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(71) Demandeur/Applicant:
GREENOVEL INC., CA

(72) Inventeurs/Inventors:
ATTIA, MAI, CA;
FARAG, SHERIF, CA;
CHAOUKI, JAMAL, CA

(74) Agent: LAVERY, DE BILLY, LLP

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(54) Title: PROCESS FOR REMOVING METALS, SULFUR AND OTHER IMPURITIES IN CRUDE OIL

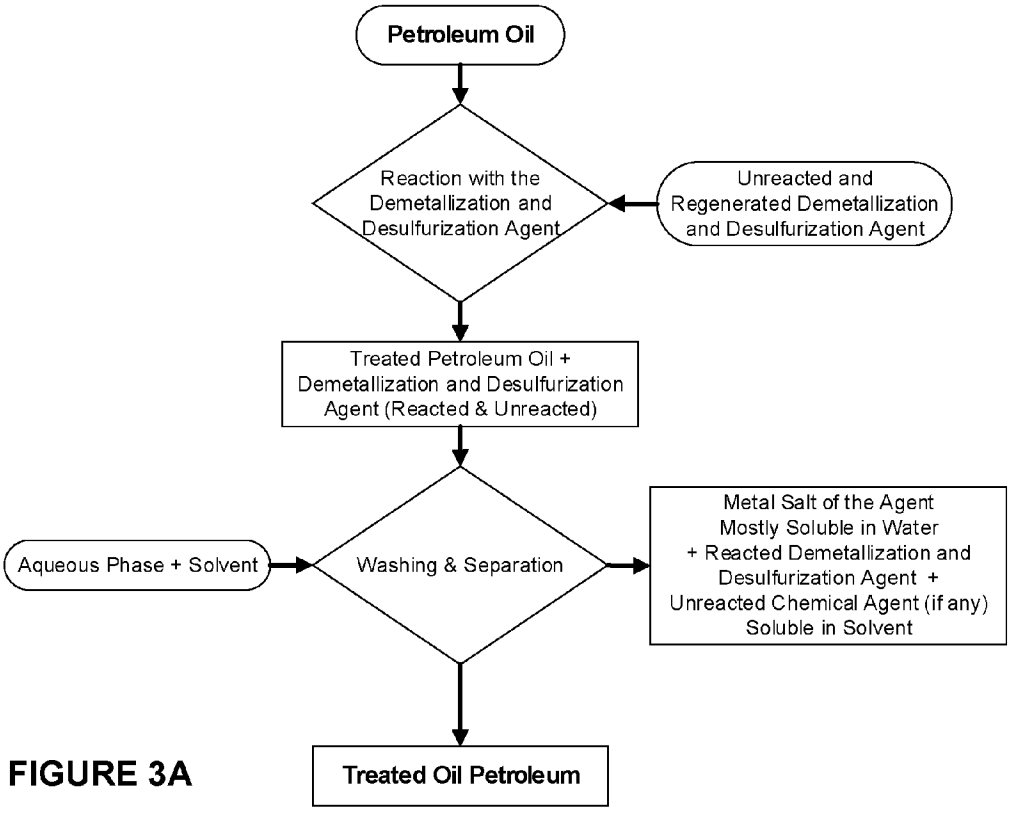

FIGURE 3A

(57) Abrégé/Abstract:
A process for removing metals and sulfur (S)-containing compounds in a crude oil material. The process comprises causing the crude oil material to react with a removing agent which comprises a phosphoric acid ester.

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(72) Inventors; and
(71) Applicants: **ATTIA, Mai** [CA/CA]; 246 Rue Rabelais, Saint-Constant, Québec J5A 0J5 (CA). **FARAG, Sherif** [CA/CA]; 246 Rue Rabelais, Saint-Constant, Québec J5A 0J5 (CA). **CHAOUKI, Jamal** [CA/CA]; 180, ave de la Présentation, Dorval, Québec H9S 3L4 (CA).

(74) Agent: **LAVERY, DE BILLY, LLP**; 1, Place Ville Marie, Bureau 4000, Montréal, Québec H3B 4M4 (CA).

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(54) **Title:** PROCESS FOR REMOVING METALS, SULFUR AND OTHER IMPURITIES IN CRUDE OIL

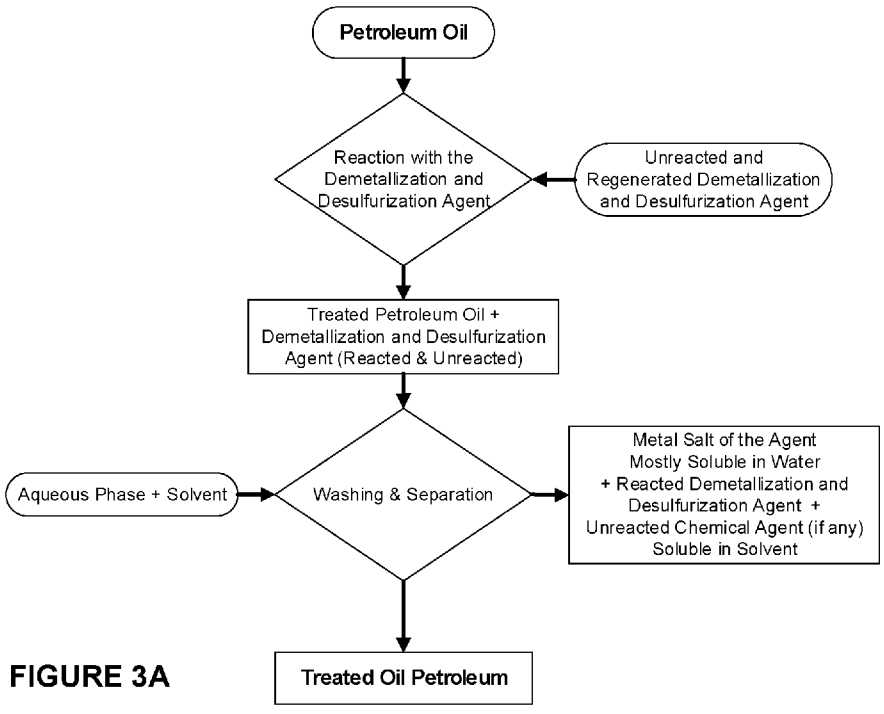

FIGURE 3A

(57) **Abstract:** A process for removing metals and sulfur (S)-containing compounds in a crude oil material. The process comprises causing the crude oil material to react with a removing agent which comprises a phosphoric acid ester.

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TITLE OF THE INVENTION

PROCESS FOR REMOVING METALS, SULFUR AND OTHER IMPURITIES IN CRUDE OIL

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims benefit of U.S. Provisional Patent Application No. 62/753,071, filed on October 31, 2018, the content of which is incorporated herein in its entirety by reference.

FIELD OF THE INVENTION

[0002] The present invention relates generally to processes for treating crude oil. More specifically, the invention relates to a process for removing metals, sulfur and other impurities in a crude oil material. The process according to the invention uses a metal and sulfur removing agent which comprises a phosphoric acid ester. The process according to the invention may be readily scaled up and integrated to industrial facilities.

BACKGROUND OF THE INVENTION

[0003] During the preceding few decades, considerable attention has been focused on petroleum heavy crude oil for use in several applications. The demand for the oil, however, has declined due to serious concerns, one of which is the unsatisfactory level of contamination by both metals and sulfur. The issue has an adverse effect throughout the refinery operations as a result of severe damage to the contact surfaces. Furthermore, it gives rise to diverse environmental issues that affect the surrounding area and society. Therefore, refining heavy crude oil is required to avoid the challenges facing crude oil and expand its commercial scale in various industrial applications.

[0004] Substantial numbers of metal contamination exist in oil, and their concentrations vary from a few parts per million (ppm) to higher than 1000 ppm. Some of the most distinct elements that have been identified in oil are cobalt (Co), nickel (Ni), copper (Cu), vanadium (V), silver (Ag), sodium (Na), potassium (K), lithium (Li), calcium (Ca), strontium (Sr) and arsenic [1,2]. Ni and V are the most abundant, and they reside predominantly in residual fuel oil fractions in an oil soluble form. The concentration of both Ni and V vary from a few ppm to 150 ppm and from less than 1 ppm to 1200 ppm, respectively [1-3].

[0005] Recently, all the attention has been directed to study the extraction of both Ni and V from crude oil. These elements exist in the core of stable organometallic compounds in the form of metalloporphyrinic and nonporphyrinc structures [4,5]. The high stability of these compounds increases the difficulty of elimination of the above metals from heavy crude oil. The subsistence of such elements in crude oil produces high volumes of coke and dry gases and decreases the liquid output [3]. In addition, the two elements poison the catalyst in a short time, ranging from 10 years for light oil to approximately one year for heavy crude oil [3,6], which is mainly due to the deposition of the two metal oxides formed on the pore of the catalyst and blocking the access site. Thus, the removal of both Ni and V from heavy oil becomes a vital objective of the crude oil industry.

[0006] Sulfur exists in crude oil as well in different forms, such as mercaptans, sulfides, disulfides, and thiophenes outlined in Erreur ! Source du renvoi introuvable. [8]. The detected percentage of sulfur in petroleum oil ranges from 0.1 wt.% to 15 wt.% and depends on several parameters, most importantly the origin of the extracted oil [7]. Sulfur is emitted to the atmosphere in the form of SOx, causing acid rain formation through its reaction with water, oxygen, and other chemicals exist in the atmosphere. The presence of sulfur in oil increases corrosion issues during the refinery process and helps in the deactivation of the catalyst in minimal time. Removal of dibenzothiophene and its alkyl derivatives is a big challenge, as the compounds cannot be transferred into H_2S due to the steric hindrance adsorption on the surface of the catalyst. The existence of sulfur in various forms, specifically the thiophinic form, is a considerable challenge due to the difficlte removal of the element from its complex structure.

[0007] Although a large number of techniques have been developed to lessen or remove the metals and sulfur from crude oil, only a few of them have been industrially applied, the main reason being the disadvantages associated with each method. For instance, the process relies on solvent extraction, which leads to removing the whole fraction containing metals, thus reducing the yield of the end-product. The distillation technique enhances the production of two grades of oils: (1) light oil, which is the primary product and contains a shallow concentration of metals; and (2) heavy oil, which includes a much higher level of contaminants that must undergo a further upgrading process. The fast catalyst deactivation, the need for an emulsification process, the high cost and long processing time are additional aspects that limit the performance of the developed demetallization and desulfurization techniques.

[0008] Ultrafiltration is a costly, value-intensive technique due to the fast fouling of the membrane used in the procedure. The bio-demetallization and bio-desulfurization processes are novel techniques for metals and sulfur removal from crude oil by the action of certain microorganisms. The process is applied directly after the burning of the fuel oil with keeping the calorific value without change. The main disadvantages of the process are the degradation of the crude oil which destroys the main skeleton of the oil. Also, the long processing time of the technique is considered a big challenge. The hydrotreatment process for both metals and sulfur removal (HDM-HDS) is the only process widely used in the industrial sector. This technique can remove around 90% of the metals and sulfur content from the oil. Although the HDM-HDS process effectively removes a large portion of the metals and sulfur, it suffers from several drawbacks. For example, they include the fast catalyst deactivation, high hydrogen consumption, which reaches H_2/Oil, Scf/bbl 300-2000 for light oil and 2000-10,000 for heavy residual oil, an elevated temperature that ranges from 300 to 400℃ for light distillate and from 340 to 425℃ for heavy residual, and elevated pressure, which ranges from 30 to130 atmosphere.

[0009] Several studies and efforts were performed on the removal of metals and sulfur from crude oil. Gould et al. developed a method for the demetallization of cold lake asphaltenes, Arabian heavy asphaltenes, and cold lake vacuum residuum [9]. Various oxidizing agents were tested to be demetallization agents, such as air at 100°C, NaOH/air, sodium hypochlorite, and peroxyacetic acid. It was found that the demetallization process is proportional to the amount of oxidant used. Air at 100°C and NaOH/air do not show any visible demetallization activity. Sodium hypochlorite and Peroxyacetic have high demetallization activity coupled with the ability to remove or destroy petroporphyrins and cause chlorine incorporation into the feed. D.A. Young proposed a new technique using $ZnCl_2$ and $TiCl_4$ for the demetallization of different hydrocarbon feedstocks [10]. The raw materials were blended with $ZnCl_2$ and $TiCl_4$ (2.0-4.5 lb/bbl oil), and the resulting mixtures were treated with hydrogen at approximately 288-482°C. A heavy Iranian residue was hydrogenated at 343°C, 1034-2500 kPa for 2 hours and a 7000 rpm stirring rate in the presence of $ZnCl_2$ (4.2 ppb). Seventy percent of the Ni and V contaminants were converted to oil-insoluble forms with coke formation of less than 3 wt.%. Young [11], Siskin [12], Michlmayr [13], Nametkin, Gubin et al. [14], and Gleim [15] have patented techniques using different demetallization agents, such as chlorinating compounds (Cl_2, $SOCl_2$), inorganic salts

($FeCl_2$, $SnCl_2$, $ZnCl_2$, $TiCl_4$, $RuCl_3$, $CrCl_3$, $COCl_2$) or their aqueous solutions. The reaction temperature ranged from 40°C to 300°C, and metals were successfully converted into insoluble constituents and removed by filtration. It was reported that the concentration of both Ni and V decreased by up to 70 wt.%. The main disadvantage of this process is the incorporation of chlorine and metal into the production and the degradation of the quality of the oil.

[0010] A novel technique has been applied by Greaney et al. [16] for demetallization and desulfurization by electrolysis using an electrochemical cell. The commercially available coulometry cell consisting of a mercury pool cathode, a platinum wire anode, a standard calomel reference electrode and a glass stirring paddle. The applied potential was set at 2.5 V. for 18 hours stirring. In the process, toluene was added to an aqueous solution of 40 wt.% tetra-butylammonium hydroxide (20 mL). It was demonstrated that the removal percentages reached to 53% of V, 50% of Ni and 65% of Fe. Yan [17] has reported a demetallization method using an aqueous solution containing a chelating agent (EDTA, N-(hydroxyethyl) ethylenediamido triacetic acid, N-[2-(bi(carboxymethyl)amino)-ethyl]-N-(2-hydroxyethyl) glycine, diethylenetriamine pentaacetic acid or its salts as a demetallization agent. A vacuum distillation residual oil was treated with 27% EDTA aqueous solution at pH 4.5. It was found that the removal percentages reached up to 99% of Ca, 35% of Fe, 4% of Ni, and 3% of V. Aldridge, R. Bearden, K. Riley [18] used a vanadium oxide supported by activated carbon for the demetallization of Arabian heavy vacuum residue. The treatment process was done at 5268 kPa and 290°C. It was noted that the activity of vanadium removal could be increased by increasing the percentage of vanadium on the activated carbon support. The reaction is highly selective with minimal occurrence of other reactions.

