RESEARCH PAPER

Demetallization of crude oil using Oxaline functionalized easily separable paramagnetic rust products

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A B S T R A C T:

The removal of catalyst poisoning compounds from crude oil or heavy oil fractions improves the efficiency of oil refineries and reduces the cost of high temperature corrosion damage during combustion. In this study, the demetallization of crude oil examined using readily separable paramagnetic rust particles functionalized with acidic choline chloride/oxalic acid (Oxaline) deep eutectic solvents (DESs). The functionalized particles were used as absorbent/adsorbents for organic and inorganic metal ions existing in crude oil specifically Ni, V, Mg, Ca, and Na. The functionalized particle samples are characterized using scanning electron microscopy /electron dispersive x-ray (SEM/EDX), x-ray fluorescence (XRF), Fourier transform infrared spectroscopy (FT-IR). The optimum conditions for the removal of metallic constituents in terms of rust particle identity, absorbent/adsorbent dosage, temperature, and the type of employed DESs are studied. Inductively coupled plasma optical emission spectroscopy (ICP-OES) and flame atomic absorption (AAS) and flame atomic emission spectrometry (AES) are used for measuring elemental analysis.

INTRODUCTION:

The demand for clean fuels, depleting supply of conventional oils and insufficient availability of sustainable energy sources have forced refineries to process heavy oil, extra heavy oil, and every heavy fraction as a response to the market demand. Crude oil is a complex mixture of hydrocarbon and non-hydrocarbon compounds. During fractionation processes, most of the non-hydrocarbon compounds concentrate in heavy fractions and more specifically in oil residues.(Al-Attas et al., 2019, Tu and Yen, 2000, Ferreira et al., 2012, Fingas, 2022, M.R. Riazi, 2013) The presence of non-hydrocarbons such as metallic constituents, acids, sulfur and nitrogen-containing compounds can cause a number of demerits such as catalyst deactivation, high temperature corrosion, contamination of petrochemical products and environmental pollution.

(Kurniawan, 2021, Dechaine and Gray, 2010) Every day, without any treatments, the direct combustion of crude oil is almost 9×10^5 barrels over the World for power production. (IEA, 2021) There are many treatment processes employed in oil refineries to reduce the amount of non-hydrocarbon compounds including metallic constituents. Among these treatment methods, the demetallization methods could be classified into non-destructive methods such as adsorption and extraction in which components containing a higher number of metals are separated physically such those practiced in solvent deasphalting process. In the destructive methods, the nature of metallic containing compounds is modified under the influence of heat such as in the coking process, or the use catalyst or chemical aims such as experienced in the catalytic hydrodemetallization. Finally, physical methods such as using radiation and electric fields are used to remove undesirable elements from oils. (Mustafin et al., 2017, Tamer et al., 2019, Dechaine and Gray, 2010) The destructive methods such as hydrocracking or

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hydrotreating are known as costly methods as they need to apply high pressure and temperature.(Yan et al., 2015, Tamer et al., 2019) Therefore, as the cost-effective approaches, scientists are encouraged to develop new methods to treat the crude oil itself, or oil residues to remove undesirable elements. Paper reviews such as (Kurniawan, 2021, Ali and Abbas, 2006, Magomedov et al., 2015, Jenifer et al., 2015, Dechaine and Gray, 2010) have covered most of the works performed for demetallization of oils and oil residues.

Over the last two decades, investigation studies and applications of both ionic liquids (ILs)(Plechkova and Seddon, 2008) and deep eutectic solvents (DESs)(El Achkar et al., 2021, Hansen et al., 2020) are considered as the most growing alternative liquids for conventional solvents. This is because their properties could be controlled via well-chosen couplings between cations and anions and/or hydrogen bond donor/acceptor.(Smith et al., 2014, Plechkova and Seddon, 2008) DESs are mixtures of quaternary ammonium salts (commonly chlorides) and hydrogen bond donors.(Smith et al., 2014) The definition has been expanded to cover more formulations as mixtures of Bronsted or Lewis acids and bases.(Abbott et al., 2021) Among their numerous applications (Smith et al., 2014, Perna et al., 2020, Shishov et al., 2017, Hansen et al., 2020) DESs have been widely used for desulfurization of liquid fuels for example; extractive desulfurization, oxidative desulfurization and absorptive desulfurization.(Tahir et al., 2021) However, to the best of our knowledge, this study could be considered as the first of this kind of works which uses small amounts of DESs covered on the surface of easy removable paramagnetic rust particles.

