

# Extractive Demetalization of Iraqi Crude Oil by using Zeolite A

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## Abstract

The feasibility of removal vanadium (V) from Iraqi crude oil using zeolite A was investigated. Different operating parameters such as adsorbent loading, vanadium loading, and operating time were studied for their effects on metal removal efficiency. Experimental results of adsorption test show that Langmuir isotherm predicts well the experimental data and the maximum zeolite A uptake of V was 30 mg/g. XRD and EDX analyses revealed the noticeable uptake of zeolite for V. In crude oil, experimental results indicated that for zeolite loading at 1g/100ml oil and within approximately 5 h, the removal efficiencies of V were 60, 45, and 33

**Index terms**— vanadium; crude oil; demetalization; isotherm models.

## 1 Introduction

In crude oil, traces of vanadium (V) are considered the most plentiful metals [1]. Serious problems can be evolved due to this metal through petroleum processing, such as catalyst poisoning which lead to acid rain, corrosion of equipment and low quality of product. It is well-known that metals in crude oils form complexes with asphaltenes [2]. Consequently, severe conditions have been applied for removal metals from crude oil in conventional technologies include; deasphalting, hydrocracking and hydrotreating [3]. Other removal processes are adsorption, acid attack, and solvent extraction [4][5][6]. Therefore efficient and effective-cost process is required to decrease the concentration of these metals before any subsequent processes. Zeolites have been utilized in many industrial implementations such as water softening, heterogeneous catalysis, separation, environmental remediation because zeolites possessing large surface area, remarkable catalytic and ionic exchange properties [7][8] and then it could be employed for the removal of these metal ions from crude oil. Zeolites are The positive ion uptake capacity of a zeolite is a consequence of the degree of exchange of Al for Si in the structure. Author concluded that the more the substitution of Al for Si, the higher the number of positive ions wanted to preserve electronic neutrality in the zeolites. Price et al. [14] conducted experimental study to investigate the adjustments in framework occurred after partly substituting the extra-framework Na<sup>+</sup> ions with monovalent, Li<sup>+</sup>, K<sup>+</sup>, Rb<sup>+</sup> and NH<sub>4</sub><sup>+</sup> and divalent, Ca<sup>2+</sup> cations. Authors concluded that solid state Nuclear Magnetic Resonance detected alterations to the internal structure of the Linde Type A framework upon ion substitute with NH<sub>4</sub><sup>+</sup> and Ca<sup>2+</sup>. Substitution with Li<sup>+</sup>, K<sup>+</sup> and Rb<sup>+</sup> ions does not considerably influence the long-range crystal order. Substitution with NH<sub>4</sub><sup>+</sup> ions compensates some of the long-range order of the zeolite A crystals because of the wastage of some structure Al as can be observed from X-ray data. Substitution with divalent Ca<sup>2+</sup> ions inserts some monodentate carbonate kinds into the structure, but no change to the long-range crystal order is noticed. Published data on the usage of zeolites for the elimination of metal ions from crude oil are scarce. In Iraq crude oil of east Baghdad field contains higher amounts of vanadium (> 75 ppm) than other heavy metals [15]. The main objective of present work was to investigate the feasibility of Zeolite type A to remove vanadium ions from crude oil. Another objective was to study the kinetics of adsorption process. Naturally occurring crystalline aluminosilicate minerals which are synthesized of 3-dimensional structures of tetrahedral molecules connected with the O<sup>2-</sup> participated atoms [9]. Zeolites are assured ion exchangers and have been effectively utilized in the elimination of heavy metals from wastewaters, and as catalyst for the catalytic cracking of heavy oils [10][11]. Ikyereve et al. [12] investigated the eclectic sharing of the natural zeolites in the elimination of these toxic metals

## 5 B) INFLUENCE OF METAL ADSORPTION ON ZEOLITE CHARACTERISTICS

from crude oil. Ikyereve [13] reported that the ion substitution reaction between positive ion A S Za , at first in solution and B Z Zb , at first in a zeolite is shown as follows:

(1) XRD-6000 Shimadzu (X-ray diffractometer with incident angle of 0.154nm using Cu-K $\alpha$  radiation) was used to examine the phase ingredients. The topographical features were accomplished by utilizing Tescan VEGA 3SB scanning electron microscope with accelerating voltage: 200V to 30kV and the magnification power from 4X to 10 5 X. The chemical composition of zeolite A was anatomized by utilizing energy dispersive X-ray analysis (EDX) Model; Inspect S50/FEI Company, Netherland. The concentration of vanadium in fluid before and after treatment was measured using atomic absorption type (AA-7000, Shimadzu, Japan) at the Petroleum Research and Development Center, Ministry of Oil, Baghdad/Iraq.