[0011] As can be seen, the removal of metals and sulfur from crude oil has received considerable attention.

[0012] There is still a need for processes for lowering the metals and sulfur contents of the crude oil. There is a need for such processes which are environmentally friendly, efficient, cost-effective and which can be readily scaled-up for industrial applications. Also, there is a need for such processes that can performed at industrial level.

SUMMARY OF THE INVENTION

[0013] The inventors have designed and conducted a process for removing metals and sulfur (S) and S-containing compounds from a crude oil material. The process uses a removing agent which is both a demetallization (DM) agent and a desulfurization (DS) agent. The demetallization and desulfurization agent (DM-DSA) according to the invention comprises a phosphoric acid ester.

[0014] In embodiments of the invention, the DM-DSA is suitable for also removing other impurities present in the crude oil. In embodiments of the invention, the DM-DSA is miscible to the crude oil. In embodiments of the invention, the DM-DSA comprises a phosphoric acid ester.

[0015] In embodiments of the invention, the reacted DM-DSA agent may be further treated such as to recover DM-DSA which is re-used in the process. Also, any unreacted DM-DSA may be recovered and re-used in the process.

[0016] The process of the invention can be readily scaled up and integrated in an industrial facility.

[0017] The invention thus provides the following in accordance with aspects thereof:

(1) A process for removing metals and sulfur (S)-containing compounds in a crude oil material, comprising causing the crude oil material to react with a removing agent which comprises a phosphoric acid ester.

(2) A process for removing metals and sulfur (S)-containing compounds in a crude oil material, comprising the steps of: (a) mixing the crude oil material with a removing agent which comprises a phosphoric acid ester, and subjecting the reaction mixture to stirring for a first period of time, at a temperature which is lower than the boiling point of the removing agent; (b) adding a first mixture of solvents including water to the reaction mixture, and subjecting the aqueous reaction mixture to stirring for a second period of time, at a temperature which is less than about 100°C; (c) allowing the aqueous reaction mixture to stand for a third period of time, thereby obtaining an oil phase comprising a treated oil and one or more phases including an aqueous phase; and (d) subjecting the aqueous reaction mixture to separation thereby yielding the treated oil.

(3) A process according to (2), further comprising the steps of: (e) washing the treated oil using a second mixture of solvents including water; and (f) retrieving a washed treated oil, optionally steps (e) and (f) is repeated one time or more.

(4) A process according to (2), wherein the treated oil is further subjected to steps (b) to (d), one time or more.

(5) A process according to (2), wherein the treated oil is further subjected to steps (a) to (d), one time or more.

(6) A process according to (3), wherein a composition of the first mixture of solvents at step (b) and the second mixture of solvents at step (d) is the same or is different; optionally the first and second mixtures of solvent each independently comprises an organic solvent; optionally the organic solvent is an alcohol such as ethanol, or benzene, or hexane, or 4-methyl-2-pentanone.

(7) A process according to (3), wherein step (f) is conducted at ambient temperature.

(8) A process according to (2) or (3), wherein steps (d) and (f) each independently comprises use of a reflux system; optionally steps (d) and (f) each independently comprises decantation, centrifugation, filtration or a combination thereof.

(9) A process according to any one of (2) to (8), wherein a length of the first period of time at step (a) and the second period of time at step (b) is the same or is different.

(10) A process according to any one of (2) to (9), wherein the aqueous phase obtained at step (c) comprises reacted removing agent, and wherein the reacted removing agent is further subjected to a regeneration treatment to yield the removing agent; optionally the regenerated removing agent is re-used at step (a); optionally the reacted removing agent comprises metal salts of the removing reacted agent.

(11) A process according to (10), wherein the regeneration treatment of the reacted removing agent comprises causing the treated reacted removing agent to react with an acid; optionally the acid is HCl.

(12) A process according to any one of (2) to (11), wherein the one or more phases obtained at step (c) comprise at least one phase comprising unreacted removing agent in an organic solvent, and wherein the unreacted removing agent is re-used at step (a).

(13) A process according to any one of (2) to (12), wherein the aqueous phase obtained at any of the steps is re-used in the process.

(14) A process according to any one of (1) to (13), wherein an amount of the removing agent is: between about 1 vol.% to about 5 vol.% an amount of the crude oil, or between about 1 vol.% to about 4 vol.% an amount of the crude oil, or between about 1 vol.% to about 3 vol.% an amount of the crude oil, or between about 1 vol.% to about 2 vol.% an amount of the crude oil, or about 2 vol.% an amount of the crude oil; or about 1 vol.% an amount of the crude oil.

(15) A process according to any one of (1) to (13), wherein an amount of the removing agent is: between about 1 wt.% to about 5 wt.% an amount of the crude oil, or between about 1 wt.% to about 4 wt.% an amount of the crude oil, or between about 1 wt.% to about 3 wt.% an amount of the crude oil, or between about 1 wt.% to about 2 wt.% an amount of the crude oil, or about 2 wt.% an amount of the crude oil; or about 1 wt.% an amount of the crude oil.

(16) A process according any one of (1) to (15), wherein other impurities in the crude oil are also removed.

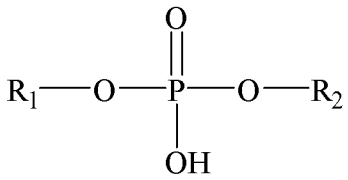
(17) A process according to (16), wherein the metals and other impurities, as measured by Neuron Activation Analysis, comprise at least one of: Cd, U, Ca, V, Ti, Sn, Sr, Ag, Mn, Si, Al, Mg, Na, Fe, K, Zn, Cr, Cl, V, Co, Ni, Cu, As, Se, Br, Rb, Zr, Mo, In, Sn, Sb, I, Cs, Ba, La, Hf, W, Hg, Th, Sc and S.

(18) A process according to (16), wherein the metals and other impurities, as measured by Neuron Activation Analysis, comprise at least one of: Ti, Mn, Al, Mg, Na, V, Ni, Cl, I, Br, Ca and S.

(19) A process according to any one of (1) to (18), wherein the metals, as measured by Neuron Activation Analysis, comprise at least one of: V and Ni.

(20) A process according to any one of (1) to (19), wherein sulfur in the crude oil is in a form selected from the group consisting of: thiol, sulfide, disulfide, thiolanes, thiophene, benzothiophene, dibenzothiophene and benzonaphtothiophene.

(21) A process according to any one of (1) to (20), wherein the removing agent is a phosphoric acid ester of general formula **I** below

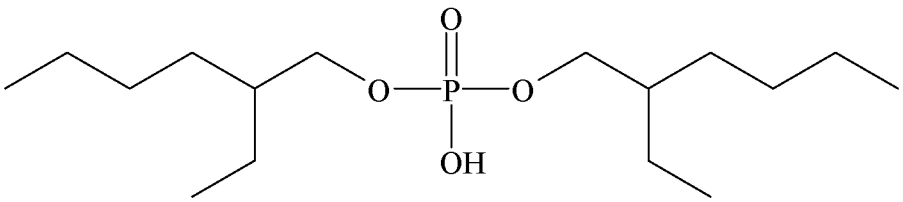


I

wherein R_1 and R_2 are each independently C_1 to C_{20} a linear or branched, cyclic or non-cyclic, saturated or unsaturated alkyl group, optionally comprising a heteroatom which is O, S or N.

(22) A process according to (21), wherein R_1 and R_2 are each independently a C_8 to C_{20} or a C_8 to C_{16} or a C_{16} a linear or branched, cyclic or non-cyclic, saturated or unsaturated alkyl group, optionally comprising a heteroatom which is O, S or N.

(23) A process according to any one of (1) to (22), wherein the metal removing agent comprises di-(2-ethylhexyl)phosphoric acid (**DEHPA** or **HDEHP**) outlined below



DEHPA or HDEHP

(24) A process according to (23), wherein the temperature at step (a) is up to about 250°C.

(25) A process according to any one of (1) to (24), wherein the metal removing agent is selected from the group consisting of: di-(2-ethylhexyl) phosphoric acid, bis(2-ethylhexyl) hydrophosphoric acid, di-(2-ethylhexyl) orthophosphoric acid, O,O-bis(2-ethylhexyl)phosphoric acid, orthophosphoric acid 2-ethylhexyl alcohol, phosphoric acid di(2-ethylhexyl) ester and Hostarex PA 216™.

(26) A process according to any one of (1) to (25), wherein the removing agent is miscible to the crude oil.

(27) A treated oil obtained by the process as defined in any one of (1) to (26).

(28) A treated oil obtained by the process as defined in any one of (1) to (26), wherein a content of the metals in the treated oil is about 75 to 90% or 80 to 90% lower than in the crude oil.

(29) A treated oil obtained by the process as defined in any one of (1) to (26), wherein a content of S and S-containing compounds in the treated oil is about 50 to 55% or about 53% lower than in the crude oil.

(30) A treated oil obtained by the process as defined in any one of (1) to (26), wherein: a content of the metals in the treated oil is about 75 to 90% or 80 to 90% lower than in the crude oil; and a content of S and S-containing compounds in the treated oil is about 50 to 55% or about 53% lower than in the crude oil.

(31) A treated oil obtained by the process as defined in any one of (1) to (26), wherein a content of V in the treated oil is about 90% lower than in the crude oil.

(32) A treated oil obtained by the process as defined in any one of (1) to (26), wherein a content of Ni in the treated oil is about 79% lower than in the crude oil.

(33) A treated oil obtained by the process as defined in any one of (1) to (26), wherein a content of S and S-containing compounds in the treated oil is about 53% lower than in the crude oil.

(34) A treated oil obtained by the process as defined in any one of (1) to (26), wherein: a content of V in the treated oil is about 90% lower than in the crude oil; a content of Ni in the

treated oil is about 79% lower than in the crude oil; a content of S and S-containing compounds in the treated oil is about 53% lower than in the crude oil.

(35) A system for treating crude oil, which is adapted for conducting the process as defined in any one of (1) to (26).

(36) An oil treatment facility, comprising the system as defined in (35); optionally the facility is an industrial facility

[0018] Other objects, advantages and features of the present invention will become more apparent upon reading of the following non-restrictive description of specific embodiments thereof, given by way of example only with reference to the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

[0019] In the appended drawings:

[0020] Figure 1: Forms of sulfur in petroleum crude oil.

[0021] Figure 2: Experimental setup of the process according to the invention.

[0022] Figure 3: Flowchart of the process according to the invention.

[0023] Figure 4: FTIR spectra of the raw heavy aromatic naphthenic crude oil (dotted line) and the treated oil using 2 vol.% DM-DSA (continuous line).

[0024] Figure 5: FTIR spectra of raw light naphthenic crude oil (dotted line) and the treated oil using 2 vol.% DM-DSA (continuous line).

[0025] Figure 6: FTIR spectra of the treated heavy aromatic naphthenic crude oil using 2 vol.% (continuous line) and using 5 vol.% DM-DSA (dotted line).

[0026] Figure 7: FTIR spectra of the treated light naphthenic crude oil using 2 vol.% DM-DSA (dotted line) and using 5 vol.% DM-DSA (continuous line).

[0027] Figure 8: Sulfur detection in the raw heavy aromatic naphthenic crude oil by elemental analysis technique.

[0028] Figure 9: Sulfur detection in the treated heavy aromatic naphthenic crude oil using 2 vol.% DM-DSA, by elemental analysis technique.

[0029] Figure 10: Sulfur detection in the raw light naphthenic crude oil by elemental analysis technique.

[0030] Figure 11: Sulfur detection in the treated light naphthenic crude oil using 2 vol.% DM-DSA, by elemental analysis technique.

[0031] Figure 12: Removal efficiency of Pennsylvania oil treated with 2 vol.% DM-DSA.

[0032] Figure 13: Removal efficiency of heavy aromatic naphthenic oil treated with 2 vol.% DM-DSA.

[0033] Figure 14: Removal Efficiency of light naphthenic oil treated with 2 vol.% DM-DSA.

[0034] Figure 15: Removal Efficiency of Iran oil treated with 2 vol.% DM-DSA.

[0035] Figure 16: Removal efficiency of Basra oil treated with 2 vol.% DM-DSA.

[0036] Figure 17: Removal Efficiency with 2 vol.% (continuous line) and 5 vol.% (dotted line) DM-DSA for heavy aromatic naphthenic oil.

[0037] Figure 18: Removal Efficiency with 2 vol.% (continuous line) and 5 vol.% (dotted line) DM-DSA for light naphthenic oil.

[0038] Figure 19: Removal efficiency of treated Iran oil with 2 vol.% DM-DSA (continuous line) against that only washed with aqueous solution (dotted line).

DESCRIPTION OF ILLUSTRATIVE EMBODIMENTS

[0039] Before the present invention is further described, it is to be understood that the invention is not limited to the particular embodiments described below, as variations of these embodiments may be made and still fall within the scope of the appended claims. It is also to be understood that the terminology employed is for the purpose of describing particular embodiments; and is not intended to be limiting. Instead, the scope of the present invention will be established by the appended claims.

[0040] In order to provide a clear and consistent understanding of the terms used in the present specification, a number of definitions are provided below. Moreover, unless defined otherwise, all technical and scientific terms as used herein have the same meaning as commonly understood to one of ordinary skill in the art to which this disclosure pertains.

[0041] Use of the word "a" or "an" when used in conjunction with the term "comprising" in the claims and/or the specification may mean "one", but it is also consistent with the meaning of "one or more", "at least one", and "one or more than one". Similarly, the word "another" may mean at least a second or more.

[0042] As used in this specification and claim(s), the words "comprising" (and any form of comprising, such as "comprise" and "comprises"), "having" (and any form of having, such as "have" and "has"), "including" (and any form of including, such as "include" and "includes") or "containing" (and any form of containing, such as "contain" and "contains"), are inclusive or open-ended and do not exclude additional, unrecited elements or process steps.

[0043] As used herein when referring to numerical values or percentages, the term "about" includes variations due to the methods used to determine the values or percentages, statistical variance and human error. Moreover, each numerical parameter in this application should at least be construed in light of the number of reported significant digits and by applying ordinary rounding techniques.