When any liquid is evaluated to be applied in industry, the use of a high portion of solvent is objectionable if the cost is taken into considerations. (Chauhan and de Klerk, 2020, Attia et al., 2020, Adebiyi and Oyedele, 2022). Thus, compared with ILs, DESs are favorable for numerous applications as they are benign, biodegradable, easy to prepare, and inexpensive as hydrophilic or hydrophobic liquids.(Hansen et al., 2020, Abbott et al., 2021) Therefore, given the sustainability and the cost of many of the methods reported, a method that is more concise will be needed for large-scale applications. In this study,

the demetallization of crude oil is addressed using cost-effective and environmentally friendly method via straightforwardly separable functionalised paramagnetic rust particles coated with a thin layer of DESs used as absorbent/adsorbent for the removal metals in crude oil.

Experimental
Experiments were conducted using a DES prepared from ChCl 1:1 dihydrate oxalic acid 99.5% (Oxaline). The DES was prepared by the method reported in the literature(Abbott et al., 2003, Abbott et al., 2004) using chemicals as received from biochem chemopharma, without any further treatment. Other chemicals such as 37% HCl from SUVCHEM, 69.5% HNO_3 from Scharlau and, and $HClO_4$ 70% from RIEDEL are used for the purpose of digestion process. The Oxaline is coated on the surface of rust particles by mixing Oxaline 2:1 rust particle. 0.1%, 0.25%. 0.5% and 1 % dosages of DESs coated rust particles were mixed with oil samples at different temperature (50°C, 75°C and 100°C) for one hour. Then rust particles have been separated from oil samples using magnetic field. Later, treated oil samples were digested based on the procedure reported in the test method ASTM D5863, and finally, the samples were analyzed for metal content using inductively coupled plasma optical emission spectroscopy (ICP-OES) flame atomic absorption spectrometer (FAAS) and flame emission spectroscopy.

Results
Crude oil characterization
Table 1 shows the results of characterized crude oil from khurmala oil field located in south west Erbil city -Iraq. The table shows that the oil is intermediate in terms of API gravity and sour in nature in terms of sulfur content. Noticeable quantity of metals is observed and this quantity of metals especially Ca, Na, Ni and V can participate significantly in issues such as high temperature corrosion and catalyst deactivation if the oil used in catalytic processes. Therefore, this issue necessitating demetallization process to done for crude oil before direct burn.

Deep eutectic solvent Oxaline
A clear liquid resulted from mixing of choline chloride (ChCl)1:1dihydrate Oxalic acid named (Oxaline) while heating the mixture moderately at temperatures lower than 80˚C. Prepared Oxaline has been characterized in terms of physical

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properties such as viscosity, density, electrical conductivity, acidity, refractive index, flash point, pour point have been determined and the results of these properties are shown in Table 2. If these properties compared with properties of traditional solvents such as polar and non-polar solvents, it is clear that the application window is somewhat different and for some applications could be used much better than traditional liquids. Here, as the liquid coated on the surface of rust particles, it is supposed to react with metallic constituents in crude oil and possibly form metal oxalates.

Absorbent/adsorbent particle characterization

Figure 2 shows SEM image of rust particles before coating with Oxaline, and Tables 3 and 4 shows elemental analysis performed by EDX for rust particles and for pure rust as a reference for the pure iron oxide. Table 5 shows results of elemental analysis collected from XRF for the same rust particles to ensure what is the exact proportions of each metal impurities. The results show that the rust has some impurities, this could be referred to the collection mechanism because the rust particles have been collected from different surfaces and places rather than collecting from the same surface made from pure iron. The presence of these metals means that the particles are products of iron alloys rather than from pure iron. The IR spectrum shown in Figure 2 are for rust particles recorded before and after coating with Oxaline which then used as absorbent/adsorbent for metals in crude oil. The spectrum shows a clear shift of IR absorbance of -OH groups toward longer wave lengths. This is indicating the change in hydrogen bonding strength resulting in the formation of eutectic mixture.(Häkkinen and Abbott, 2021)