### 2 III.

## 3 Results and Discussion

### 4 a) Kinetic study of adsorption

The maximum adsorption capacity of zeolite A was estimated by conducting adsorption experiments. Different concentrations (5,10,20, 30, and 50 mg/L) of an aqueous solution of VCl<sub>4</sub> in distilled water was prepared. Then 100ml of each concentration is placed in a 250ml flask separately with 1g of zeolite A. The amount of vanadium adsorbed at equilibrium, (mg/g) was estimated using Eq. 1.  $q_e = (C_o - C_e) \cdot V / W$

Where  $C_o$  and  $C_e$  : concentrations of vanadium at initial and at equilibrium (mg/ L), respectively, V: volume of the heavy oil used, and W: mass of zeolite A used (gm). The Freundlich and Langmuir equations are the most widely used models for isotherm [16], the correlation of Freundlich and Langmuir isotherms are represented by Eqns. 2 and 3, respectively.  $q_e = K_F \cdot C_e^{1/n}$  and  $q_e = K_L / (1 + K_L \cdot C_e)$

Where  $q_m$  : maxima quantity of metal V adsorbed per unit mass of zeolite (mg gm<sup>-1</sup>),  $q_e$  : concentration of V at equilibrium (mg L<sup>-1</sup>).  $K_L$  is the Langmuir constant (L mg<sup>-1</sup>) and  $K_F$  is Freundlich constant (mg gm<sup>-1</sup>) (L mg<sup>-1</sup>)<sup>-n</sup>. Figure ?? plots the experimental results of vanadium and nickel adsorption at equilibrium on zeolite A sample respectively. To predict which one of these two models will well represent the experimental data of metal (V) removal, a linearization technique would be applied on equations 2 and 3, respectively. Equations 4 and 5 represent the linearized form for equations 2 and 3 respectively. This outcome depicts that the maximum uptake of V metal was 30mg g<sup>-1</sup>, this may be attributed to the capability of the usable zeolite structural frame with high percentage of pore volume.  $1/q_e = 1/q_m + 1/(K_F \cdot q_m) \cdot C_e$  (4)  $1/q_e = 1/q_m + 1/(K_L \cdot q_m) \cdot \ln C_e$  (5)

### 5 b) Influence of metal adsorption on zeolite characteristics

i. XRD analysis Figure ?? shows XRD images of zeolite A before and after vanadium adsorption. According to [17], the XRD pattern (Fig. ??a) for the zeolite shows excellent match with typical zeolite A while the XRD image of the vanadium-zeolite (see Fig. ??b) shows a breakdown of structure which indicates an effective exchanger (zeolite A). This collapsing in peaks may be attributed to the replacement of Si ions by larger vanadium ions which could induce an extension in the unit cell. This attitude is compatible with the existence of vanadium in the structure of zeolite which caused by the difference between V-O and Si-O ligament tallness [18]. Gallezot and Leclerc [19] found that vanadium promotes the (1) (2) (3) b) Experimental method

The experimental setup is shown in Figure ?? . Zeolite A particles was grounded. Figure ?? shows the Zeolite A particles before and after grounding. 1 gram of the sieved zeolite A was added into 100 mL of the crude oil in a separating flask with 5mL of EDTA. This mixture was well mixed by a magnetic stirrer at 100 rpm for an hour at room temperature (~25°C). Zeolite A was separated from the mixture in a vacuum separator (Rocker 300A Vacuum Filtration System, New Star Environmental & Laboratory Products). The liquid mixture was then transferred to a high speed centrifuge (Type Centrisart @ D-16C, Sartorius Co.) where the demetalized crude oil (DMCO) layer was separated and analyzed for the metal ions. ii. EDX analysis EDX analysis of the zeolites was carried out, before and after vanadium uptake, to estimate the percentage weight of elements existed. Moreover, the proportion of Si/Al in the zeolites can be determined. Table 2 presents the percentage weight of elements as measured by the SEM-EDX (XRD-6000 Shimadzu) and the proportion of Si/Al in the zeolites. Figure ??(a-b) shows EDX images of zeolite A before and after vanadium uptake. As be seen from images, that all Na, and some of Al and Si are ion exchanged with vanadium on the zeolite surface. The percentage weight of elements displays that the whole Na + inside the zeolite were substituted and furthermore, about 76% of ions of silicon which formed the structure were also replaced the ions of vanadium while only 26% of Al ions were exchanged. (Gomes et al., [20] stated that ion radius plays an important effect on the ionic exchange. Shannon [21] published a revised crystallographic data on ionic radii. He estimated the ionic radii of Na<sup>+</sup>, Al<sup>3+</sup>, Si<sup>4+</sup>, and V<sup>4+</sup> as equal to 116, 67.5, 54, and 72 picometer, respectively (1 Angstroms = 100 picometer). These values suggest that vanadium ions could exchange any ions of equal or larger of its size which clearly explains the drastic effect of Na and Si ions exchanged and breakdown of zeolite structure noticed after vanadium ion exchange.