[0044] As used herein, the term "removing agent" or "demetallization-desulfurization agent (DM-DSA)" refers to a suitable agent that mixes with the crude oil and is adapted to removing both metals and sulfur (S)-containing compounds from the crude oil. Such agent may also be adapted to removing S in free form. Such agent is also adapted to removing other impurities in the crude oil. Such agent comprises a phosphoric acid ester.

[0045] As used herein, the term "sulfur (S)-containing compounds" refers to any compound in the crude that comprises a sulfur atom. The term also refers to S in free form.

[0046] As used herein, the term "demetallization agent" refers to a suitable agent that mixes with the crude oil and is adapted to removing metals from the crude oil. Such agent is also adapted to removing other impurities in the crude oil. Such agent comprises a phosphoric acid ester.

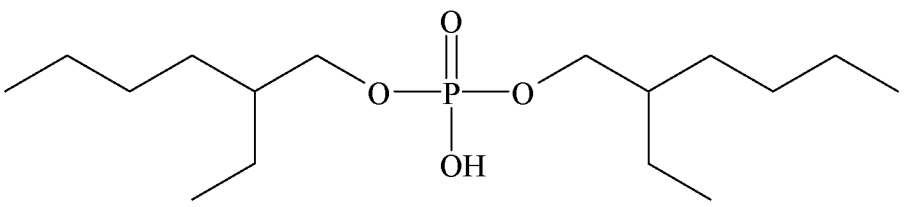
[0047] As used herein, the term "desulfurization agent" refers to a suitable a suitable agent that mixes with the crude oil and is adapted to removing sulfur (S)-containing compounds. Such agent may also be adapted to removing S in free form. Such agent is also adapted to removing other impurities in the crude oil. Such agent comprises a phosphoric acid ester.

[0048] The inventors have designed and conducted a process for removing metals and sulfur (S) and S-containing compounds from a crude oil material. The process uses a removing agent which is both a demetallization (DM) agent and a desulfurization (DS) agent. The demetallization and desulfurization agent (DM-DSA) according to the invention comprises a phosphoric acid ester.

[0049] The present invention is illustrated in further details in the Experiment Work section below. The section includes non-limiting examples.

Experimental work conducted

[0050] Materials: The demetallization-desulfurization (DM-DS) process according to the invention has been implemented on a number of petroleum crudes obtained from several countries. Iran and Basra oils were obtained directly from the tanks of the TOTAL refinery station in France with a high concentration of V, Ni and S. Heavy aromatic naphthenic crude oil, light naphthenic crude oil, and Pennsylvania crude oil were purchased from the ONTA company, in Ontario. The concentrations of V, Ni and S varied from low to high in the ONTA samples, as it is desired to gain deeper insight into the removal efficiency using the DM-DSA for the high and low metal concentrations. Other chemical agents, such as the DM-DSA and the solvents, were purchased from Sigma-Aldrich, Canada; di-(2-ethylhexyl)phosphoric acid (**DEHPA** or **HDEHP**) outlined below was generally used as DM-DSA in the experiments conducted.



DEHPA or HDEHP

[0051] The concentration of metals and sulfur in the oil samples was determined by the neutron activation analysis technique (NAA) using the SLOWPOKE reactor at Polytechnique Montréal, QC, Canada. The other required information archived directly from the supplier, Iran and Basra oils, are presented in **Table 1** below.

[0052] Table 1 – Characteristic of the processed oils.

Property	Unit	Basra Oil	Iran Heavy	Light naphtha	Heavy aromatic naphtha
Density (15°C)	kg/m^3	886.8	881.2	873.5	953.0
API	-	27.98	28.99	30.0	16.4
Viscosity (10°C)	mm^2/s	23.8	18.4	-	-
Viscosity (37,8°C)	mm^2/s	9.32	10.6	-	-
Viscosity (50°C)	mm^2/s	6.79	8.67	-	-
S_{total}	mg/kg	26354	22795	33557	18385
Ni	mg/kg	12	25	61.1	35.3
V	mg/kg	40	85	331	383.1
CCR	%W	7.845	6.88	H/C= 1.668	H/C= 1.558

[0053] Experimental setup: The experimental setup shown in **Figure 2** was employed to carry out the experimental work. The reference numerals in **Figure 2** are as follows: batch reactor (1), conventional heating source (2), heating zone (3), electric stirrer (4), heat reflux (5), water cooler (6), treated oil tank (7), washing liquids tank (8), analytical techniques (9), thermometer (10) and three-ways valve (11). Also, on **Figure 2** "NAA" denotes Neutron activation analysis and "FTIR" denotes Fourier transform infrared.

[0054] The mixture of the crude oil and the reactants is poured into the batch reactor equipped with a stirring technique. The reactor is attached to a water-cooled Liebig or Vigreux condenser fitted onto the top. The condensation system, in other words, reflux, works at a temperature of -5°C and ambient pressure. The central role of the reflux is to condense the lower molecular weight compounds that might be vaporized during the reaction time due to increasing temperature. The reactor is heated conventionally to a temperature lower than the

boiling point of the DM-DSA yet enough to perform the removal reaction. The temperature was controlled not only based on the electric oven temperature, but also as a direct measurement by using a thermometer immersed inside the oil. The experiment was carried out utilizing the conventional heating mechanism to control the reaction temperature and other aspects.

[0055] Experiment procedures: A flowchart illustrating the process according to the invention is presented in **Figure 3A** and **Figure 3B**, also showing the regenarations of various components of the process. The process comprises: treatment of the crude oil with the DM-DSA (reaction); separation of the treated oil from the reacted and/or unreacted DM-DSA (in aqueous phase); and washing the treated oil. More details on each of the steps of the process are outlined herein below.

[0056] Treatment of crude oil with the DM-DSA (reaction): A weight/volume amount of the crude oil was mixed with the DM-DSA. An amount of DM-DSA between about 2 wt.% and 5 wt.% of the amount of the crude oil was generally used. The mixture of crude oil and DM-DSA was poured into the reactor as outlined in **Figure 2**. It is worth mentioning that the described process does not need an emulsification process, which is contrary to most of the existing chemical demetallization techniques. The principal reason for this aspect is the good miscibility of the DM-DSA according to the invention with crude oil. Electric stirring is applied during the reaction for mixing the reactants and for properly distributing the heat inside the reactor. This enhances the replacement reaction taking place between the treated oil and the DM-DSA. The mixture is heated for about 1 hour at a temperature of up to 250℃ under stirring conditions of up to 700 rpm.

[0057] Separation: Efforts were made to separate the treated oil from the reacted DM-DAS in the form of metal salts thereof and any unreacted DM-DSA. The challenge is due to the fact that all the components involved, namely, the treated oil, DM-DSA in the form of salts thereof and any unreacted DM-DSA are all present in the same vessel. The separation process was performed using a mixture of solvents comprising organic solvents and water. In embodiments of the invention, an organic solvent such as an alcohol was used together with water. A first solvent was used mainly to dissolve any unreacted DM-DSA and separate it from the treated oil. A second solvent, preferably in aqueous phase, was used to dilute the metal salts of DM-DSA. In embodiments of the invention ethanol and water were used. The

mixture of the first and second solvents and the treated oil was then subjected to heating at a temperature of less than about 100°C under stirring conditions of up to 700 rpm for about 1 hour. The separation is generally performed in a reflux system to avoid the evaporation of the solvent which would allow for the precipitation of the dissolved compounds back into the oil. After the separation time, a mixture of three phases could be observed in the reactor. The upper phase comprising the treated oil, the lower phase comprising both the metal salts of DM-DSA dissolved in the aqueous phase and unreacted DM-DSA dissolved in ethanol. Eventually, the two obtained phases were separated by decantation and, then, centrifugation. The organic solvent phase comprising the unreacted dissolved DM-DSA was further separated from the aqueous phase to regenerate the unreacted DM-DSA.

[0058] Washing the treated oil: After the separation, the collected oil phase was subjected to washing in order to ensure a complete removal of the metal salts of DM-DSA and any unreacted DM-DSA. More than one washing was performed, generally about three washings were performed. In embodiments of the invention, the first and second solvents used in the separation step were also used in the washings. Washing was performed at room temperature with vigorous stirring or shaking for approximately a few minutes. The mixture was then poured into a separation system where it was left to stand until complete detachment of the two phases. A centrifugal separation system was eventually used for the aqueous phase/oil phase separation; then the treated oil was sent for the analytical techniques.

[0059] Analytical techniques: Various analytical techniques were performed to validate the performance of the DM-DSA according to the invention as well as to gain a better understanding of the process efficiency. The following three analytical techniques were applied: (1) Fourier transform infrared (FTIR), (2) Neutron activation analysis (NAA) and (3) Elemental analysis C, H, N, and S.

[0060] FTIR technique: Fourier transform infrared spectroscopy analysis was undertaken using a Perkin Elmer 65 FTIR-ATR instrument (PerkinElmer, Woodbridge, ON, Canada). A sum of 128 scans was accumulated for the signal averaging of each IR spectral measurement with a 4 cm^{-1} resolution. The spectra of the samples were recorded over a wavenumber range of 4000-650 cm^{-1} to detect the transformation of N-M bond to the N-H bond. FTIR can detect the characteristic vibration frequencies for each bond, functional group, side chain, and cross-link inside the molecule. The demetallization reaction is primarily founded on the conversion

of N-M bonds into the N-H bond. The FTIR technique is a good candidate to observe the changes taking place in the N-M bond. Unfortunately, the FTIR instrument used in the detection process could not detect peaks lower than 600 cm^{-1}; consequently, the peaks of N-M bonds at less than 400 cm^{-1} have not been recorded.

[0061] Elemental analysis technique: It is desirable to detect the sulfur concentration in the crude oil to record the change that occurs after the demetallization-desulfurization process. To observe the change, the elemental analysis technique is applied to find out the variation in sulfur concentration before and after the extraction process. The sulfur detection was performed using the Elemental Analyzer EA3000 (EuroVector) instrument. The data were processed using Callidus software interface version 5.1. Callidus. The 5.1 software fully controls the device, integrates peaks, reprocesses sample data, and reports result selecting one of the pre-arranged formats. The Callidus is based on the autorun concept as the samples cannot analyze in isolation but must be in association with standards (for calibration purposes), blanks (for the determination of potential trace contaminants) and bypasses (for conditioning purposes).

[0062] Neutron activation analysis: Neutron activation analysis is a nuclear technique used to determine the compactness of each element existing in vast numbers of chemical compounds. The analysis was performed in a slowpoke lab at Polytechnique Montréal, QC, Canada. In this technique, a neutron source is required for bombarding the sample with neutrons. Due to this bombardment, the element transfers to its isotopic form. According to the radioactive emission and decay data known for each element, the spectra of emission of gamma rays for all the elements can be easily studied. Quantifying various metals in crude oil is indeed a challenge, due to the complex matrix of crude oil, which includes vast numbers of metals and different elements. In addition, the depressed concentration of each metal remains a considerable issue to be determined by most of the analytical techniques. Many of the metals and elements are interfering as well, which affects the accuracy of the measurements. The NAA technique is characterized by high accuracy in quantifying a wide assortment of metal elements in the complex matrix of crude oil. Its proficiency is indirectly dealing with the oil itself without any digestion process or dilution, such as the ICP-MS technique, which has several factors for error production in the measurements. The drawbacks, the uncertainty, and the limitations were determined for the NAA measurements to heighten the accuracy of the technique. An optimum method that can be used for metals

quantification using the NAA technique is the k0-Neutron Activation analysis (k0-NAA). This method is a single-comparator standardized method used for high accuracy quantification of elements in any type of materials. By applying this method, the calibration of each element by changing the matrix or the detector is not required.

[0063] Quantification method: For the quantification of the metals and sulfur in the crude and treated oil, the extraction efficiencies in the case of each oil were calculated. The extraction efficacy percentage was determined using the following equation:

$$\text{Extraction efficacy (\%)} = \frac{((\text{C crude} - \text{C treated})}{\text{C crude}} * 100,$$

where the C_{crude} is the concentration of an element in the crude oil before the treatment process, $C_{treated}$ is the concentration of the element in the treated oil after the treatment process.

[0064] Results and discussion: The DM-DSA according to the invention has the ability to form an ionic liquid while it is present in oil at a lower temperature. The DM-DSA is not miscible with water, but it forms salts that are soluble in water at low and high temperatures. Thus, the unreacted part of the DM-DSA can be recovered and recycled. The immiscibility of the agent with water may be attributed to the presence of long side chains in the agent (R_1 and R_2 in formula **I** are between about C_8 and C_{10} chains), which reduces its polarity.

[0065] The FTIR of the DM-DSA indicates that the DM-DSA has peaks appearing in regions that are different from what appeared in the treated oil, in particular, between 4000cm^{-1} and 3000 cm^{-1}. This allows us to conclude that peaks appearing in these regions after the process do indeed relate to the treatment process.

[0066] The FTIR shows a difference in the absorption frequencies between the treated and untreated oil. It is supposed to transfer the metalloporphyrin ring into free based porphyrin; accordingly, new frequencies for the N-H bonds should appear instead of the N-M bonds.

[0067] Figure 5 shows the deviation in the IR absorption frequencies between the untreated and treated heavy aromatic naphthenic crude oil. There is a peak located at 3320 cm^{-1}, which is attributed to the N-H bond stretching frequency. The peak located around 1600 cm^{-1} is related to another vibrational mode of N-H [19]. There are two other peaks appearing at

around 1110 cm^{-1} and 740 cm^{-1} in the treated oil, which are relative to in-plane N−H and out-of plane bending N−H, respectively [20]. It should be noted that these two peaks do not exist in the crude oil or in the DM-DSA. The bands around 2922 cm^{-1} were assigned to the C-H bond of the benzene ring and pyrrole ring. Bands at ~1458 and ~1379 cm^{-1} are attributed to the C=C stretching mode and the C=N stretching vibration, respectively. The bands at around 800 cm^{-1} and 750 cm^{-1} were respectively assigned to the C-H bond bending vibration of the para-substituted and molecule ortho-substituted phenyl ring.

[0068] **Figure 5** shows the same peaks appearing in **Figure 4** but for light naphthenic crude oil. The FTIR results confirm that new peaks appeared in the treated oil which related to the N-H bond. This finding, in turn, confirms that the treatment process using the DM-DSA according to the invention was successfully implemented and the N-M bond transferred to N-H bond. Similar results were obtained in all processed oil samples.

[0069] An increased concentration of DM-DSA, to about 5 vol.%, was also applied during the treatment process of both heavy aromatic naphthenic crude oil and light naphthenic crude oil. This experiment performed to determine the variation in the removal efficiency when a higher amount of the DM-DSA was used. The difference can be determined by comparing the intensity of the peak for both 2 vol.% and 5 vol.% using the FTIR technique. It was found that there is no significant increase in the removal efficiency by applying 5 vol.% of DM-DSA during the treatment process, as presented in **Figure 6** and **Figure 7**.