Demetallization process

Metallic constituents could be found in different chemical structures, such as organic metal complexes, inorganic salts, metal soaps, and metals attached to asphaltenes.(Fingas, 2022) Organic metal complexes are mostly in the forms of either metal-porphyrins or metal-nonporphyrins, that exist in native crude oil, and mainly concentrates in heavy parts of petroleum. Typically, metal-porphyrins are known as stable metal sources that compromise 5-34% of most crudes, these are complexes of porphyrin ligands with central metals such as nickel (Ni) and vanadium (V). (Tu and Yen, 2000, Fingas, 2022) On the other hand, non-porphyrins metals could be metal complexes of other mixed ligands such

as mixed tetradentate ligands, or ligands which derived from decomposed porphyrin and poly aromatic porphin chelate compounds. The most common inorganic metals found in oil are in the form of water dissolved salt ions such as Mg, Na and Ca.(Tu and Yen, 2000, Fingas, 2022) Among common metals, V and Ni as the most troublesome and abundant metallic constituents are known to cause catalyst poisoning even when their existence is very low. (Fingas, 2022, Tu and Yen, 2000) Additionally, along with sodium they often cause serious corrosion damage in installations using high sulfur content crudes and fuel oils.(S. Abbas et al., 2010) Accordingly, avoiding the issue, is connected directly to the removal of metallic constituents in crude oils or oil residues before their direct use for burning as in power generation installations and in marine fuels. Removal of Ni and V, considered as a one of the real challenges facing refineries due to the detrimental influence on refinery efficiencies as the removal process is rather difficult as they complexed with large molecules.(Chauhan and de Klerk, 2020, Tu and Yen, 2000, Al-Attas et al., 2019, Ferreira et al., 2012)

Table 6 shows the results of metallic analysis for raw crude blend and removal percentage of metals after treating with functionalized rust particles namely A, B, and C having Fe content 95.7%, 89.6% and 88.7% respectively with Oxaline. The results illustrate that, coated brown rust is better than the other two rusts for the removal of all metals. This shows somewhat little reverse relationship between metal removal and iron percentage in rust particles. However, for Mg a clear reverse relationship is exist among three rust particles and Mg removal. This means that the identity of rust does not participate in the removal of V. However, the difference in metal removal could be rationalized by the way of the interaction between Oxaline on the surface of rust particles with V in porphyrin compounds and possibly forming vanadium Oxalate.

Oxaline (one of the type III DES) used in this study is hydrophilic in nature (immiscible with oil), thus it cannot absorb oil soluble metal compounds such as metal-porphyrins or metal-non-porphyrins. However, it can readily absorb inorganic metals such as Na and Ca as the size of Na is relatively small compared with the size of Ca and Mg ions. For removal of organic metals such as Ni and V, it could be envisioned that demetallization efficiency of absorbent/adsorbent

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species depends strongly on the way in which metal ions or metal compounds exist in the oil interacts with Oxaline found on the surface of rust particles. As reported in literature for the desulfurization of fuels by DESs, and solubility power of DESs for metal oxides, the interaction can be related strongly to the formation of hydrogen bonding between active-hydrogen atom found on the HBD from DES and electrons from porphyrin molecules holding Ni and V ions. On the other hand, the interaction could be rationalized strongly for transition metal ions such as Ni and V, by the complexation of metal ions with electron lone pairs exist on chlorine and oxygen atoms of DES employed. (Tahir et al., 2021, Abbott et al., 2006). Thus, the former interaction is only a physical interaction, and the latter is a chemical interaction.

(John G. Reynolds 1989) has reported before that oxalic acid or the salts of the acid can complicate with metal ions in aqueous mediums, nonetheless, they have little or no influence on Petro-porphyrin metal ions. However, when the acid is converted to DES, the nature of acid shown to bet altered toward the removal of metal ions in this study. Thus, Oxaline shows a considerable power for the removal of metallic constituents. The removal mechanism is not clear at this stage of study. Here, the removal percent is pointed out rather than the mechanism by which the metals were interacting with the coat on the surface of rust particles. However, the interaction could be related somewhat to the solubility power of acidic DESs as those found for 17 metal oxides in acidic DESs such as malonic acid (comparable structures with oxalic acid) (Abbott et al., 2006). Based on their study, the formation of some metal ion complexes are responsible for the stabilizing metal ions and hence performing metal removal. (Abbott et al., 2006) The relative low removal percentage of Mg, could be related to the solubility issue. These metal ions are relatively large in size and solubility is rather difficult due to the void size exist in liquids such as Oxaline. This difference in ion size and void sizes makes difficulties in holding such those relatively large ions comparing with smaller ions such as Na. (Abbott, 2004) Considerable removal of Ca could be rationalized by the anion exchange between naphthenic acid anion from the salts of Ca exist in native crude oil(John G. Reynolds 1989) with stronger anion like oxalate from Oxaline.

