



## Extractive demetallization of Iraqi crude oil by using zeolite A

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**Abstract:** The feasibility of the removal of 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 1 g/100 mL oil and within approximately 5 h, the removal efficiencies of V were 60, 45, and 33% at vanadium loadings of 75, 85, and 95 ppm respectively. While at 10, 20, 40, and 50 h the removal efficiency was 68, 75, 78 and 78% for 75 ppm of V loading. The equilibrium concentration of V in crude oil was attained after 40 h of operation. Long-term tests revealed the high stability of zeolite A for vanadium removal. Results depict that zeolite A could be advantageous for removal of V in the crude oil hydrotreating units.

**Keywords:** Vanadium, crude oil, demetallization, isotherm models.

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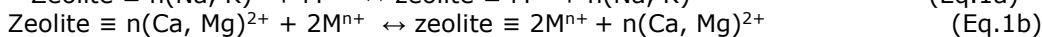
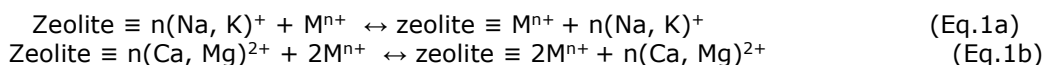
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### INTRODUCTION

In crude oil, traces of vanadium are considered the most plentiful metal (1). Serious problems can be evolved due to this metal through petroleum processing, such as catalyst poisoning which leads to reducing sulfur removal from petroleum fractions and consequently to acid rain due to increase emissions of sulfur oxides to the environment, corrosion of equipment and low quality of the product. It is well known that metals in crude oils form complexes with asphaltenes (2). Consequently, high temperature and pressure have been applied for removing metals from crude oil in conventional technologies, including deasphalting, hydrocracking, and hydrotreating (3). Other removal processes are adsorption, acid attack, and solvent extraction (4-6). Therefore an 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 a catalyst for the catalytic cracking of heavy oils (10-11). Benhammou *et al.* (12) reported that ion exchange reaction takes place between exchangeable cations ( $Na^+$ ,  $K^+$ ,  $Ca^{2+}$ , and  $Mg^{2+}$ ) located in zeolite structure and cations ( $M^{n+}$ ) in solution and can be given by Eqns. 1a and 1b:



During the ion exchange process, metal ions have to move through the pores and channels of zeolite and they have to replace exchangeable cations ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$ ). Thus the cation exchange capacity of a zeolite is a result of the degree of substitution of Al for Si in the framework. Thus the greater the degree of substitution of Al for Si, the greater the number of cations required to maintain electronic neutrality in the zeolites. These charge balancing cations are capable of exchanging with external cations from solution (13). Price *et al.* (14) conducted an experimental study to investigate the adjustments in framework occurred after partly substituting the extra-framework  $\text{Na}^+$  ions with monovalent,  $\text{Li}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$  and  $\text{NH}_4^+$  and divalent,  $\text{Ca}^{2+}$  cations. The authors concluded that solid-state Nuclear Magnetic Resonance detected alterations to the internal structure of the Linde Type A framework upon ion substitution with  $\text{NH}_4^+$  and  $\text{Ca}^{2+}$ . Substitution with  $\text{Li}^+$ ,  $\text{K}^+$  and  $\text{Rb}^+$  ions does not considerably influence the long-range crystal order. Substitution with  $\text{NH}_4^+$  ions compensates some of the long-range order of the zeolite A crystals because of the wasting of some structure Al as can be observed from X-ray data.

Substitution with divalent  $\text{Ca}^{2+}$  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 the adsorption process.

## MATERIALS AND METHODS

### 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 ( $\text{VCl}_4$ ), EDTA, HCl, and NaOH flakes were supplied from Ava Chemicals Private Limited, India. Table 1 lists the physicochemical properties of crude oil of east Baghdad field.

**Table 1:** Physicochemical properties of crude oil of eastern Baghdad field (15)

Item	Property	Value
1	Density @ 15 °C $\text{g}/\text{cm}^3$	0.932
2	Sulfur content %wt	75.970
3	Vanadium, ppm	25.340
4	Nickel, ppm	2.684
5	Asphaltenes %wt x	6.412

### Experimental method

The experimental setup is shown in Figure 1. Zeolite A particles were ground. 1 gram of the sieved zeolite A was added into 100 mL of the crude oil in a separating flask with 5 mL of EDTA solution. This mixture was mixed well by a magnetic stirrer at 100 rpm for an hour at room temperature ( $\sim 25$  °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 demetallized crude oil (DMCO) layer was separated and analyzed for the metal ions. According to the published data (16-18), the best pH range of adsorption of heavy metals onto zeolite has been varied between 3 and 6. In the present study, the selected pH was  $\sim 4.5$ , adjusted using NaOH and HCl.