[0070] The elemental analysis was carried out to detect the variation in sulfur concentration before and after the treatment process, and to record the effect of the DM-DSA on sulfur removal. **Figure 8** depicts a clear peak for sulfur in the region between 144 and 180 cm^{-1} on the heavy aromatic naphthenic crude oil and **Figure 9** shows the change performed for the sulfur peak after the process. The strength of the peak was reduced, which indicates the decrease in the concentration of sulfur in the treated oil.

[0071] This shows that the DM-DSA eliminated a portion of the sulfur compounds from the crude oil during the demetallization-desulfurization process. The same decrease in the sulfur content was obtained in the light naphthenic crude oil. **Figure 10** and **Figure 11** also confirm the reduction in sulfur concentration that took place after the demetallization-desulfurization process.

[0072] To accurately determine the metal content in the oils, the NAA technique was performed. The analysis was carried out on the crude oil, the treated oil and the aqueous phase produced after the washings. A difference in the metal content between the crude oil and the treated oil was detected. In addition, the analysis of the aqueous phase showed the presence of metals in the aqueous phase after the washing step. It is worth mentioning that almost all the metals concentrations have been reduced compared to the crude oils, specifically, V and Ni, which are known in the art to be difficult to eliminate. Pennsylvanian crude oil is a light oil with low metals concentrations. Thus, it was used to test the removal efficiency of the DM-DSA in the case of the lower levels of metals in crude oil. The NAA results are presented in **Table 2** below and **Figure 12** confirming that the DM-DSA has a high removal efficiency in the case of Ti, I, Al and Ca, which reaches more than 90 wt.%. The removal efficiency for Br, Mg, V and Cl was detected at higher than 70 wt.%. The treatment process also included removal of sulfur alongside metals, which reached 27%.

[0073] **Table 2** – NAA results of Pennsylvania oil treated with 2 vol.% DM-DSA.

Element	Raw oil (ppm)	Treated oil (ppm)
Ti	7	0.3
I	0.6	0.03
Br	0.5	0.06
Mn	0.02	0.01
Al	12	0.50
Mg	15	1.6
Na	6	2.6
V	0.03	0.01
Cl	12	3.2
Ca	44	2.7
S	839	612

[0074] The NAA results of the heavy aromatic naphthenic oil are tabulated in **Table 3** below. **Figure 13** displays the removal efficiency of the treated heavy aromatic naphthenic crude oil using 2 vol.% DM-DSA. All three of Ti, Mg, and Na have a higher removal efficiency, which reached more than 80%, followed by Cl and Ca with more than 65%. The concentration of S decreased as well with a removal efficiency of around 15%.

[0075] Table 3 – NAA results of heavy aromatic naphthenic oil treated with 2 vol.% DM-DSA.

Element	Raw oil (ppm)	Treated oil (ppm)
Ti	20.4	2.05
Mn	0.23	0.15
Mg	41	3.37
Na	5.88	0.85
V	383.1	233.6
Cl	100.8	27.02
Ca	54.16	16.66
S	18385	15513.8

[0076] Figure 14 and **Table 4** below demonstrate the results of the light aromatic naphthenic oil.

[0077] Table 4 – NAA results of light naphthenic oil treated with 2 vol.% DM-DSA.

Element	Raw oil (ppm)	Treated oil (ppm)
Ti	34	3
Mn	0.2	0.1
Mg	74	10
Na	9	7
V	331	307
Cl	106	18
Ca	55	17
S	33557	23812

[0078] The NAA analysis shows a high removal efficiency of both Iran and Basra oils in spite of the high complexity of the two oils. In the case of Iran oil, the removal efficiency presented in **Figure 15** and **Table 5** below.

[0079] Table 5 – NAA results of Iran oil treated with 2 vol.% DM-DSA.

Metals	Raw oil (ppm)	Treated oil (ppm)
Ti	6	0.5
Mn	0.02	0.01
Mg	17	6
Na	13	0.1
V	88	59

Ni	30	8
Cl	22	17
Ca	5	0
S	22795	14816

[0080] V, Ni and S reached 33%, 73% and 35%, respectively. For Basra oil, the removal efficiency was more prominent than in Iran oil, as all of V, Ni and S have been eliminated with 90%, 79% and 63% efficiency, respectively; see **Table 6** below and **Figure 16**.

[0081] Table 6 – NAA results of Basra oil treated with 2 vol.% DM-DSA.

Metals	**Raw oil (ppm)**	**Treated oil (ppm)**
Ti	4	0.6
Mn	0.05	0.008
Mg	5	1
Na	14	5.5
V	37	3.6
Ni	10	2
Cl	25	10
Ca	8	2.6
S	26354	9751

[0082] It is essential to distinguish the variation that could take place for the metals and sulfur concentrations if the dosage of the DM-DSA rose to more than 2 vol.%. Therefore, another batch of experiments was carried out on the heavy aromatic naphthenic crude oil and light naphthenic crude oil applying 5 vol.% DM-DSA, **Figure 17**, **Table 7** below, **Figure 18** and **Table 8** below. It was found from the NAA analysis that there is an adequate discrepancy in the removal efficiency of some metals when raising the DM-DSA dosage, specifically Na and Mn. This reduction could be due to the simple structure of the metals in the oil, which make them much smoother to attach to the DM-DSA than the other metals complexes. Regarding S, it is reasonable to enhance the removal efficiency of S by increasing the DM-DSA dosage, because S compounds will encounter more ionic liquids with which to connect.

[0083] Table 7 – comparison between heavy aromatic naphthenic crude oil and treated oils with 2 vol.% and 5 vol.% DM-DSA.

Metal	Raw oil (ppm)	Treated oil 2 vol.% (ppm)	Treated oil 5 vol.% (ppm)
Ti	20.4	2.05	3.06
Mn	0.23	0.15	0.1
Mg	41	3.37	2.5
Na	5.88	0.85	2.24
V	383.1	233.6	222.6
Cl	100.8	27.02	26.76
Ca	54.16	16.66	14.72
S	18385	15514	10090

[0084] Table 8 – NAA analysis of light naphthenic crude oil and treated oils with 2 vol.% and 5 vol.% of DM-DSA.

Metal	Raw oil (ppm)	Treated oil 2 vol.% (ppm)	Treated oil 5 vol.% (ppm)
Ti	33.66	2.7	1
Mn	0.169	0.105	0.03
Mg	73.99	10.33	0.45
Na	9.4	7.82	2.85
V	331	307.26	300.15
Cl	100.8	18.46	44.68
Ca	54.955	17.48	8.88
S	33557	23812.9	23602.6

[0085] It was desired to confirm that the decrease in metals concentrations after the treatment process was due to the reaction of the metals with the DM-DSA and not because of the washing step. A comparison between the treated oil with the process according to the invention and the same oil exposed only to the washing step was therefore carried out. Iran oil was used, and the results were analyzed by the NAA technique. **Figure 19** illustrates the comparison in removal efficiency between the treated and washed Iran oil. It was noted that

all the metals decreased due to the high removal efficiency reaching up to 100% for some metals, whereas employing just the washing step did not show any drop in the metals except those that can be extracted just by washing, such as Ca and Ba. This confirmed that the treatment process is indeed responsible for the decline that took place for the metal concentrations.

[0086] The DM-DSA according to the invention acts as a proton donor and, thus, provides the porphyrin ring with the needed hydrogen ions to occupy the vacancies created during the metal extraction reactions. The DM-DSA also helps to extract the metals from the porphyrin ring forming the metal salt of the agent. Behind the demetallization and desulfurization processes, there are a set of complex chemical reactions taking place. Effort was made to better understand these chemical reactions.

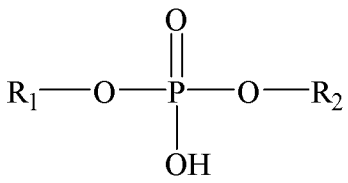
[0087] The main idea behind the demetallization reaction is the ion exchange mechanism that happens very quickly in homogeneous solutions. In the reaction (cation exchanger), the agent acts as a proton donor for the metalloporphyrin ring after the four nitrogen atoms extract the electron bonds between the metals, due to the high electronegativity of the nitrogen atoms, which reaches up to 3.04 compared to 1.63 for the V atom. The high electronegativity of the four nitrogen atoms plays an essential role in leaving the metal atom as a positive metal ion after the electron bond extraction. This, in turn, forms four negative nitrogen ions, which directly bond with the hydrogen protons from the agent forming the pure porphyrin ring. At the same time, the negative side of the agent robustly extracts the positive metal ion from the media creating the metal salt of the agent.

[0088] The DM-DSA used for the demetallization process is one of the most famous cations that can form ionic liquids with several anions. Both anion and cation species can interact forming an ionic liquid, or the cation can interact with a chloride anion from the oil medium forming another ionic liquid. The ionic liquid is formed by stirring both of the DM-DSA with the crude oil [21]. It was demonstrated that there are some factors affected by the melting point and the physical state in general of the ionic liquid at room temperature, importantly, the lengths of the alkyl chain and the central atom of the cation [22]. Platzer et al. have indicated that larger side chain cations tend to reduce the melting point of the ionic liquid [23].

[0089] When the ionic liquid is formed, it bonds with the thiophen compounds [24] in the oil through two different bonds: (1) through the H-bond between the S and the H from the agent,

and (2) through the electrostatic force between the different charges of the high molecular weight part of both the agent and the thiophen compounds.

[0090] The process according to the invention allows for the removal of metals, sulfur and other impurities in a crude material. The removing agent or DM-DSA used in the process is a phosphoric acid ester such as di-(2-ethylhexyl)phosphoric acid (**DEHPA** or **HDEHP**) outlined above. As will be understood by a skilled person, the DM-DSA may be any suitable phosphoric acid ester, for example of general formula **I** below. In embodiments of the invention, the DM-DSA is miscible with the crude oil.



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wherein R_1 and R_2 are each independently C_1 to C_{20} a linear or branched, cyclic or non-cyclic, saturated or unsaturated alkyl group, optionally comprising a heteroatom which is O, S or N; optionally R_1 and R_2 are each independently a C_8 to C_{20} or a C_8 to C_{16} or a C_{16} linear or branched, cyclic or non-cyclic, saturated or unsaturated alkyl group, optionally comprising a heteroatom which is O, S or N.

[0091] The process according to the invetntion comprises: at least one reaction step, at least one separation step, and at least one washing step. As will be understood by a skilled person these steps may invoved other steps such as decantation, centrifugation, filtration.

[0092] The process according to the invention allows for the regeneration of the DM-DSA from the reacted DM-DSA. This is performed by causing the reacted DM-DSA to react with an acid such as HCl. The regenerated DM-DSA is re-used in the process. Also, any unreacted DM-DSA is recovered and re-used in the process. Moreover, the aqueous phases steming from the separations are recovered and re-used in the process.

[0093] A content of metals in an oil treated by the process of the invention may be between about 75 to 90% or between about 80 to 90% lower than in the crude oil. A content of S and

S-containing compounds in an oil treated by the process of the invention may be between about 50 to 55% or about 53% lower than in the crude oil. As will be understood by a skilled person, such treated oils are with the scope of the present invention.

[0094] The process according to the invention embodies a system and may be readily scaled up and integrated in an industrial facility. As will be understood by a skilled person, such system and facility are within the scope of the present invention.

[0095] The scope of the claims should not be limited by the preferred embodiments set forth in the examples; but should be given the broadest interpretation consistent with the description as a whole.

[0096] The present description refers to a number of documents, the content of which is herein incorporated by reference in their entirety.

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CLAIMS:

1. A process for removing metals and sulfur (S)-containing compounds in a crude oil material, comprising causing the crude oil material to react with a removing agent which comprises a phosphoric acid ester.

2. A process for removing metals and sulfur (S)-containing compounds in a crude oil material, comprising the steps of:

(a) mixing the crude oil material with a removing agent which comprises a phosphoric acid ester, and subjecting the reaction mixture to stirring for a first period of time, at a temperature which is lower than the boiling point of the removing agent;

(b) adding a first mixture of solvents including water to the reaction mixture, and subjecting the aqueous reaction mixture to stirring for a second period of time, at a temperature which is less than about 100°C;

(c) allowing the aqueous reaction mixture to stand for a third period of time, thereby obtaining an oil phase comprising a treated oil and one or more phases including an aqueous phase; and

(d) subjecting the aqueous reaction mixture to separation thereby yielding the treated oil.

3. A process according to claim 2, further comprising the steps of:

(e) washing the treated oil using a second mixture of solvents including water; and

(f) retrieving a washed treated oil,

optionally steps (e) and (f) is repeated one time or more.

4. A process according to claim 2, wherein the treated oil is further subjected to steps (b) to (d), one time or more.

5. A process according to claim 2, wherein the treated oil is further subjected to steps (a) to (d), one time or more.

6. A process according to claim 3, wherein a composition of the first mixture of solvents at step (b) and the second mixture of solvents at step (d) is the same or is different;

optionally the first and second mixtures of solvent each independently comprises an organic solvent;
optionally the organic solvent is an alcohol such as ethanol, or benzene, or hexane, or 4-methyl-2-pentanone.

7. A process according to claim 3, wherein step (f) is conducted at ambient temperature.

8. A process according to claim 2 or 3, wherein steps (d) and (f) each independently comprises use of a reflux system;
optionally steps (d) and (f) each independently comprises decantation, centrifugation, filtration or a combination thereof.

9. A process according to any one of claims 2 to 8, wherein a length of the first period of time at step (a) and the second period of time at step (b) is the same or is different.

10. A process according to any one of claims 2 to 9, wherein the aqueous phase obtained at step (c) comprises reacted removing agent, and wherein the reacted removing agent is further subjected to a regeneration treatment to yield the removing agent;
optionally the regenerated removing agent is re-used at step (a);
optionally the reacted removing agent comprises metal salts of the removing reacted agent.

11. A process according to claim 10, wherein the regeneration treatment of the reacted removing agent comprises causing the treated reacted removing agent to react with an acid;
optionally the acid is HCl.

12. A process according to any one of claims 2 to 11, wherein the one or more phases obtained at step (c) comprise at least one phase comprising unreacted removing agent in an organic solvent, and wherein the unreacted removing agent is re-used at step (a).

13. A process according to any one of claims 2 to 12, wherein the aqueous phase obtained at any of the steps is re-used in the process.