No.	Test description	Unit	Test Method	Results
	Table 1: Properties of crude oil blend.			
1	Specific Gravity at 15.56 $^{\circ}$C	----	ASTM D1298	0.8596
2	API Gravity at 15.56 $^{\circ}$C	----	ASTM D1298	33.12
3	Density at 20 $^{\circ}$C	gm/cm^3	ASTM D4052	---
4	Total Sulfur	wt %	ASTM D4294	2.3844
5	Pour point	$^{\circ}$C	ASTM D97	Bellow-20
6	Kinematic viscosity at 20 $^{\circ}$C	cSt	ASTM D445	9.53
7	Kinematic viscosity at 40 $^{\circ}$C	cSt	ASTM D445	5.71
8	Water content, Free water	vol%	ASTM D4007	Not detected
9	Sediments	vol%	ASTM D4007	Trace
10	Flash Point, Tag CC	$^{\circ}$C	ASTM D56	+4
11	Salt content	Ptb	ASTM D3230	12.9
12	Reid Vapor pressure at 37.8 $^{\circ}$C	Kpa	ASTM D323	28
13	Copper strip corrosion	----	ASTM D130	2a
14	Calorific value (gross)EST	Kcal/kg	Calculated	10856
15	Vanadium	ppm	ASTM D3605 and	35.70
16	Nickel	ppm	ASTM D3605 and ASTM D5600	17.56
17	Calcium	ppm	ASTM D3605 and	8.001

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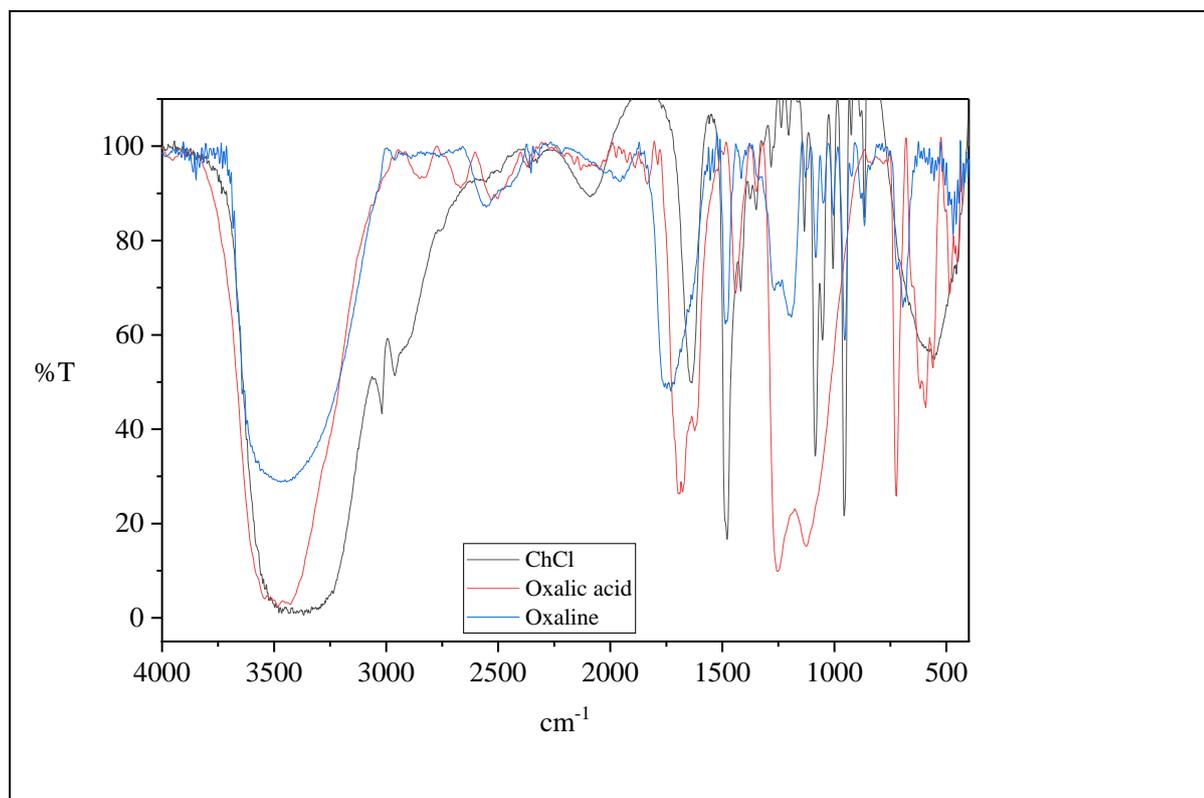| 18 | Sodium | ppm | ASTM D3605 | 4.079 |
| 19 | Magnesium | ppm | ASTM D5600 | 1.59 |

