



GLOBAL JOURNAL OF RESEARCHES IN ENGINEERING: C
CHEMICAL ENGINEERING

Volume 19 Issue 1 Version 1.0 Year 2019

Type: Double Blind Peer Reviewed International Research Journal

Publisher: Global Journals

Online ISSN: 2249-4596 & Print ISSN: 0975-5861

Extractive Demetalization of Iraqi Crude Oil by using Zeolite A

By Luma H. Mahmood & Mohammad F. Abid

University of Technology

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GJRE-C Classification: *FOR Code: 090499*



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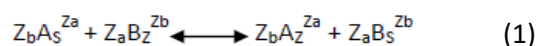
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1. INTRODUCTION

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, sever 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 [4-6]. 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

naturally occurring crystalline aluminosilicate minerals which are synthesized of 3-dimensional structures of tetrahedral molecules connected with the O_2 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 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:



B_z^{Zb} & A_z^{Za} are the positive ions inside the zeolite crystal; Za & Zb are the valences of the seions; A_s^{Za} & B_s^{Zb} are positive ions in solution. The positive ionuptake 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^+ ions with monovalent, Li^+ , K^+ , Rb^+ and NH_4^+ and divalent, Ca^{2+} 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_4^+ and Ca^{2+} . Substitution with Li^+ , K^+ and Rb^+ ions does not considerably influence the long-range crystal order. Substitution with NH_4^+ 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^{2+} 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.

Author ^α ^σ: Department of Chemical Engineering, University of Technology. e-mails: 80152@uotechnology.edu.iq, 80005@uotechnology.edu.iq

II. MATERIALS AND METHODS

a) Materials

Zeolite A ($\text{Na}_{12}(\text{AlO}_2)_{12}(\text{SiO}_2)_{12} \times 27\text{H}_2\text{O}$) was purchased from GCMIL, India. Crude oil was received from Al-Daura Oil Refinery, Baghdad. Vanadium tetrachloride (VCl_4) and EDTA were supplied from Ava Chemicals Private Limited, India. Table 1 lists the physicochemical properties of crude oil of east Baghdad field

b) Experimental method

The experimental setup is shown in Figure 1. Zeolite A particles was grounded. Figure 2 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 ($\sim 25^\circ\text{C}$). 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.

c) Analysis techniques

XRD-6000 Shimadzu (X-ray diffractometer with incident angle of 0.154nm using $\text{Cu-K}\alpha$ 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 10^5X . 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.

III. RESULTS AND DISCUSSION

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_4 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.

$$q_e = \frac{(C_o - C_e)V}{W} \quad (1)$$

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.

$$q_e = K_F C_e^{1/n} \quad (2)$$

$$q_e = \frac{q_m \cdot K_L \cdot C_e}{(1 + K_L \cdot C_e)} \quad (3)$$

Where q_m : maxima quantity of metal V adsorbed per unit mass of zeolite (mg gm^{-1}), q_e : concentration of V at equilibrium (mg L^{-1}). K_L is the Langmuir constant (L mg^{-1}) and K_F is Freundlich constant (mg gm^{-1}) (L mg^{-1})ⁿ. Figure 3 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.

$$\frac{1}{q_e} = \frac{1}{q_o} + \frac{1}{b q_m C_e} \quad (4)$$

$$\ln q_e = \ln K_F + \frac{\ln C_e}{n} \quad (5)$$

Figure (4a) represents a plot of $\frac{1}{q_e}$ vs $\frac{1}{C_e}$ with a correlation coefficient (R^2) = 0.9738. Mean while Figure (4b) represents a plot of $\ln q_e$ vs $\ln C_e$ with a correlation coefficient (R^2) = 0.9484. These results assure the viability of Langmuir isotherm in our study. This outcome depicts that the maximum uptake of V metal was $\approx 30\text{mg g}^{-1}$, this may be attributed to the capability of the usable zeolite structural frame with high percentage of pore volume.

b) Influence of metal adsorption on zeolite characteristics

i. XRD analysis

Figure 5 shows XRD images of zeolite A before and after vanadium adsorption. According to [17], the XRD pattern (Fig. 5a) for the zeolite shows excellent match with typical zeolite A while the XRD image of the vanadium-zeolite (see Fig. 5b) 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

collapse of zeolite frame work because it joins with other ions which stabilize the framework of zeolite.