### Kinetic study of adsorption

The amount of vanadium adsorbed at equilibrium, (mg/g) was estimated using Eq. 2.

$$q_e = \frac{(C_o - C_e)V}{W} \quad (\text{Eq. 2})$$

Where  $C_o$  and  $C_e$  are concentrations of vanadium at initial and at equilibrium (mg/L), respectively,  $V$ : volume of the heavy oil used,  $q_e$ : concentration of V at equilibrium (mg  $\text{L}^{-1}$ ), and  $W$ : the mass of zeolite A used (g). The Freundlich and Langmuir equations are the most widely used models for isotherm (16), the correlation of Langmuir and Freundlich isotherms are represented by Eqns. 3 and 4, respectively.

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

$$q_e = K_F \cdot C_e^{1/n} \quad (\text{Eq. 4})$$

Where  $q_m$ : maximum quantity of metal V adsorbed per unit mass of zeolite (mg  $\text{g}^{-1}$ ),  $K_L$  is the Langmuir constant (L  $\text{mg}^{-1}$ ) and  $K_F$  is Freundlich

constant ( $\text{mg gm}^{-1}$ ) ( $\text{L mg}^{-1}$ )<sup>-n</sup>. 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 3 and 4, respectively. Equation 5 represents the linear form of equation 3, and equation 6 represents the linear form of equation 4.

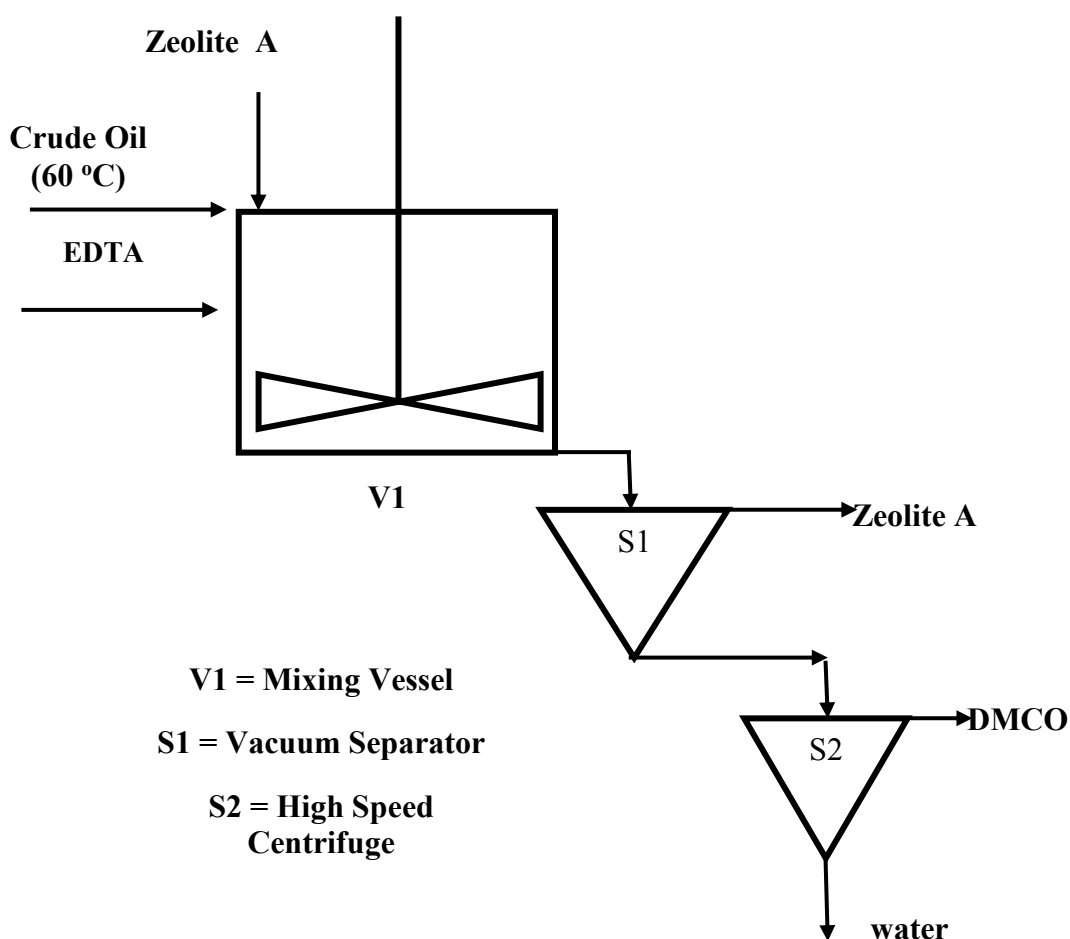
$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m K_L C_e} \quad (\text{Eq.5})$$