Figure 1: IR spectrum for hydrogen bond donor oxalic acid and hydrogen bond acceptor choline chloride and their corresponding deep eutectic solvent Oxaline.

Table 2: Observed physical properties of Oxaline.

Physical properties	units	Results
Flash point	˚C	112.00
Pour point	˚C	3.00
Density	g/cm^3	1.24
Viscosity at 25 ˚C	mm^2/ s	4.73
Refractive index at 100 ˚C	………….	1.4637
Conductivity at 25˚C	mS/cm	83.20
Surface tension at 25˚C	mNm^{-1}	155
pH	………….	0.00

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Table 3A: Elemental analysis of black rust particles by EDX.					
Element	App Conc.	Intensity Corrn.	Weight%	Weight% Sigma	Atomic%
C K	2.44	0.3330	7.31	0.44	44.72
O K	5.52	0.5392	10.25	0.38	47.06
Al K	0.04	0.7150	0.05	0.03	0.14
Si K	0.49	0.8165	0.60	0.04	1.56
Mn K	0.11	0.7883	0.14	0.07	0.19
Fe K	3.67	0.8044	4.56	0.22	6.00
Zn K	0.06	0.7605	0.08	0.15	0.09
Pb M	0.43	0.6560	0.65	0.14	0.23
Totals			23.64		

Table 3B: Elemental analysis of red rust particles by EDX.					
Element	App Conc.	Intensity Corrn.	Weight%	Weight% Sigma	Atomic%
C K	0.77	0.3116	2.47	0.23	47.97
O K	1.41	0.5503	2.57	0.19	37.41
Al K	0.02	0.6727	0.04	0.02	0.30
Si K	0.03	0.7866	0.03	0.03	0.28
Ca K	0.03	0.9658	0.03	0.03	0.18
Mn K	0.03	0.8228	0.04	0.06	0.18
Fe K	2.66	0.8410	3.17	0.18	13.21
Cu K	0.01	0.7882	0.01	0.10	0.04
Pb M	0.25	0.6653	0.38	0.10	0.43
Totals			8.74		

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Table 3C: Elemental analysis of brown rust particles by EDX.					
Element	App Conc.	Intensity Corrn.	Weight%	Weight% Sigma	Atomic%
C K	1.18	0.3288	3.58	0.33	38.70
O K	3.83	0.6033	6.36	0.28	51.66
Al K	0.06	0.6892	0.08	0.03	0.40
Si K	0.08	0.7949	0.10	0.03	0.45
Ca K	0.05	0.9452	0.05	0.03	0.18
Mn K	0.01	0.8005	0.02	0.06	0.04
Fe K	2.83	0.8176	3.46	0.19	8.05
Zn K	0.09	0.7716	0.12	0.13	0.24
Pb M	0.30	0.6595	0.46	0.12	0.29
Totals			14.23		