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 6(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 by 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^+ , Al^{3+} , Si^{4+} , and V^{4+} 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.

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 7 illustrates vanadium removal efficiency as a function of operating time at different loading of vanadium. As can be seen in Figure 6, 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.

IV. 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.

ACKNOWLEDGEMENTS

Authors are grateful to the Department of Chemical Engineering, University of Technology for providing space and facilities. Thanks are also due to the Petroleum Research Center, Iraqi Ministry of Oil for their assistance.

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

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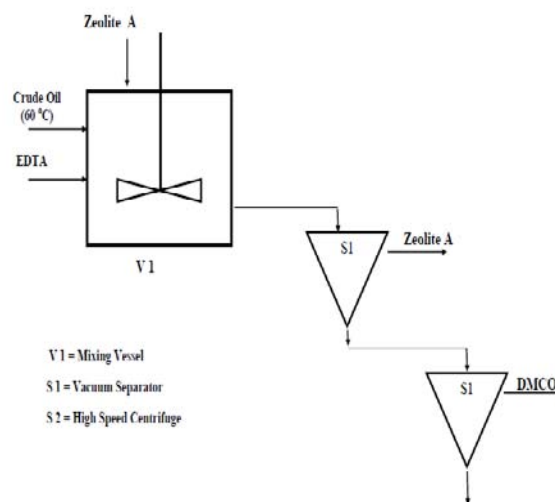


Fig. 1: Schematic of the experimental setup

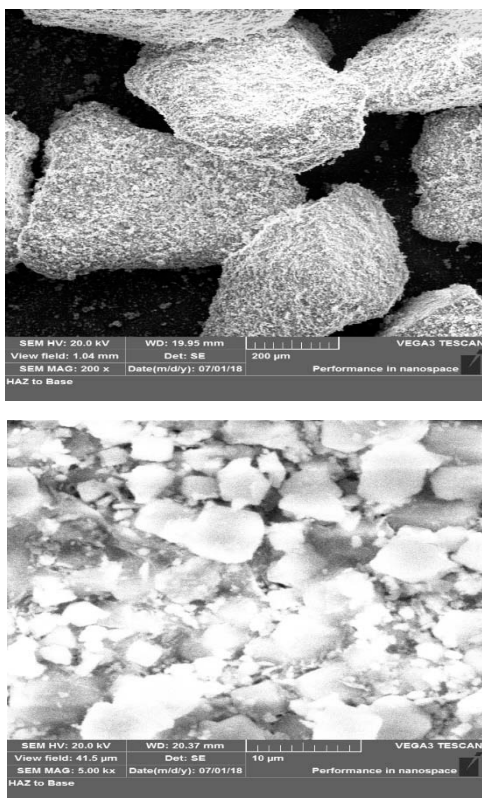


Fig. 2: Electron Image of zeolite A particles (top) before grounded and after grounded (bottom)

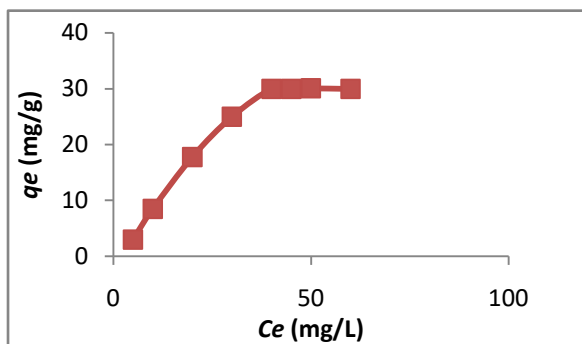
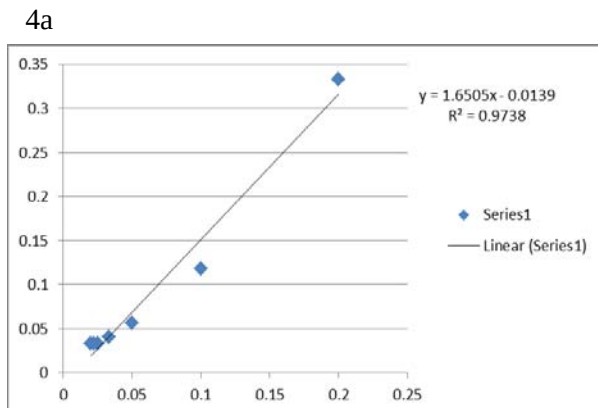