14. A process according to any one of claims 1 to 13, wherein an amount of the removing agent is: between about 1 vol.% to about 5 vol.% an amount of the crude oil, or between about 1 vol.% to about 4 vol.% an amount of the crude oil, or between about 1 vol.% to about 3 vol.% an amount of the crude oil, or between about 1 vol.% to about 2 vol.% an amount of the crude oil, or about 2 vol.% an amount of the crude oil; or about 1 vol.% an amount of the crude oil.

15. A process according to any one of claims 1 to 13, wherein an amount of the removing agent is: between about 1 wt.% to about 5 wt.% an amount of the crude oil, or between about 1 wt.% to about 4 wt.% an amount of the crude oil, or between about 1 wt.% to about 3 wt.% an amount of the crude oil, or between about 1 wt.% to about 2 wt.% an amount of the crude oil, or about 2 wt.% an amount of the crude oil; or about 1 wt.% an amount of the crude oil.

16. A process according any one of claims 1 to 15, wherein other impurities in the crude oil are also removed.

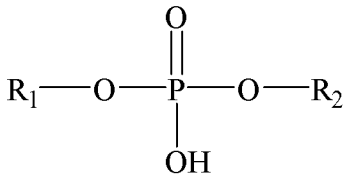
17. A process according to claim 16, wherein the metals and other impurities, as measured by Neuron Activation Analysis, comprise at least one of: Cd, U, Ca, V, Ti, Sn, Sr, Ag, Mn, Si, Al, Mg, Na, Fe, K, Zn, Cr, Cl, V, Co, Ni, Cu, As, Se, Br, Rb, Zr, Mo, In, Sn, Sb, I, Cs, Ba, La, Hf, W, Hg, Th, Sc and S.

18. A process according to claim 16, wherein the metals and other impurities, as measured by Neuron Activation Analysis, comprise at least one of: Ti, Mn, Al, Mg, Na, V, Ni, Cl, I, Br, Ca and S.

19. A process according to any one of claims 1 to 18, wherein the metals, as measured by Neuron Activation Analysis, comprise at least one of: V and Ni.

20. A process according to any one of claims 1 to 19, wherein sulfur in the crude oil is in a form selected from the group consisting of: thiol, sulfide, disulfide, thiolanes, thiophene, benzothiophene, dibenzothiophene and benzonaphtothiophene.

21. A process according to any one of claims 1 to 20, wherein the removing agent is a phosphoric acid ester of general formula **I** below

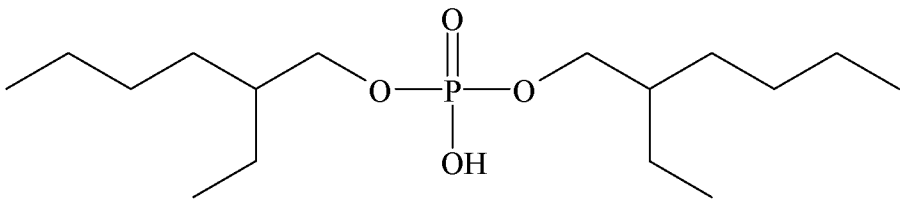


I

wherein R_1 and R_2 are each independently C_1 to C_{20} a linear or branched, cyclic or non-cyclic, saturated or unsaturated alkyl group, optionally comprising a heteroatom which is O, S or N.

22. A process according to claim 21, wherein R_1 and R_2 are each independently a C_8 to C_{20} or a C_8 to C_{16} or a C_{16} a linear or branched, cyclic or non-cyclic, saturated or unsaturated alkyl group, optionally comprising a heteroatom which is O, S or N.

23. A process according to any one of claims 1 to 22, wherein the metal removing agent comprises di-(2-ethylhexyl)phosphoric acid (**DEHPA** or **HDEHP**) outlined below



DEHPA or HDEHP

24. A process according to claim 23, wherein the temperature at step (a) is up to about 250°C.

25. A process according to any one of claims 1 to 24, wherein the metal removing agent is selected from the group consisting of: di-(2-ethylhexyl) phosphoric acid, bis(2-ethylhexyl) hydrophosphoric acid, di-(2-ethylhexyl) orthophosphoric acid, O,O-bis(2-ethylhexyl)phosphoric acid, orthophosphoric acid 2-ethylhexyl alcohol, phosphoric acid di(2-ethylhexyl) ester and Hostarex PA 216™.

26. A process according to any one of claims 1 to 25, wherein the removing agent is miscible to the crude oil.

27. A treated oil obtained by the process as defined in any one of claims 1 to 26.

28. A treated oil obtained by the process as defined in any one of claims 1 to 26, wherein a content of the metals in the treated oil is about 75 to 90% or 80 to 90% lower than in the crude oil.

29. A treated oil obtained by the process as defined in any one of claims 1 to 26, wherein a content of S and S-containing compounds in the treated oil is about 50 to 55% or about 53% lower than in the crude oil.

30. A treated oil obtained by the process as defined in any one of claims 1 to 26, wherein: a content of the metals in the treated oil is about 75 to 90% or 80 to 90% lower than in the crude oil; and a content of S and S-containing compounds in the treated oil is about 50 to 55% or about 53% lower than in the crude oil.

31. A treated oil obtained by the process as defined in any one of claims 1 to 26, wherein a content of V in the treated oil is about 90% lower than in the crude oil.

32. A treated oil obtained by the process as defined in any one of claims 1 to 26, wherein a content of Ni in the treated oil is about 79% lower than in the crude oil.

33. A treated oil obtained by the process as defined in any one of claims 1 to 26, wherein a content of S and S-containing compounds in the treated oil is about 53% lower than in the crude oil.

34. A treated oil obtained by the process as defined in any one of claims 1 to 26, wherein: a content of V in the treated oil is about 90% lower than in the crude oil; a content of Ni in the treated oil is about 79% lower than in the crude oil; a content of S and S-containing compounds in the treated oil is about 53% lower than in the crude oil.

35. A system for treating crude oil, which is adapted for conducting the process as defined in any one of claims 1 to 26.

36. An oil treatment facility, comprising the system as defined in claim 35; optionally the facility is an industrial facility.

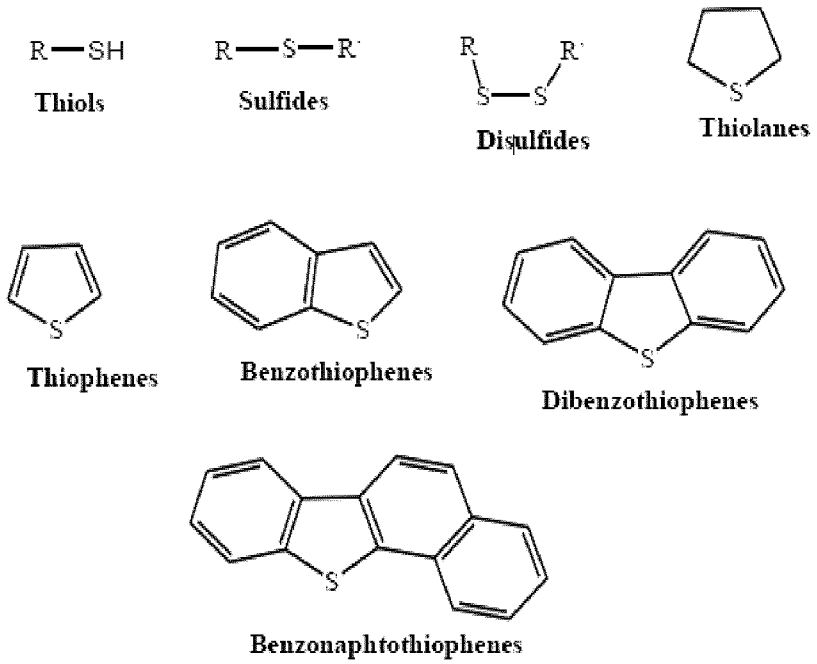


FIGURE 1

(PRIOR ART)

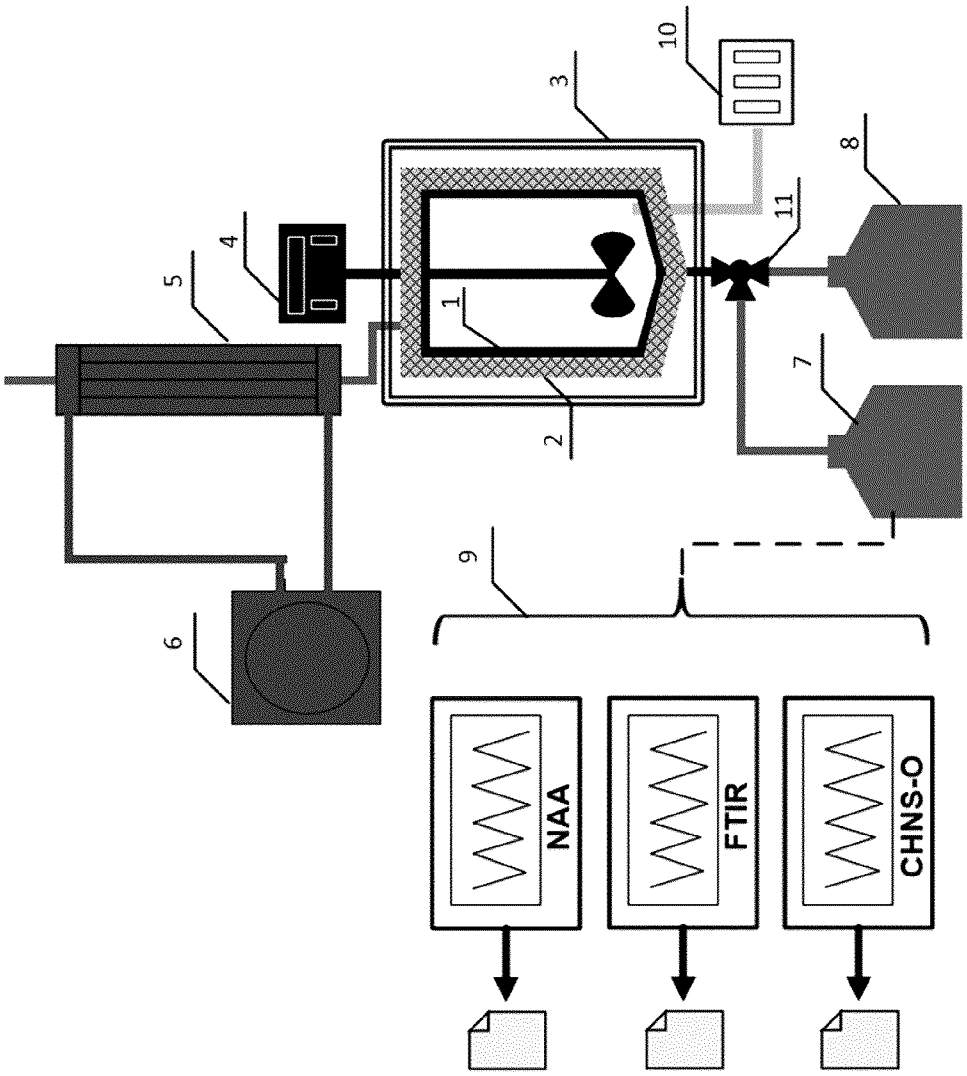


FIGURE 2

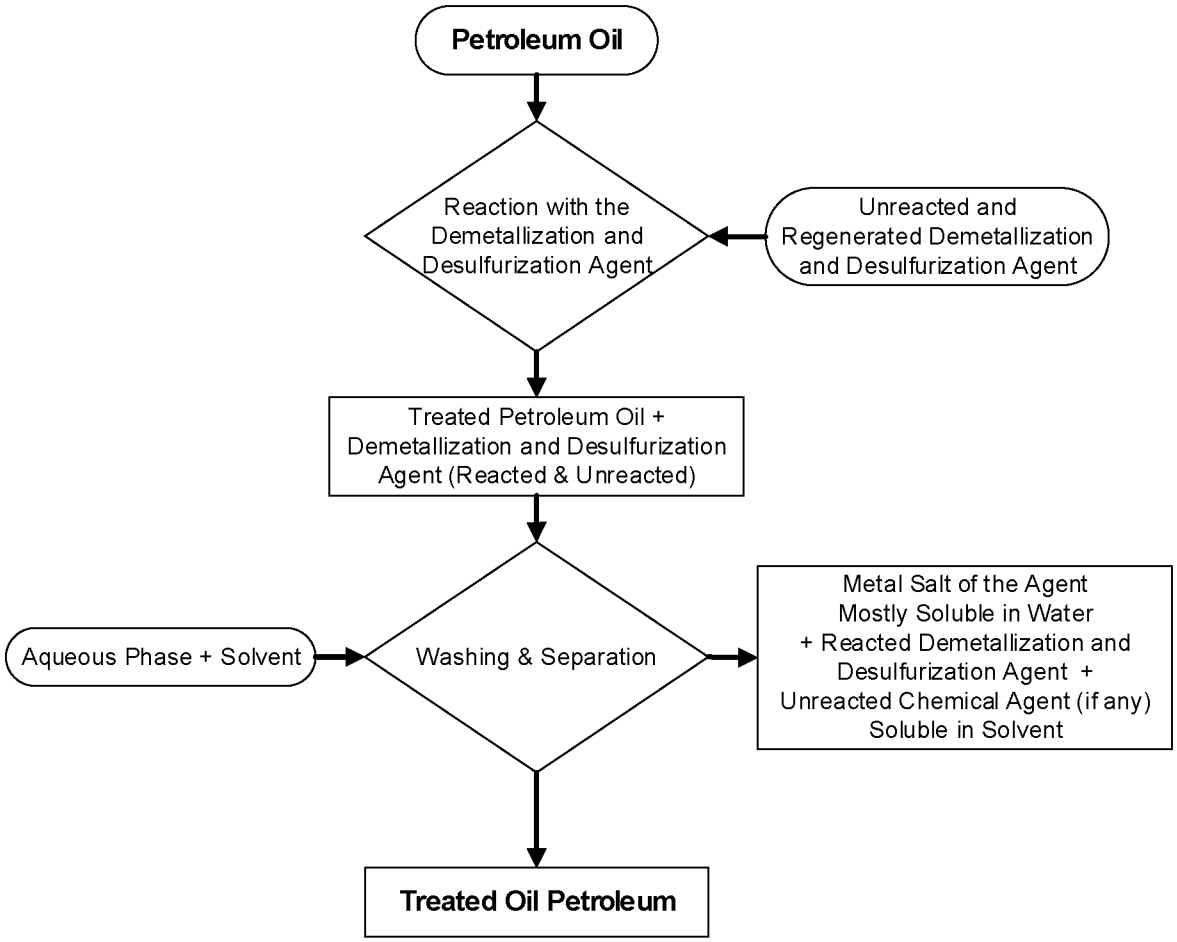

Petroleum Oil
Reaction with the Demetallization and Desulfurization Agent
Unreacted and Regenerated Demetallization and Desulfurization Agent
Treated Petroleum Oil + Demetallization and Desulfurization Agent (Reacted & Unreacted)
Aqueous Phase + Solvent
Washing & Separation
Metal Salt of the Agent Mostly Soluble in Water + Reacted Demetallization and Desulfurization Agent + Unreacted Chemical Agent (if any) Soluble in Solvent
Treated Oil Petroleum