Table 4: Elemental analysis of pure rust particles by EDX.								
Element	App Conc.	Intensity Corrn.	Weight %	Weight % Sigma	Atomic %	Compd %	Formula	Number of ions
C K	3.73	0.4930	4.32	0.90	10.51	15.83	CO_2	1.52
Fe K	105.75	0.9221	65.42	1.31	34.23	84.17	FeO	4.96
O			30.25	1.24	55.26			8.00
Totals			100.00					
							Cation sum	6.48

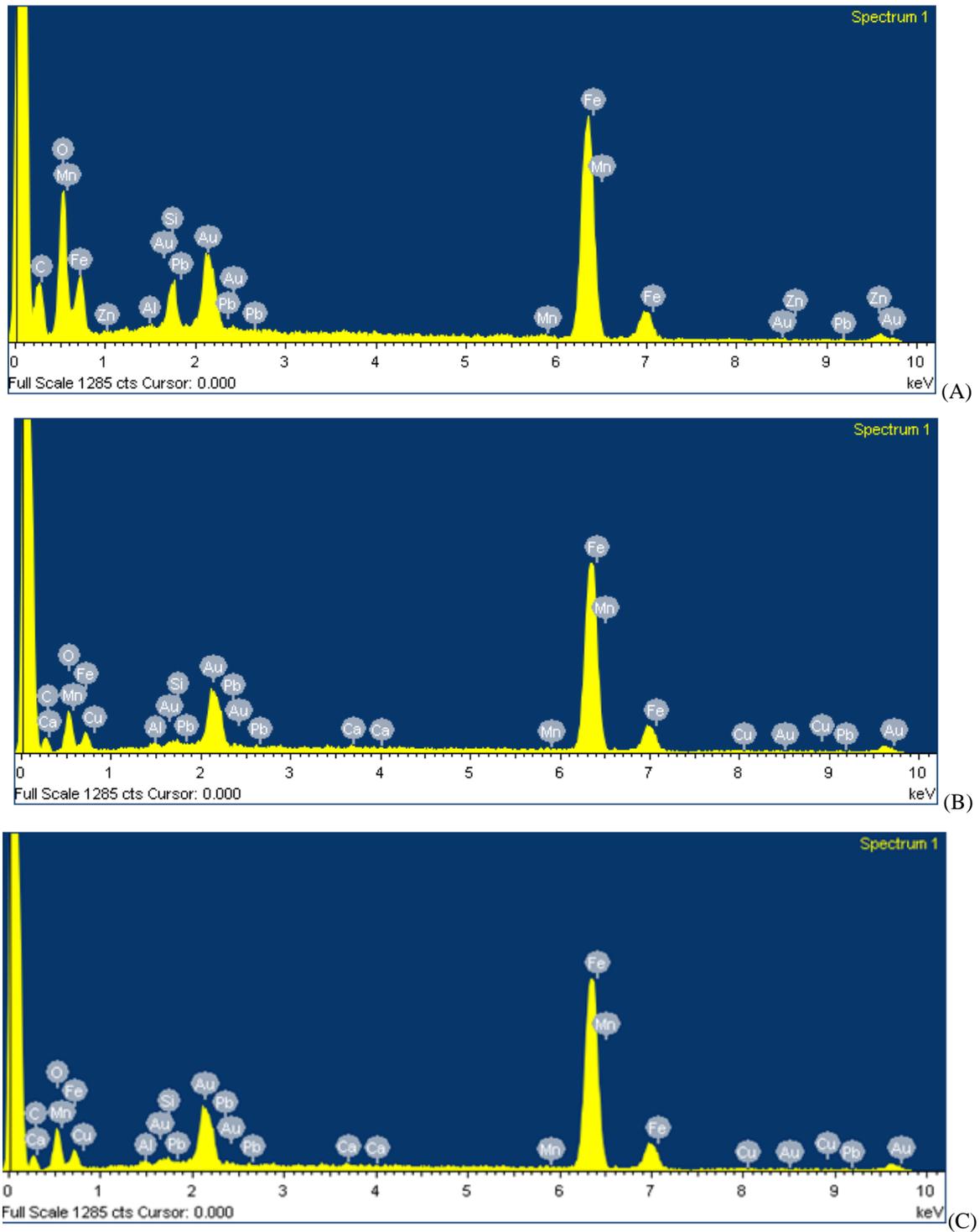| Table 5: Elemental analysis of rust particles by XRF.			
Metal %	Black rust (A)	Red rust (B)	Brown rust (C)
Fe	95.700	89.600	88.700
Cr	0.260	0.210	0.170
Cu	0.093	0.087	0.080
Mn	0.600	0.300	0.600
Co	0.070	0.078	0.080
Pb	0.020	0.013	0.012
Zn	0.005	0.14	0.140

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Figure 2: EDX elemental analysis for rust particles A, B, C respectively.