$$\ln q_e = \ln K_F + \frac{\ln C_e}{n} \quad (\text{Eq.6})$$

### Analysis techniques

XRD-6000 Shimadzu X-ray diffractometer (with an incident angle of 0.154 nm 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: 200 V to 30 kV and the magnification power from 4X to 10<sup>5</sup>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 with a model AA-7000 Flame atomic absorption spectrometer (FAAS) with graphite technique, Shimadzu with flame of N<sub>2</sub>O-C<sub>2</sub>H<sub>2</sub> and the instrument settings were according to the manufacturer's recommendations (Lighting conditions: Current; 10 mA/0 mA. Wavelength; 318.4 nm. Slit width; 0.5 nm. Lighting mode; BGC-D2). Measurements of vanadium's concentration were conducted at the Petroleum Research and Development Center, Iraqi Ministry of Oil, Baghdad. pH measurements were performed using an on-line pH meter Model Excel 25PH/mV/ISL.



**Figure 1:** Schematic of the experimental setup.

RESULTS AND DISCUSSION

Results for Kinetic study

The maximum adsorption capacity of zeolite A was estimated by conducting adsorption experiments. Different concentrations (5, 10, 20, 30, and 50 mg/L) of  $VCl_4$  in distilled water were prepared. Then 100 mL of each concentration is placed in a 250 mL

flask separately with 1 g of zeolite A. Figure 2 plots the experimental results of vanadium adsorption at equilibrium on zeolite A. Figure 2 depicts that the maximum uptake of V metal was  $\approx 30 \text{ mg g}^{-1}$ , this may be attributed to the capability of the zeolite framework which having a high percentage of pores.

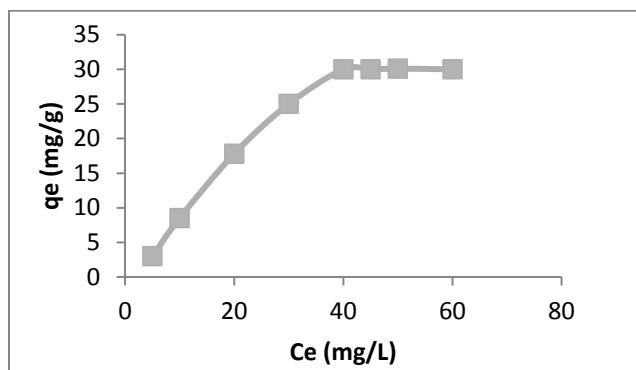


Figure 2: Experimental results of vanadium adsorption at equilibrium over Zeolite A.

Figure (3a) represents a plot of  $\frac{1}{q_e}$  versus  $\frac{1}{C_e}$  with a correlation coefficient ( $R^2$ ) = 0.9738. Meanwhile, Fig. (3b) represents a plot of  $\ln q_e$  versus  $\ln C_e$  with a correlation coefficient ( $R^2$ ) = 0.9711. The linear equations are

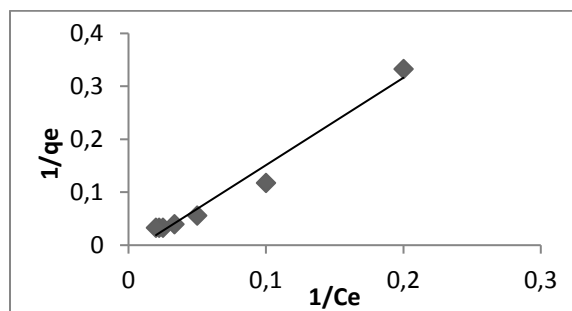
$$\frac{1}{q_e} = 1.6505 \frac{1}{C_e} - 0.0139 \quad (6)$$

for Langmuir isotherm, and

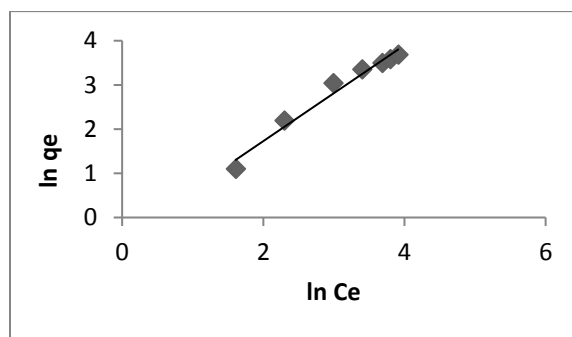
$$nq_e = 1.0848 \ln C_e - 0.4412 \quad (7)$$

for Freundlich isotherm.