## 6 c) Removal of vanadium from crude oil

A series of experiments was conducted to test the capability of Zeolite to remove Vanadium ions from crude oil. Figure ?? illustrates vanadium removal efficiency as a function of operating time at different loading of vanadium. As can be seen in Figure ??, a remarkable increase in vanadium removal within a short time was observed for all loadings of vanadium after then a slight increase with operating time was shown. Within approximately 5 h, the vanadium removal efficiencies were 33, 45, and 60% at vanadium loadings of 10, 30, and 40 ppm respectively. Further processing of crude oil with 10 ppm vanadium shows a continuous slight increase in metal removal with operating time. At 10, 20, 40, and 50 h the removal efficiency was 68, 75, 78 and 78%. As can be seen, an equilibrium concentration of the vanadium was attained after 40 h. For other vanadium loading (i.e., 30 and 40 ppm), the equilibrium concentration of vanadium was attained at approximately 20 h. Salman et al. [22] reported that the differences in zeolite adsorption capacities for heavy metal ions can be attributed to different factors i.e. physicochemical factors, hydration energy, and diameter. In general zeolites and ion exchanges prefer high valent ions [23]. Thus high selectivity of zeolite for vanadium was due to electrostatic attraction between high valent vanadium cations and cations of solid adsorbent. Fig. 8 plots the effect of zeolite loading (g/100ml oil) on vanadium removal (%). As can be seen in this Figure, zeolite loading has a positive impact on removal efficiency. The increase in vanadium removal with the zeolite A loading is due to the higher number of active sites available over the adsorbent [24]. It is interesting notice that at higher loading of zeolite a constant value of vanadium removal was attained. This may be attributed to that equilibrium is established between the adsorbed ions of vanadium onto zeolite and that which still existed into the treated crude oil.

## 7 IV.

## 8 Conclusion

In present work different operating parameters such as vanadium loading, zeolite type A loading, and operating time were investigated for their effects on vanadium removal efficiency from crude oil. Results revealed that zeolite loading and operating time have positive impact on removal efficiency while vanadium loading showed different trend. Experimental results of adsorption test show that Langmuir isotherm predicts well the experimental data. RDX and EDX analyses confirm the high tendency of zeolite A to remove vanadium ions from crude oil. Long term tests revealed the high stability of zeolite A for vanadium removal.

## 9 Acknowledgements

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## 10 Nomenclature C o :

Concentrations of vanadium at initial, (mg/ L) C e : Concentrations of vanadium at equilibrium, (mg/ L) V: Volume of the heavy oil used, (ml) W: Mass of zeolite A used, (gm) q m : Maxima quantity of metal V adsorbed per unit mass of zeolite, (mg/ gm) q e : Concentricity of V at equilibrium, (mg/ L) K L : Langmuir constant, (L/ mg) K F : Freundlich constant (mg/ gm) (L/ mg) -n Year 2019 <sup>1</sup>



Figure 1:

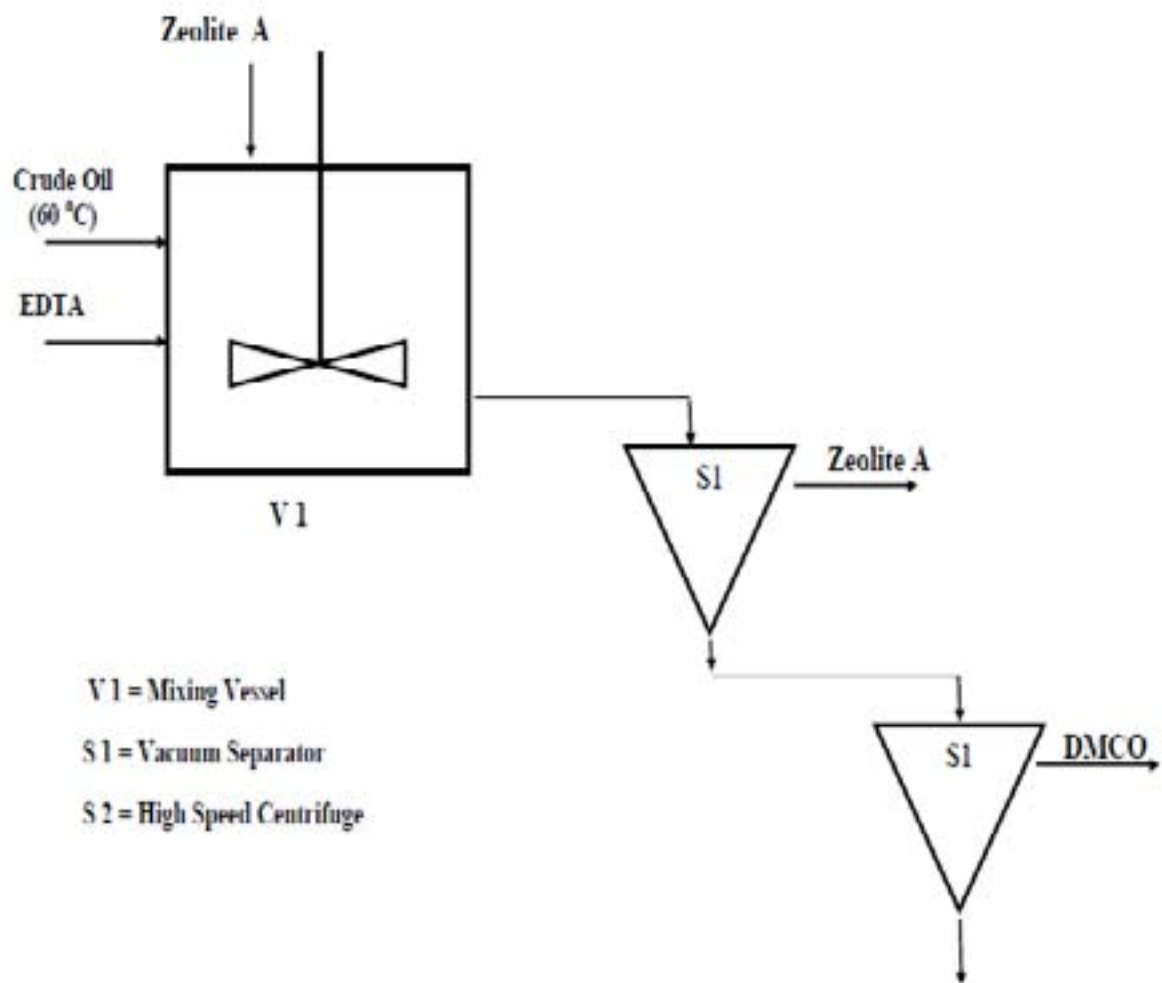


Figure 2: Figure