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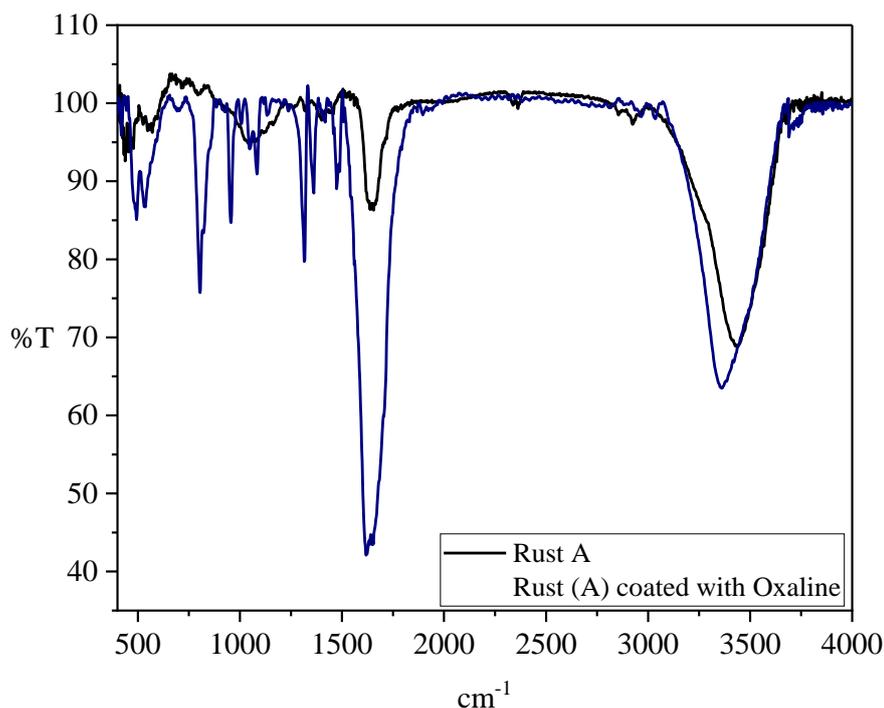
Figure 3: The IR spectrum of rust before and after coating with Oxaline.

Matals	Metallic content (ppm) of raw crude	Metal removal of treated crude oil with different rusts (wt%).		
		Black rust (A)	Red rust (B)	Brown rust (C)
V	35.70	56.94	55.43	69.41
Ni	17.56	84.33	84.33	88.60
Ca	8.001	96.58	95.63	96.71
Na	4.079	92.98	92.98	92.98
Mg	1.59	20.87	31.74	36.90

Table 6: Elemental analysis of raw crude and demetalized crude using Oxaline wetted rust particles.

Conclusions

The demetallization of crude oil samples have been studied using functionalized rust particles with a thin layer of DES Oxaline. Significant demetallization of oil samples have been observed for some metals ions such as Ni, V, Ca, and Na and to less extent Mg. The efficiency of DESs functionalized rust particles as demetallization agent has been evaluated and compared. Results revealed that 84-88 % of Ni and 55-69 % of V, 92.98% of Na, 95-96% of Ca and 20.87-36.90% of Mg could be removed using 0.1% absorbent/adsorbent/crude. The advantages of this processes lie in the easily removable of absorbent/adsorbent coated particle physically using magnetic force and using only small amount of DES. The results show that the functionalized particles were very useful if Oxaline is used, because metal ions could be stabilized by the formation Oxalate salts for transition metals such as Ni and V. Sodium and calcium ions as exist in crude oil in the form of dissolved salt in water removed easily, possibly by the action polarity nature of Oxaline which is compatible with water. The low demetallization activity of some metal ions such as Mg, could be rationalized by the noncomputability of ion sizes and void size exist in Oxaline. The size of voids is strongly related to the strength of intermolecular forces within the liquid.

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Acknowledgment

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