FIGURE 3A

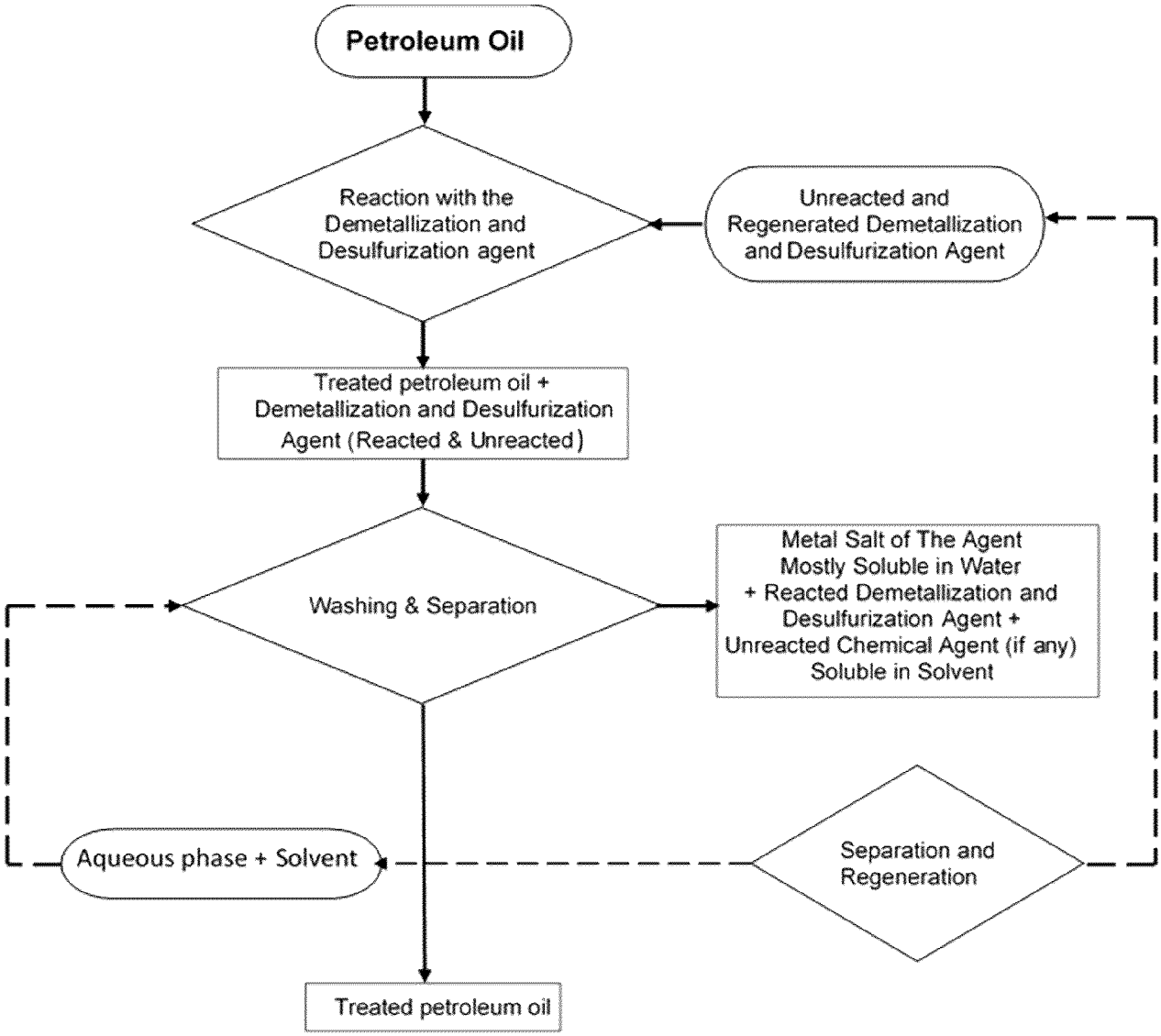

Petroleum Oil
Reaction with the Demetallization and Desulfurization agent
Unreacted and Regenerated Demetallization and Desulfurization Agent
Treated petroleum oil + Demetallization and Desulfurization Agent (Reacted & Unreacted)
Washing & Separation
Metal Salt of The Agent Mostly Soluble in Water + Reacted Demetallization and Desulfurization Agent + Unreacted Chemical Agent (if any) Soluble in Solvent
Aqueous phase + Solvent
Separation and Regeneration
Treated petroleum oil