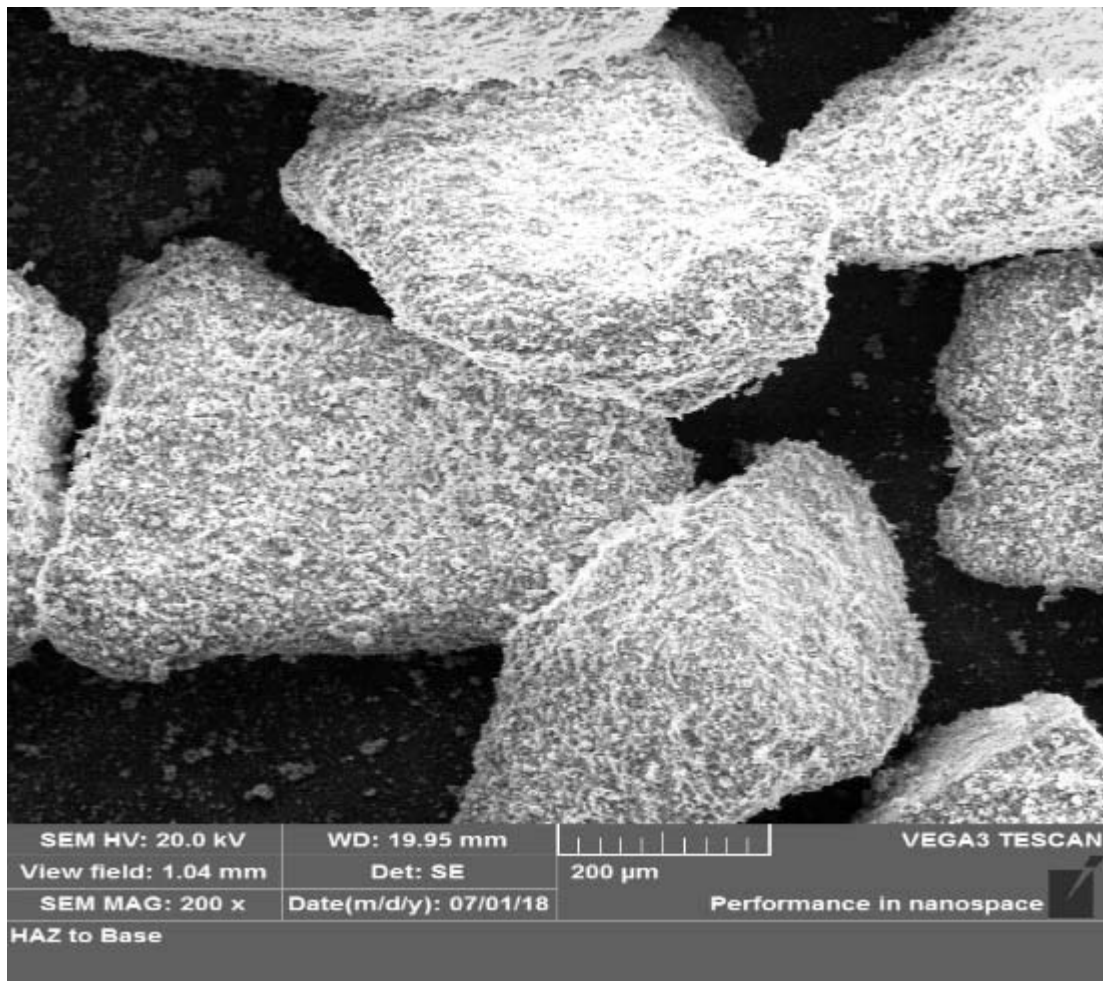
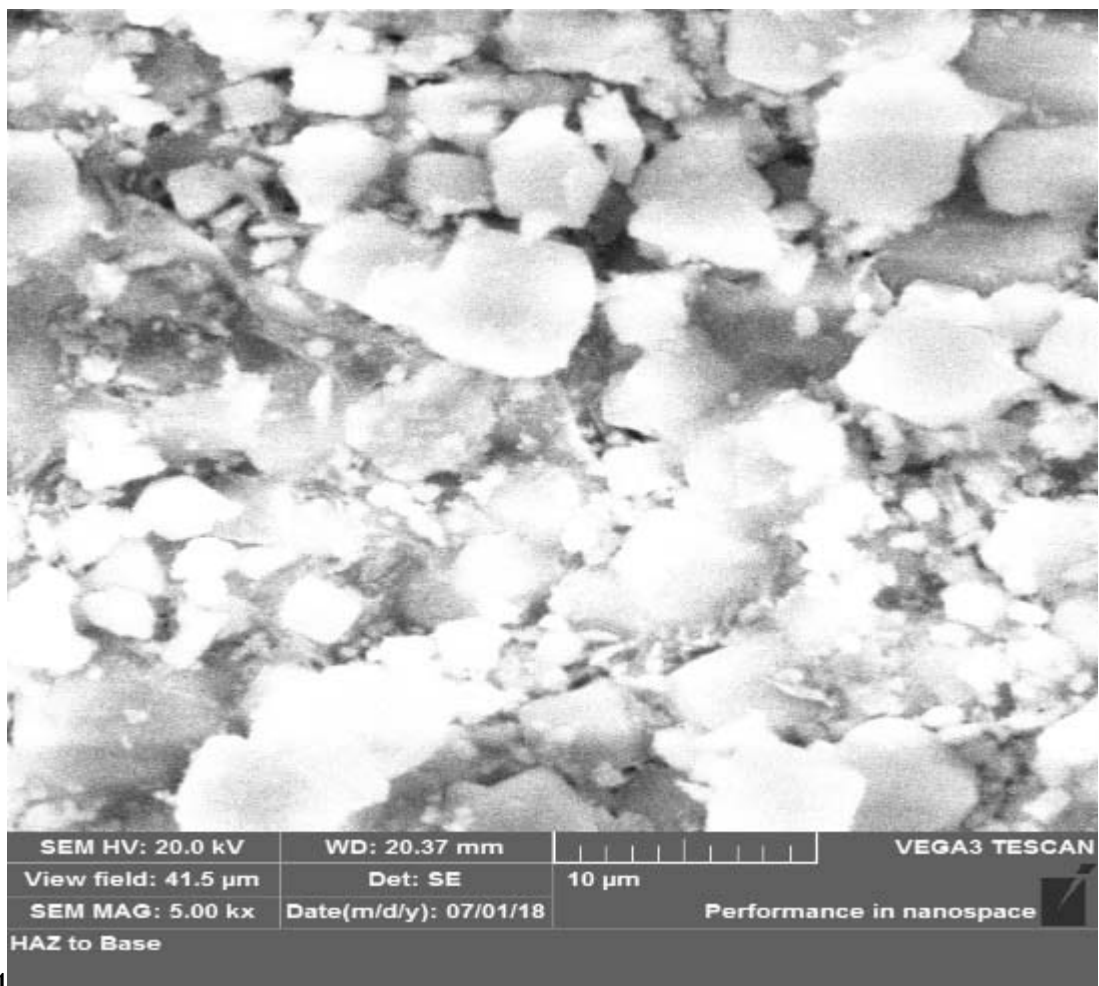