Fig. 3: Experimental results of adsorption of vanadium at equilibrium on Zeolite A



4b

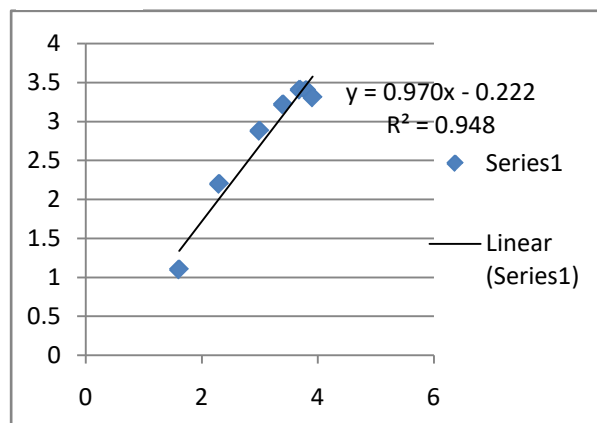


Fig. 4: Linearization plots of Langmuir isotherm model (4a) and Freundlich isotherm model (4b) for vanadium adsorption on Zeolite A.

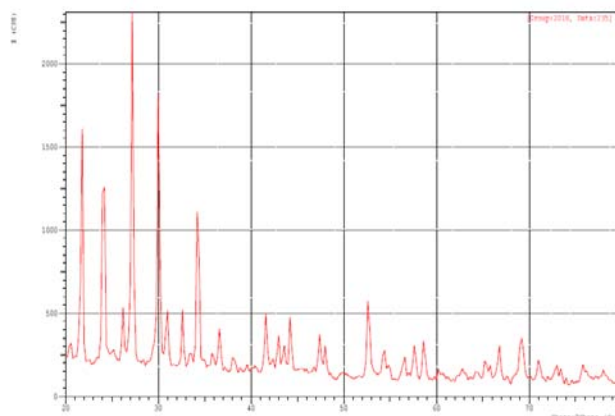


Fig. 5a: XRD image of zeolite A before vanadium uptake

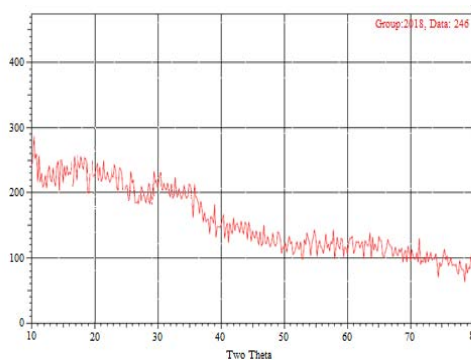


Fig. 5b: XRD image of zeolite A after vanadium

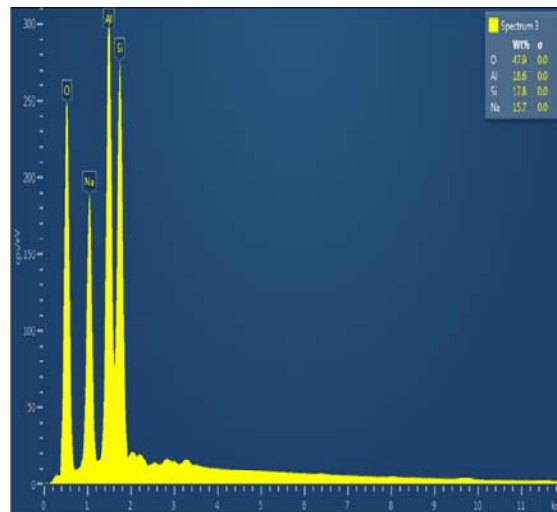


Fig. 6a: EDX image of zeolite before vanadium uptake

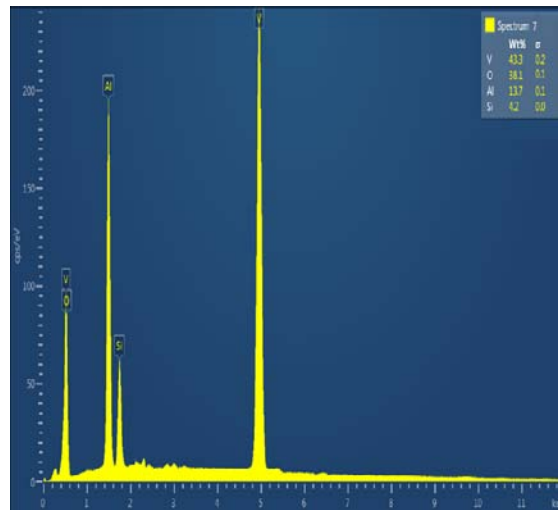


Fig. 6b: EDX image of zeolite after vanadium uptake

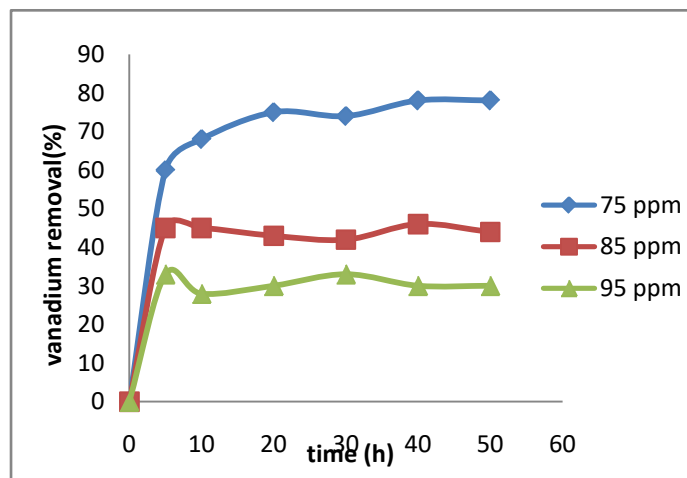