FIGURE 3B

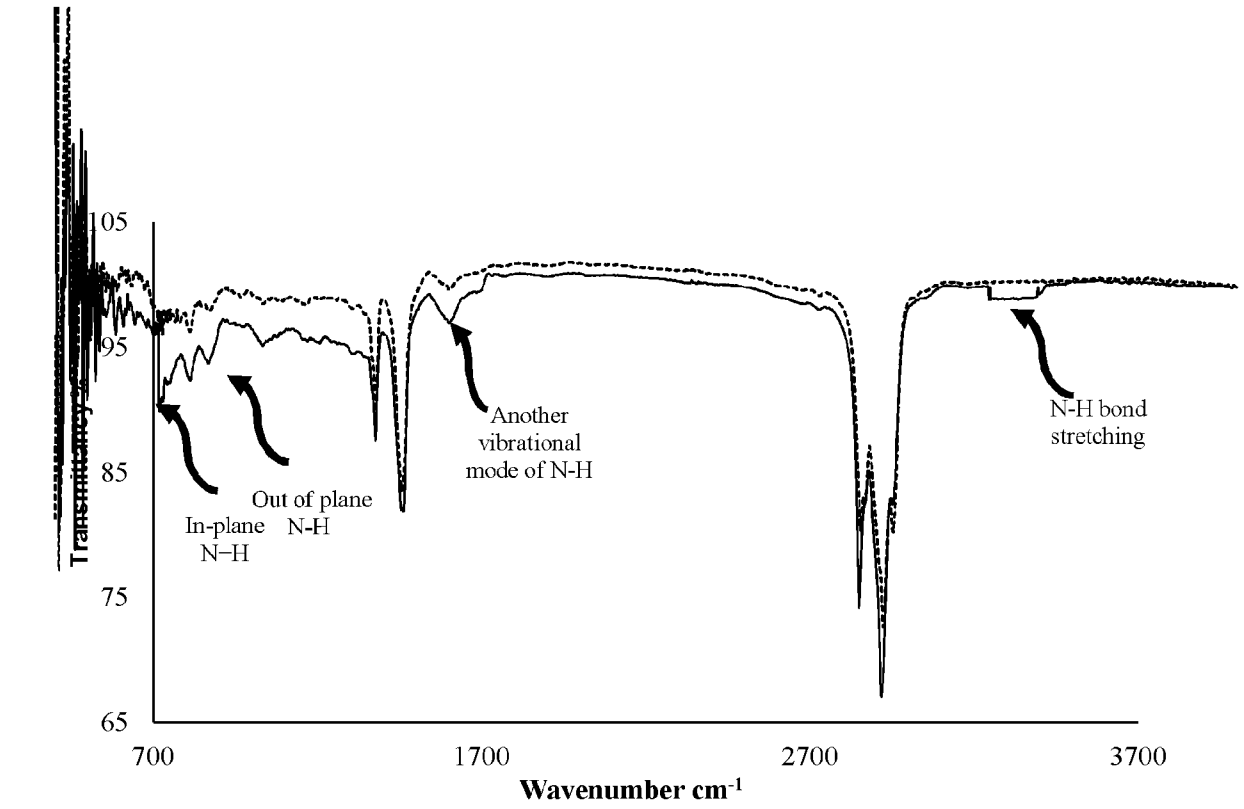


FIGURE 4

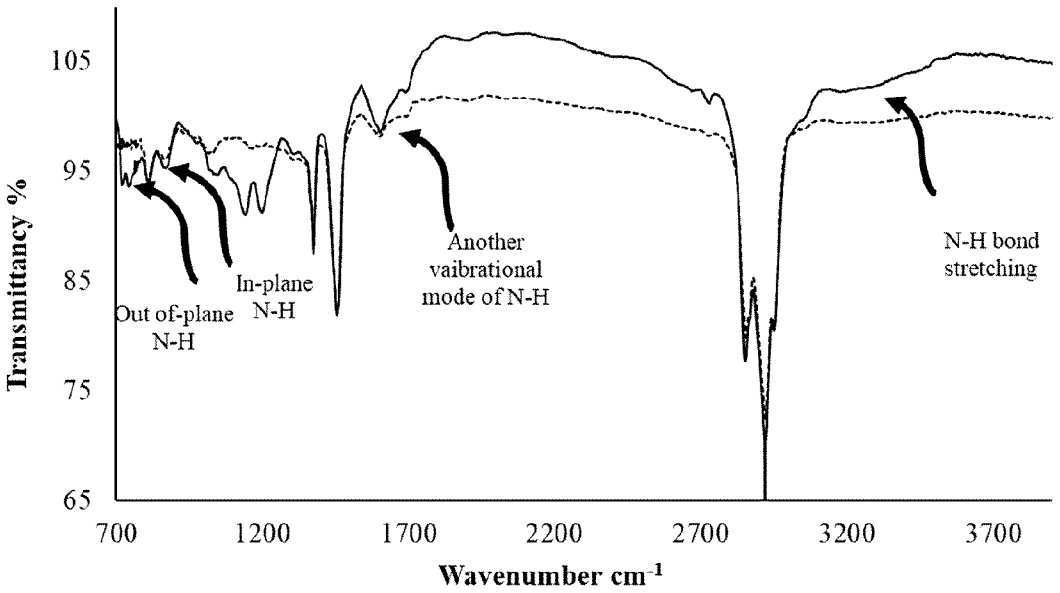


FIGURE 5

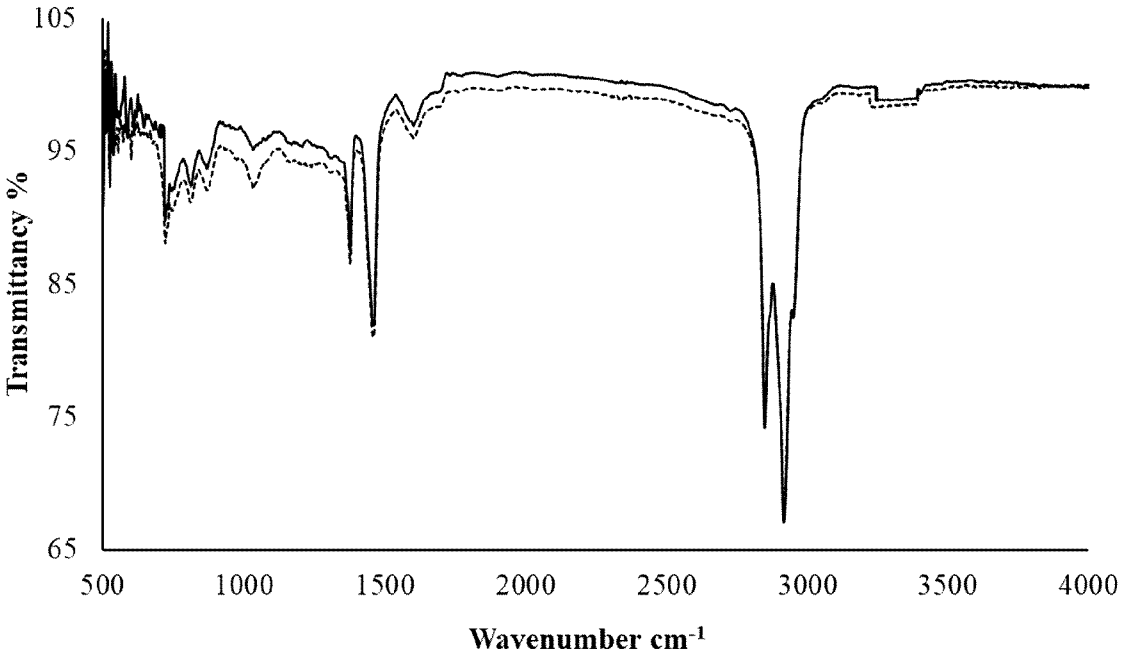


FIGURE 6

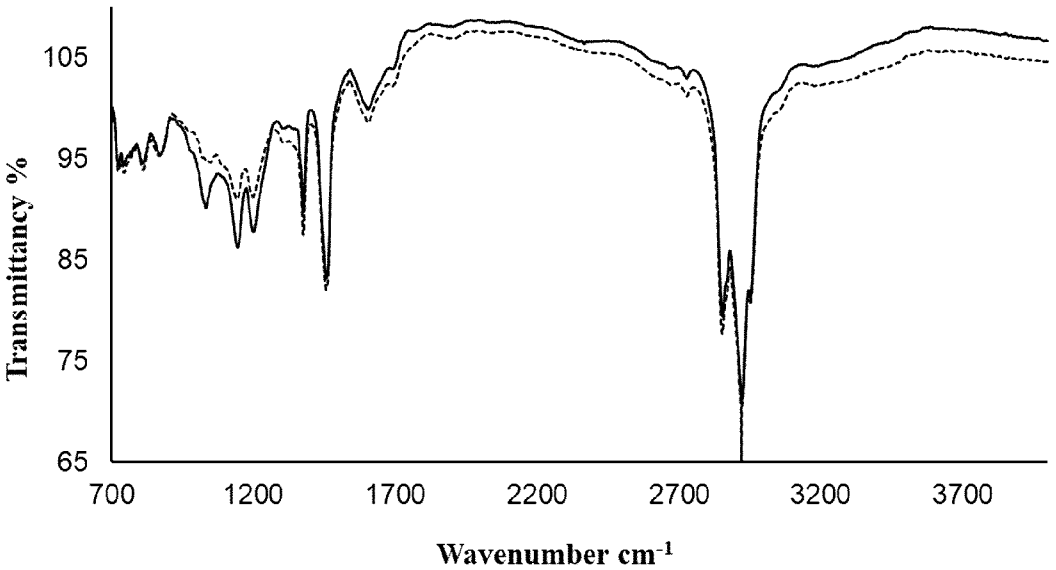


FIGURE 7

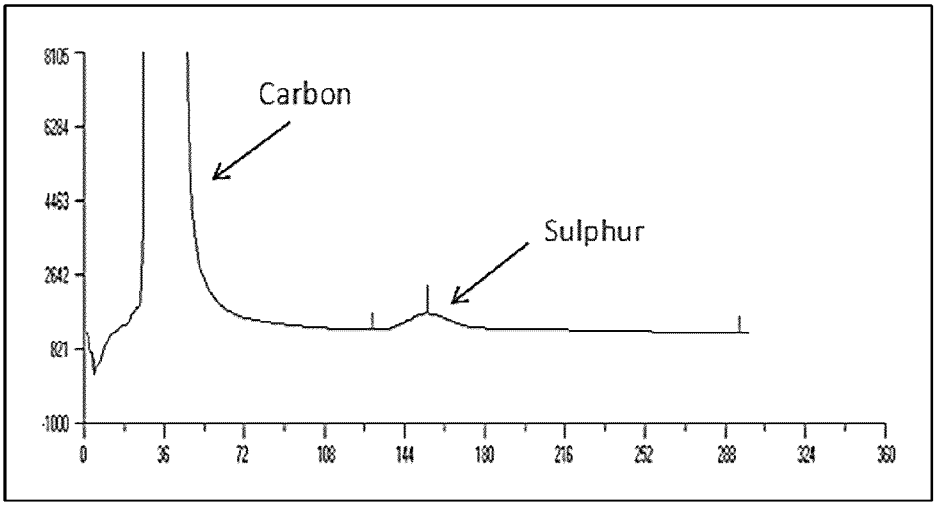


FIGURE 8

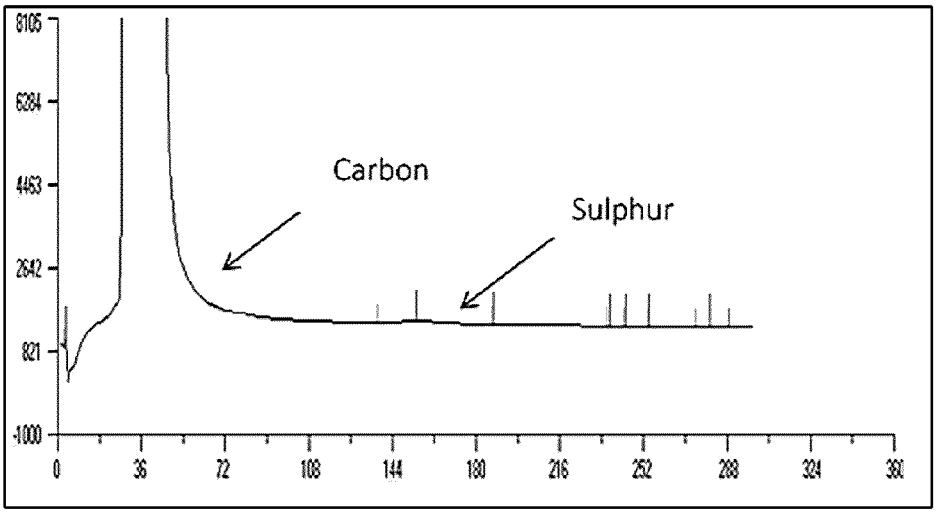


FIGURE 9

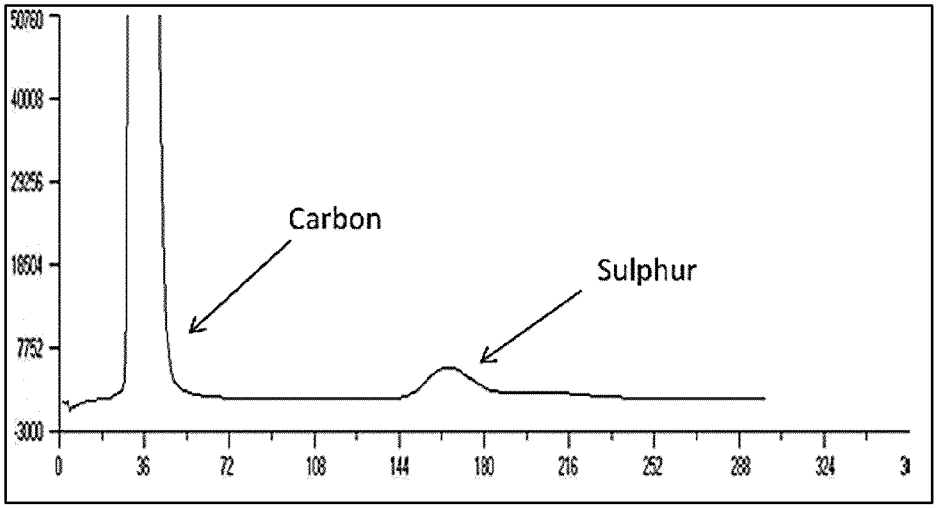


FIGURE 10

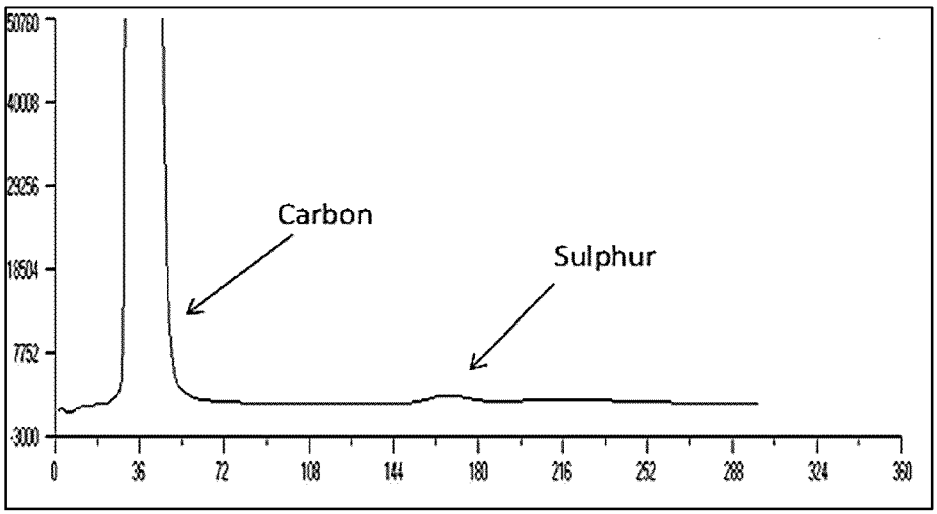


FIGURE 11

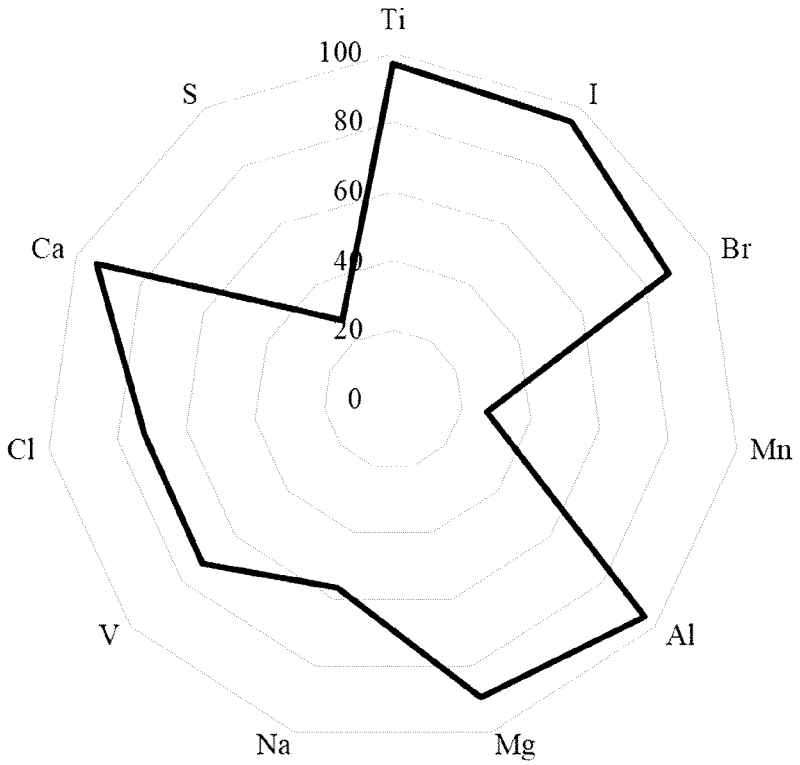


FIGURE 12

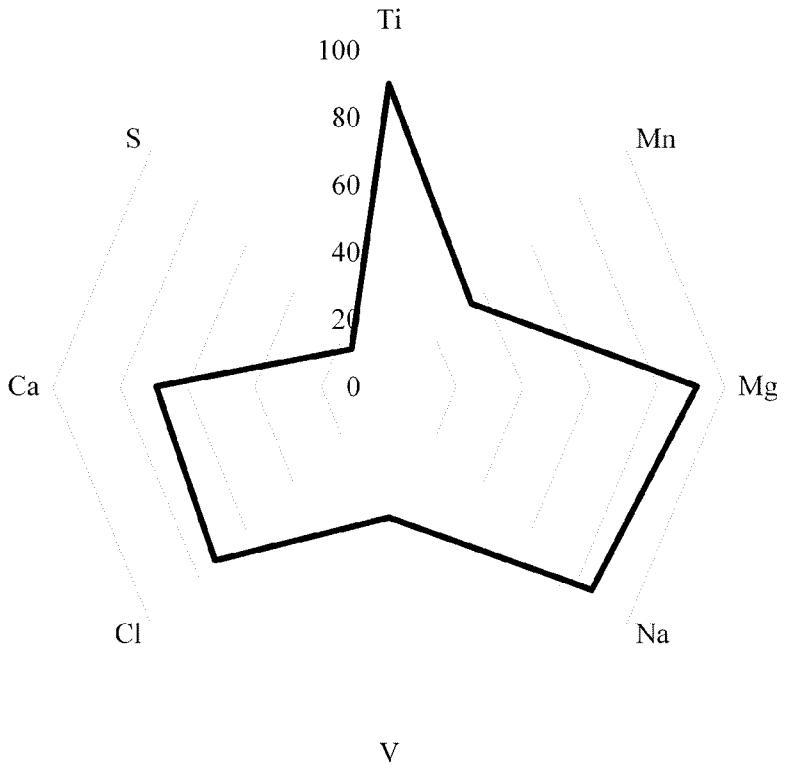


FIGURE 13

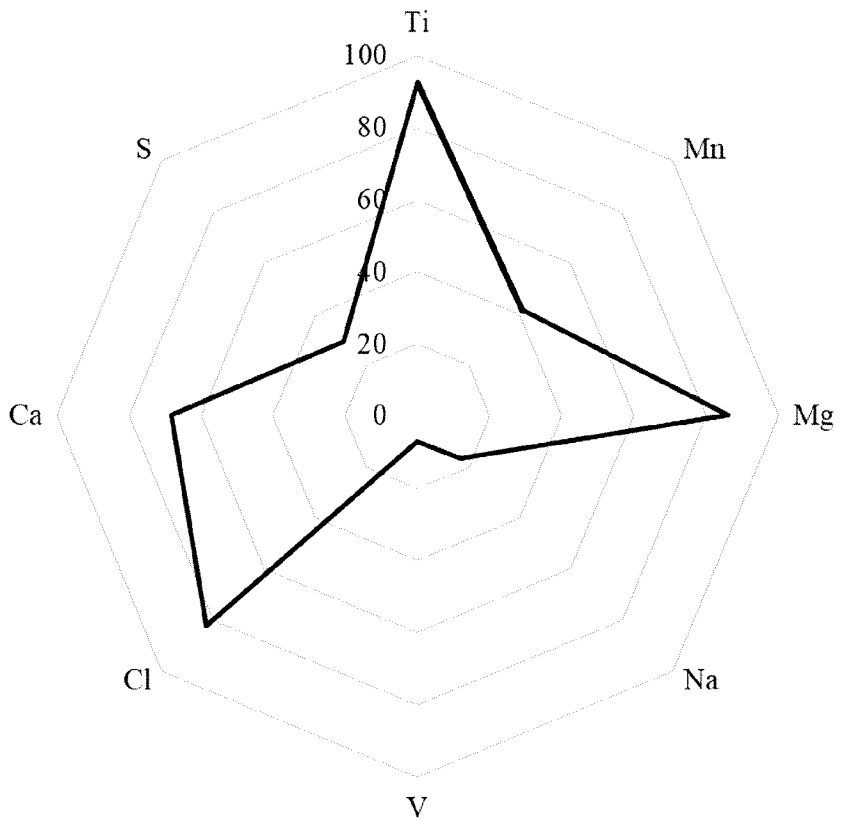


FIGURE 14

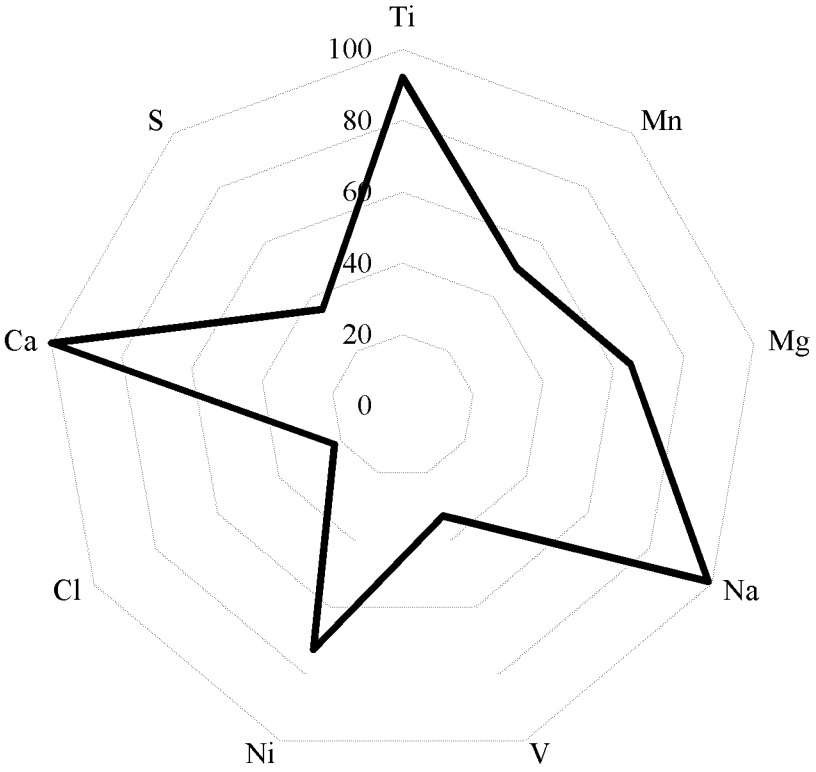


FIGURE 15

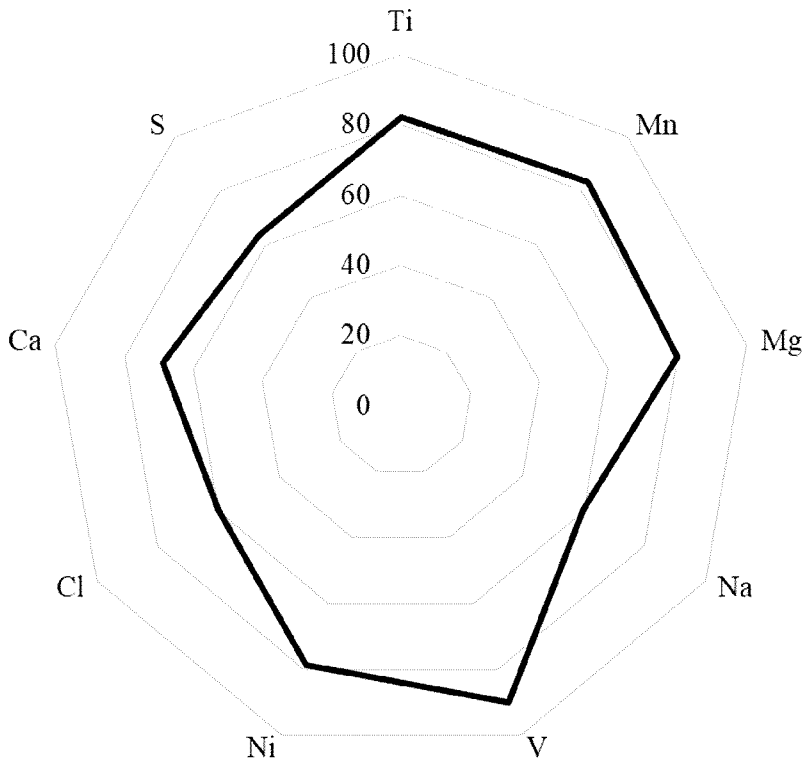


FIGURE 16

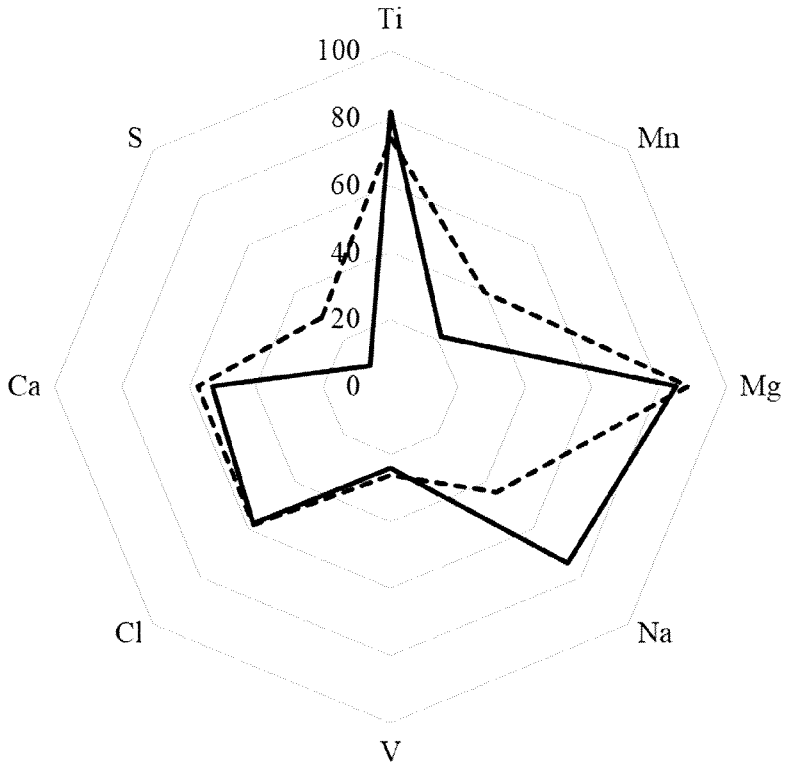


FIGURE 17