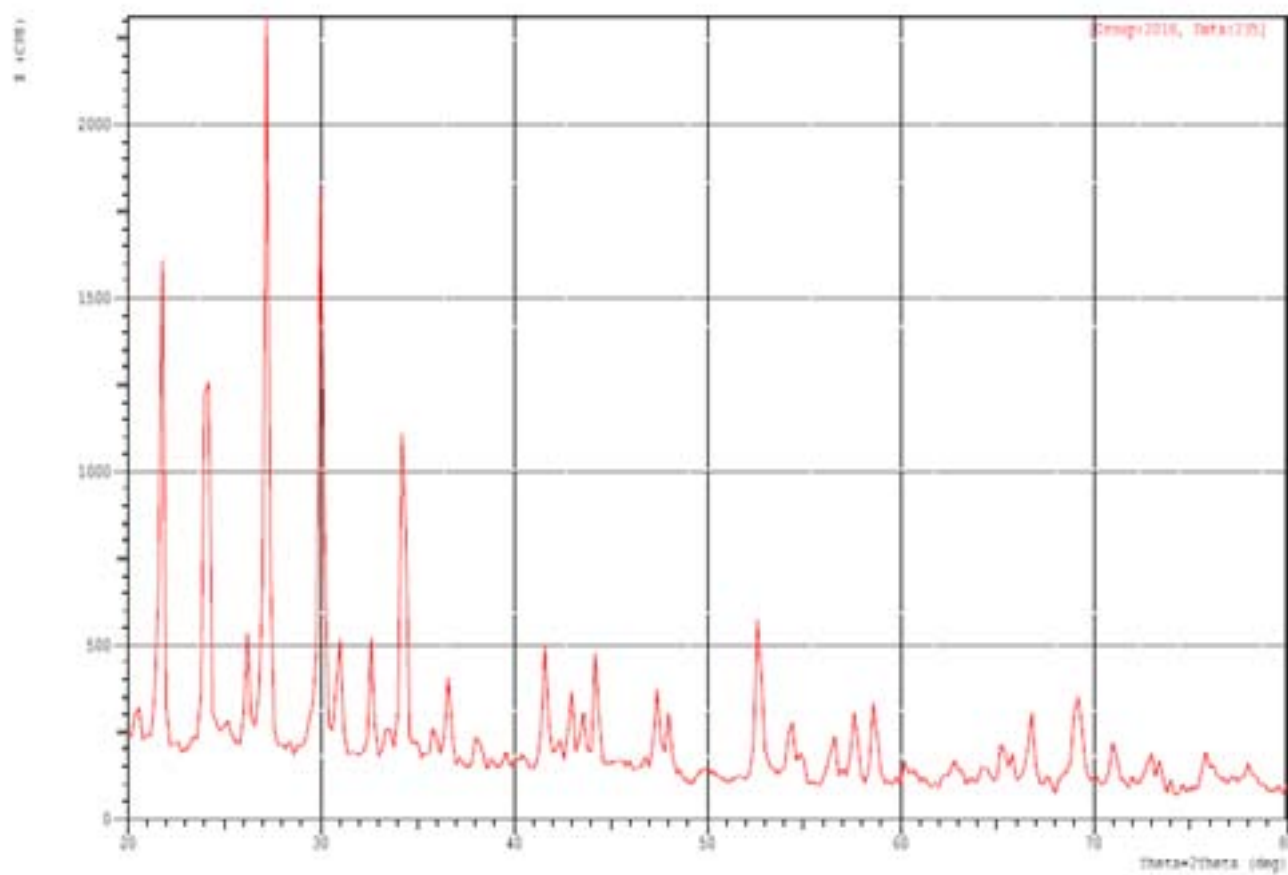


