso*-propanol, and methanol have frequently been applied [48]. Moreover, a small amount of sulfonic or sulfuric acid is sometimes added to ensure the protonation of nitrogen atoms present in porphyrin and to further weaken the metal-porphyrin bonds. This removal technique is, unfortunately, suitable for only crude oil with low resin-asphaltene fraction. Also, the high viscosity instils difficulty for the diffusion process to reach an equilibrium state, and the porphyrin removal process ultimately becomes also time-consuming [31]. As an example, the removal of vanadium-porphyrins from heavy oil using solvent extraction technique only gave 45% removal at 303 K [49]. Therefore, larger solvent quantity and energy are required to improve feasibility, which is unfavorable.

The principle of metal chelation with chemical agents involves the use of suitable chemical agents characterized by a higher complexation tendency towards vanadium and nickel, followed by the possible release from the porphyrin framework [50-51]. A study by Mokhtari and Pourabdollah [52] showed the vanadyl-porphyrin extraction process, using calix[4]arene, a nano-basket dicarboxylic acid. This compound and its derivatives demonstrate outstanding discrimination capacity in line with metal ions, due to the strong complexation energy resulting from electrostatic interactions and size exclusions [53-58]. Remarkably, about 96% of the vanadium is reportedly removed over a 90 min operation period [52]. Shang et al. [59] reported a shorter removal time for vanadium- and nickel-porphyrins by 85 and 83%, respectively, while using a sulfonyl acid chemical in a microwave electric field set at 600 Watts for 3 min. The high removal percentage was attributed to the porphyrin framework deformation observed during microwave irradiation, and further facilitates the demetallization reaction [60].

Supercritical extraction is advanced technology using supercritical fluid as the extracting solvent at above critical temperature and pressure. Mandal et al. [61] investigated the supercritical water extraction of nickel and vanadium from heavy oils, under conditions operated at 22.1 MPa, 763 K, and without a catalyst. Therefore, about 80% of the metallic porphyrins were respectively removed. Based on kinetic and thermodynamic studies, hydroxyl and hydrogen radicals were proposed to play a pivotal role in the demetallization process. The attachment to vanadium and nickel occurs in the hydride and hydroxyl forms, and consequently weaken the metal-porphyrin bonds. Conversely, these radicals also attacked porphyrin rings, and therefore instigates conformational changes, as well as weakens the chelating capacity towards both vanadyl and nickel ions [62]. However, supercritical extraction technology is not economically feasible due to its requirement for high temperature and pressure.

In addition, several demetallization procedures have been exploited over the past several years, including the oxidative [63], bio- [64-65], electrolytic [66], ultrasonic [67], and photo-demetallation [68]. These have however been recognized as ineffective resulting from the intrinsic tendency to change the crude oil physicochemical properties, which is unfavorable. Oxidative demetallation of crude oil was studied by Gould [63], however, a significant change in the physicochemical properties of crude oil happened. Bio-demetallation offers up to 55% of vanadyl-porphyrins [64] and 11% of nickel-porphyrins [65] demetallization percentage from crude oil after 24 h process at 328 K due to metabolic inhibition of microorganism in the presence of a large amount of vanadyl-porphyrins. The tolerance level of microorganisms for bio-demetallation is very low, around 20 mg kg^{-1} vanadyl-porphyrins in crude oil making bio-demetallation technology is not applicable for commercial process.

Electrolytic-demetallation was reported for Orinoco Belt crude oil with 73% demetallization percentage at 0.01 A cm^{-2} current density, however, this technology is energy-consuming [66]. Ultrasonic-demetallation was reported for crude oil at 423 K in 1-methyl naphthalene solvent yielding 35% demetallation percentage, however, a heavy part of crude oil was decoagulated and depolymerized into maltene fraction [67]. Meanwhile, a photo-demetallation process in a liquid-liquid extraction reactor was reported for metallic porphyrins removal from crude oil under ultraviolet irradiation for 10 h. This technology exhibits high demetallation percentages, i.e. 75 and 96% for commercial light oil and light gas oil. Unfortunately, some aromatic parts of crude oil were also decomposed thus the physicochemical properties of the crude oil were changed [68].