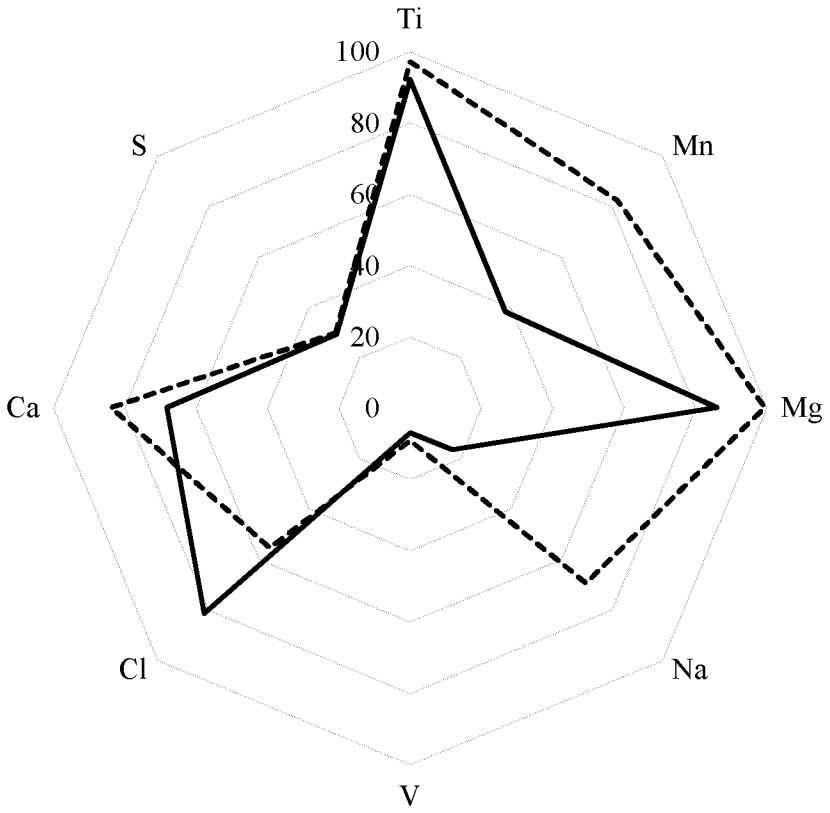


FIGURE 18

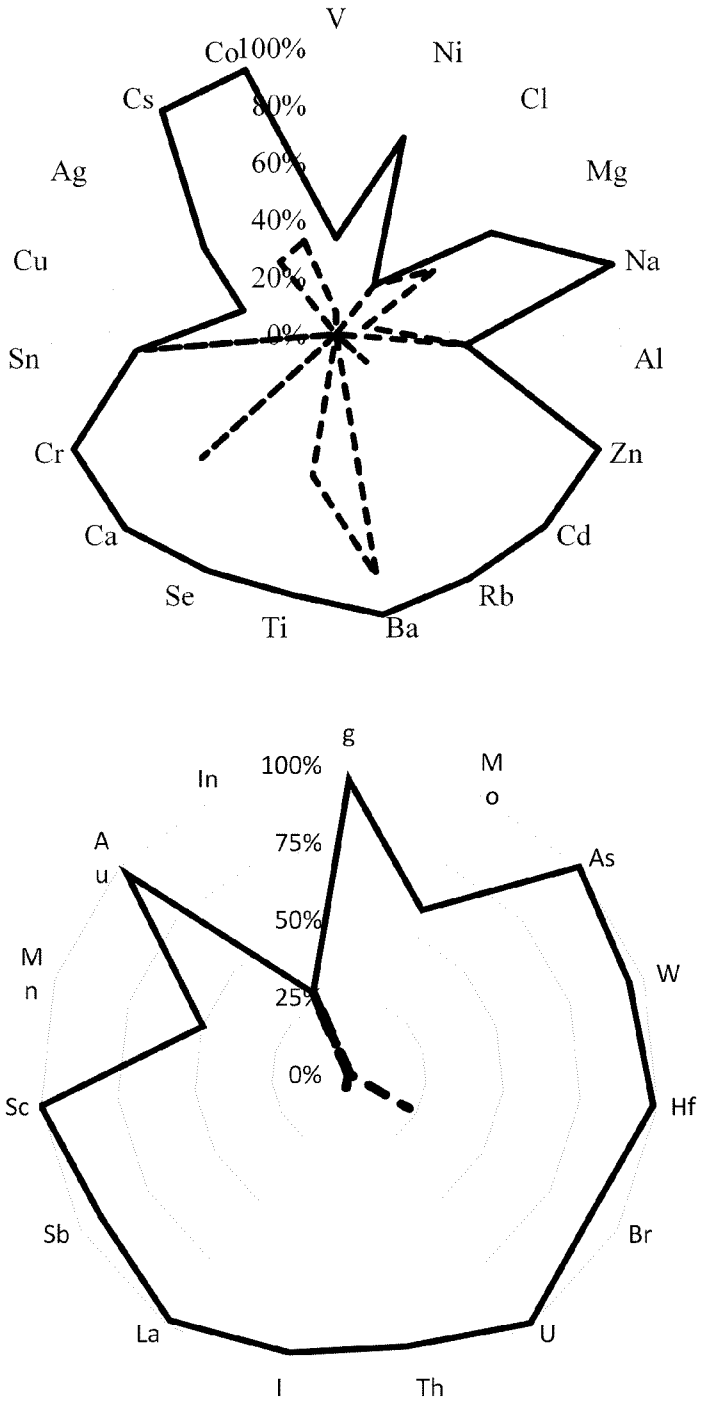

V
Co
Ni
Cs
Cl
Ag
Mg
Cu
Na
Sn
Al
Cr
Zn
Ca
Cd
Se
Rb
Ti
Ba
100%
80%
60%
40%
20%
0%
g
In
Mo
Au
As
Mn
W
Sc
Hf
Sb
Br
La
U
I
Th
100%
75%
50%
25%
0%

FIGURE 19

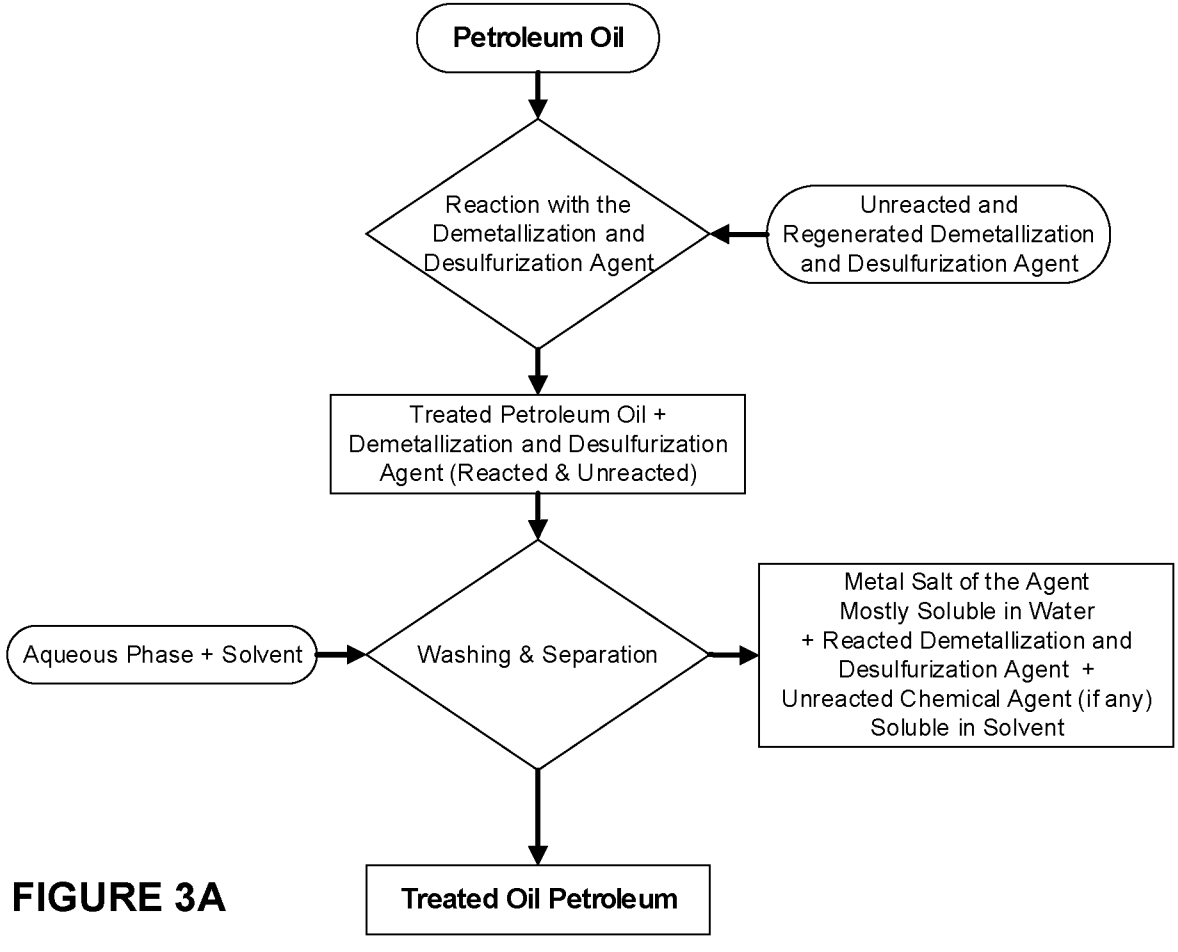

Petroleum Oil
Reaction with the Demetallization and Desulfurization Agent
Unreacted and Regenerated Demetallization and Desulfurization Agent
Treated Petroleum Oil + Demetallization and Desulfurization Agent (Reacted & Unreacted)
Aqueous Phase + Solvent
Washing & Separation
Metal Salt of the Agent Mostly Soluble in Water + Reacted Demetallization and Desulfurization Agent + Unreacted Chemical Agent (if any) Soluble in Solvent
Treated Oil Petroleum

FIGURE 3A