Figure 3:



24

Figure 4: Fig. 2 :Fig. 4 :



5a37

Figure 5: Fig. 5a :Fig. 3 :Fig. 7 :

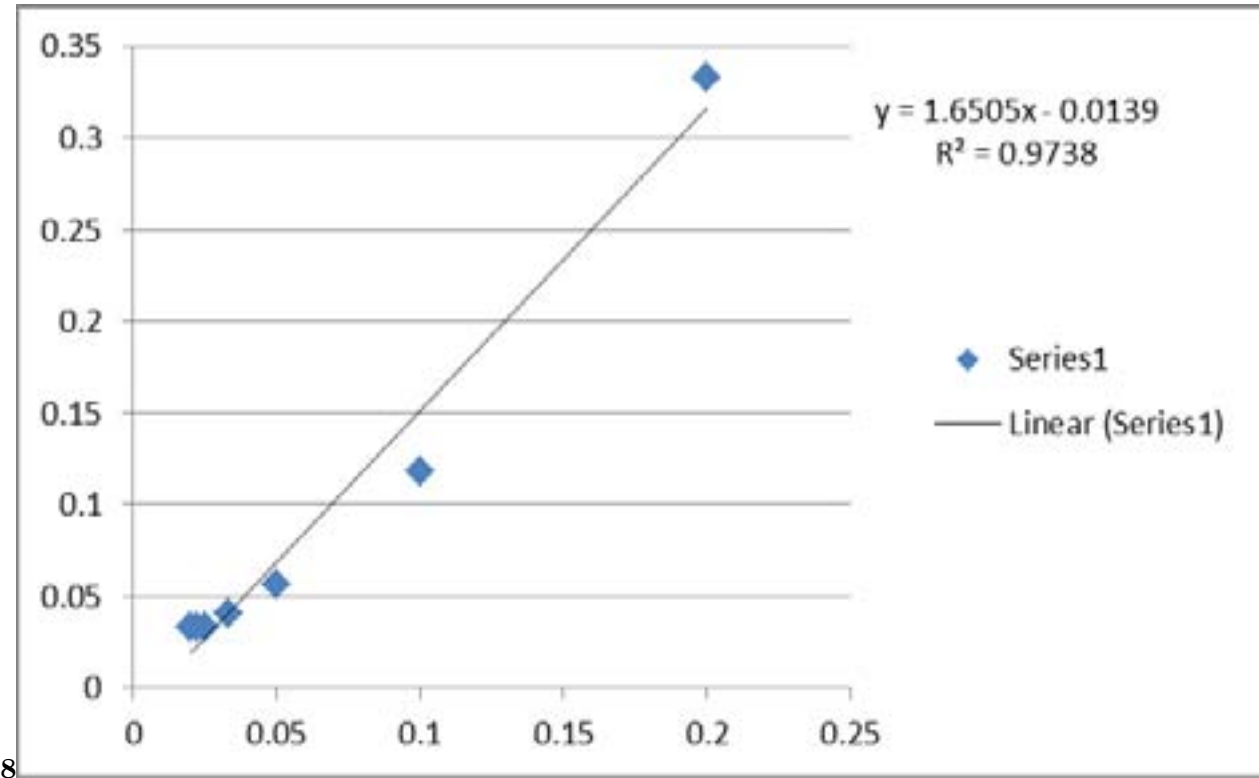


Figure 6: Fig. 8 :

1

	Year 2019
	0.932
Sulfur content %wt	3.998
Vanadium, ppm	75.970
Nickel, ppm	25.340
Aluminum, ppm	2.684
Asphaltenes %wt	6.412

Figure 7: Table 1 :

2

Figure 8: Table 2 :