Comparably, hydrodemetallization processes are highly selective targets for metallic porphyrins which could be applied for a wide coverage of crude oil samples [69]. Despite the propensity to hydrogenate the hydrocarbon parts, the products obtained remain significantly satisfying [70]. The demetallation percentage is around 60-90% using metal oxides in the aluminium oxide or sodium aluminium silicate as the catalyst materials in the hydrodemetallization process. As an example, as much as 71% demetallation percentage was achieved for Lago crude oil using hydrodemetalation process at 739 K using 3.5% CoO and 10% MoO_3 catalyst at Al_2O_3 support. On the other hand, vanadyl- and nickel-porphyrins were successfully removed in 85 and 68%, respectively, from European crude oil at 683 K [71-72]. Unfortunately, some of the drawbacks experienced during hydrodemetallization include large heat and hydrogen gas consumption, which leads to an elevated operational cost. Furthermore, it is possible to gradually deposit vanadium or nickel metals on the used catalyst, and consequently lower catalyst activity by increasing operation time [12].

Lee et al. [73] successfully converted the vanadyl-porphyrins present in the asphaltene fractions of crude oil to vanadium(III) sulfide (V_2S_3) before the potential application as a hydrocracking catalyst. Therefore, the cracking phase ensued at 693 K and 11.0 MPa H_2 to obtain middle distillates, naphtha, gas, vacuum gas oils, and coke fractions in 30% yield. The strategy devised in this study is significantly useful while the asphaltene fraction during a suitable recycling process. This outcome is attributed to the activity of vanadium as a catalyst material. Langeslay et al. [74] also acknowledged the moderate catalytic activity of vanadium sulfide during the hydrodesulfurization of thiophene, hydrodenitrogenation, and hydrogenation of pyridine and toluene, respectively. This technology significantly influences the removal of metallic porphyrins from crude oils and the consequent utility as active catalyst materials during petrochemical processing.

■ CONCLUSION

The metallic porphyrins present in crude oil samples originate from evolution reactions involving chlorophyll and heme compounds. In addition, isolation and purification processes were followed by characterization using UV-Vis spectroscopy and Fourier transform ion cyclotron resonance mass spectrometry. The results showed a propensity to distinguish alkyl-, oxygen-, nitrogen-, and sulfur-containing porphyrins. Also, a total of six vanadyl classes have been discovered, including $C_nH_{2n\text{-}y}N_4VO$, $C_nH_{2n\text{-}y}N_4VO_2$, $C_nH_{2n\text{-}y}N_4VO_3$, $C_nH_{2n\text{-}y}N_4VO_4$, $C_nH_{2n\text{-}y}N_4VSO$, and $C_nH_{2n\text{-}y}N_5VO$ types. The several analytical methods established to detect and quantify metallic porphyrins comprise gel permeation chromatography, UV-Vis spectroscopy, ICP-MS analysis, and electron paramagnetic resonance. Moreover, the porphyrin presence is undesirable, as observed with the negative effects on the petrochemical's physicochemical properties, used catalyst deactivation, contamination of desired products, and the corrosion of metal equipment during processing. Therefore, it is essential to remove the metallic porphyrins through solvent extraction, supercritical water extraction, chelation with chemical agents, or hydrodemetallization processes. Each removal technology has its own advantages and disadvantages. Solvent extraction is the most applied technology today, however, this technique is only suitable for crude oil with a low resin-asphaltene amount. Hydrodemetallization offers a promising way due to its wide application and high selectivity, however, hydrodemetallization is inevitably high-cost technology. Further research and development for these technologies still open to establishing an efficient technology for the removal of metallic porphyrins from crude oil.

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