Fig. 7: Vanadium removal efficiency from crude oil as a function of operating time at zeolite loading 1 g/100ml oil

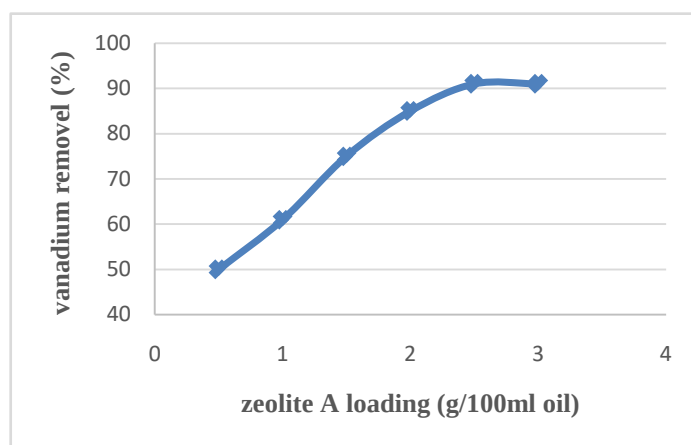


Fig. 8: Vanadium removal (%) as a function of zeolite A loading (g/100ml oil) at vanadium loading = 75 ppm and operating time=5 h

Table 1: Physicochemical properties of crude oil of east Baghdad field [15]

Item	Property	Value
1	Density @ 15 °C g/cm ³	0.932
2	Sulfur content %wt	3.998
3	Vanadium, ppm	75.970
4	Nickel, ppm	25.340
5	Aluminum, ppm	2.684
6	Asphaltenes %wt	6.412

Table 2: Percentage weight of elements before and after vanadium uptake

Elements	O		Na		Al		Si		Si/Al		V	
%weight	before	after	before	after	before	after	before	after	before	after	before	after
	47.9	38.1	15.7	0.0	18.6	13.7	17.8	4.2	0.957	0.306	0.0	43.3