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- [1: Schematic of the experimental setup] 1: *Schematic of the experimental setup*,
- [Flores and Cabassud ()] 'A hybrid membrane process for Cu (II) removal from industrial wastewater, comparison with a conventional process system'. V Flores , C Cabassud . *Desalination* 1999. 126 p. .
- [Ali and Abbas ()] 'A review of methods for the demetallization of residual fuel oils'. M F Ali , S Abbas . *Fuel Processing Technology* 2006. 87 (7) p. .
- [Rana et al. ()] 'A review of recent advances on process technologies for upgrading of heavy oils and residua'. M S Rana , V Sámano , J Ancheyta , J A I Diaz . *Fuel* 2007. 86 (9) p. .
- [Sahu et al. ()] 'Adsorption of furfural from aqueous solution onto activated carbon: kinetic, equilibrium and thermodynamic study'. A K Sahu , V C Srivastava , I D Mall , D H Lataye . *Separation Science and Technology* 2008. 43 p. .
- [Motsi et al. ()] 'Adsorption of heavy metals from acid mine drainage by natural zeolite'. T Motsi , N A Rowson , M J Simmons . *International Journal of Minerals Processing* 2001. 92 p. .
- [Treacy and Higgins ()] *Collection of Simulated XRD Powder Patterns for Zeolites*, M M J Treacy , J B Higgins . 2001. Amsterdam: Elsevier. (Fourth Revised Edition)
- [Gallezot and Leclercq (ed.) ()] *Conventional and analytical electron microscopy. In Catalyst Characterization: Physical Techniques for Solid Materials*, P Gallezot , C Leclercq . Boris Imelik, Jacques C. Vedrine (ed.) 1994.
- [Gomes et al. ()] 'Easily tunable parameterization of a force field for gas adsorption on FAU zeolites'. V A M Gomes , J A Coelho , H R Peixoto , S M P Lucena . *Adsorption* 2015. 21 p. .
- [Gawel et al. ()] 'Effects of asphaltenes on hydroprocessing of heavy oils and residua'. I Gawel , D Bociaska , P Biskupski . *Applied catalysis* 2005. 295 p. .
- [Auerbach et al. ()] *Handbook of Zeolite Science and Technology*, S M Auerbach , K A Carrado , P K Dutta . 2003. New York: Marcel Dekker.
- [Smith and Lai ()] 'Heavy oil microfiltration using ceramic monolith membranes'. K J Smith , W C Lai . *Fuel* 2001. 80 p. .
- [Kim ()] 'Hydrothermal crystallization and secondary synthesis of vanadium containing zeolites'. G J Kim . *Journal of Korean Association of Crystal Growth* 1997. 7 (3) p. .
- [Ding et al. ()] 'Hydrotreating of light cycled oil using WNi/Al<sub>2</sub>O<sub>3</sub> catalysts containing zeolite beta and/or chemically treated zeolite Y'. L Ding , Y Zheng , Z Zhang , Z Ring , J Chen . *Journal of Catalysis* 2006. 241 (2) p. .
- [Ding et al. ()] 'Hydrotreating of light cycled oil using WNi/Al<sub>2</sub>O<sub>3</sub> catalysts containing zeolite beta and/or chemically treated zeolite Y'. L Ding , Y Zheng , Z Zhang , Z Ring , J Chen . *Journal of Catalysis* 2006. 241 (2) p. .
- [Ikyereve ()] *Investigations into the pretreatment methods for the removal of Nickel (II) and Vanadium (IV) from crude oil*, R E Ikyereve . 2014. Loughborough University. (PhD dissertation)
- [Al-Daura ()] *Laboratory analyses daily log-sheet*, Al-Daura . Oil Refinery, 2017. Midland Refineries Company, Baghdad.
- [Price et al. ()] 'Local and Average Structural Changes in Zeolite A upon Ion Exchange'. L Price , K M Leung , S Asel . doi:10.3390/ Magnetochemistry 3040042. *Magneto chemistry* 2017. 3 (42) .
- [Thompson ()] 'Molecular Sieves'. R W Thompson . *Science and Technology* Weitkamp, I. J. (ed.) 1998. Springer.
- [Kuzmcki et al. ()] 'Natural zeolite bitumen cracking and upgrading'. S M Kuzmcki , W C Mccaffrey , J Brian , E Wangen , A Koenig , C C H Lin . *Microporous and Mesoporous materials* 2007. 105 p. .
- [Ikyereve et al. ()] 'Performance of Natural Zeolites in the Removal of Metal ions from Crude oil'. R E Ikyereve , A Mohammed , C Nwankwo . *ARNP Journal of Science and Technology* 2014. 4 (3) p. .
- [Abid et al. ()] 'Removal of toxic organic compounds from synthetic wastewater by a solar photocatalysis system'. M F Abid , S T Hamiedi , S I Ibrahim , S K Al-Nasri . *Desalination and Water Treatment* 2018. 105 p. .
- [Shannon ()] 'Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides'. R D Shannon . doi: 10. 1107/S0567739476001551. *Acta. Cryst* 1976. 1976AcCrA. 32 p. .
- [Fergusson ()] *The Heavy Elements: Chemistry, Environmental Impact and Health Effects*, J E Fergusson . 1990. Pergamon, Oxford.
- [Keane ()] 'The removal of copper and nickel from aqueous solution using Y zeolite ion exchangers'. M A Keane . *Colloids Surface A: Physicochem. Eng. Aspects* 1998. 138 p. .
- [Salman et al. ()] 'Use of Syrian natural zeolite for heavy metals removal from industrial waste water: Factors and mechanism'. H Salman , H Shaheen , A Ghaiath , N Khalouf . *Journal of Entomology and Zoology Studies* 2017. 5 (4) p. .