These results assure the applicability of Langmuir isotherm in our study.



(3a)



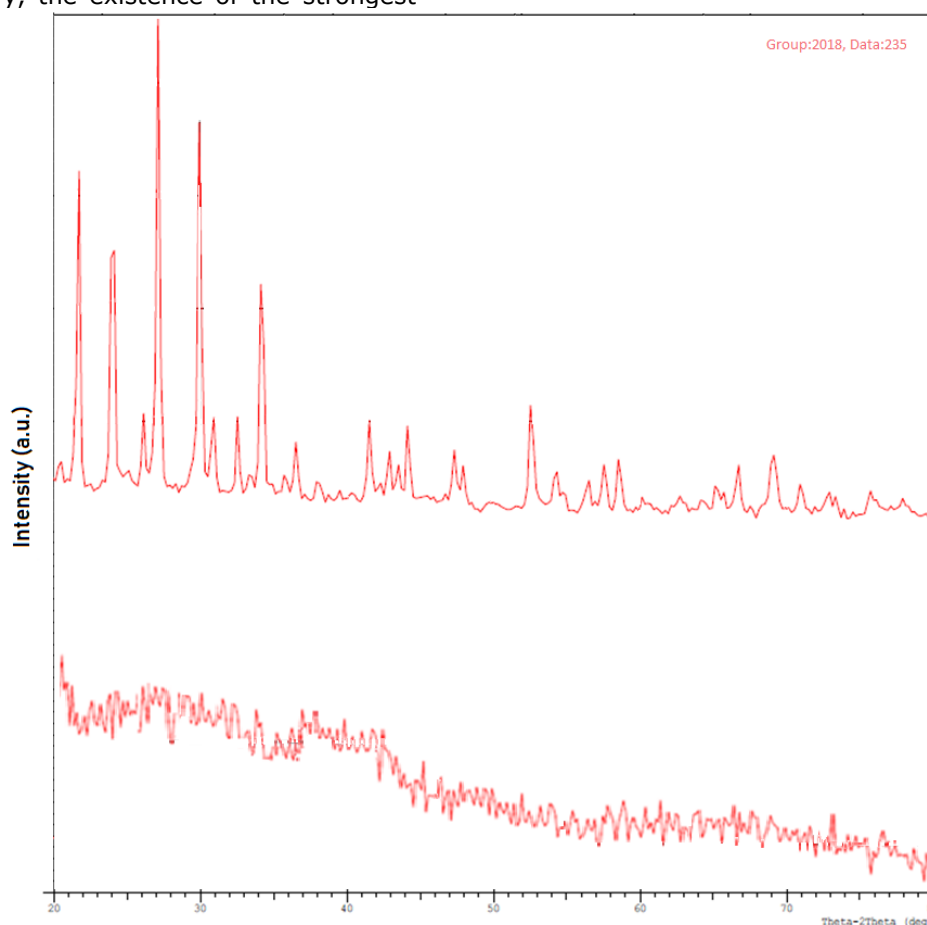
(3b)

Figure 3: Linearization plots of Langmuir isotherm model (3a) and Freundlich isotherm model (3b) for vanadium adsorption on Zeolite A.

**Influence of metal adsorption on zeolite characteristics**

*XRD analysis:* Figure 5 shows XRD images of zeolite A before and after vanadium adsorption. According to (19), the upper XRD pattern in Figure 5 shows an excellent match with typical zeolite A. As can be seen in Figure 5 (upper image), there are 3 strongest peaks, followed by another 2 weaker peaks. The position of the five peaks can be summarized in Figure 5 (upper), and its details can be seen in Table 2. In Table 2, the strongest 3 peaks were found at  $2\theta$  of  $29.550^\circ$ ,  $27.9583^\circ$ , and  $21.385^\circ$ , where the ratio of  $I/I_0$  were 95, 49, and 38 respectively. The other 2 peaks were shown at  $2\theta$  of  $24.211^\circ$  and  $34.440^\circ$ . The ratio of  $I/I_0$  were 38 and 27, respectively. According to ICDD 47-1870 data library, the existence of the strongest

peaks may indicate that the mineral was appropriate with sodium aluminum silicate hydrate of clinoptilolite-Na. Meanwhile, the lower XRD image of Figure 5 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 (20). Gallezot and Leclerc (21) found that vanadium promotes the collapse of the zeolite framework because it joins with other ions which stabilize the framework of the zeolite.



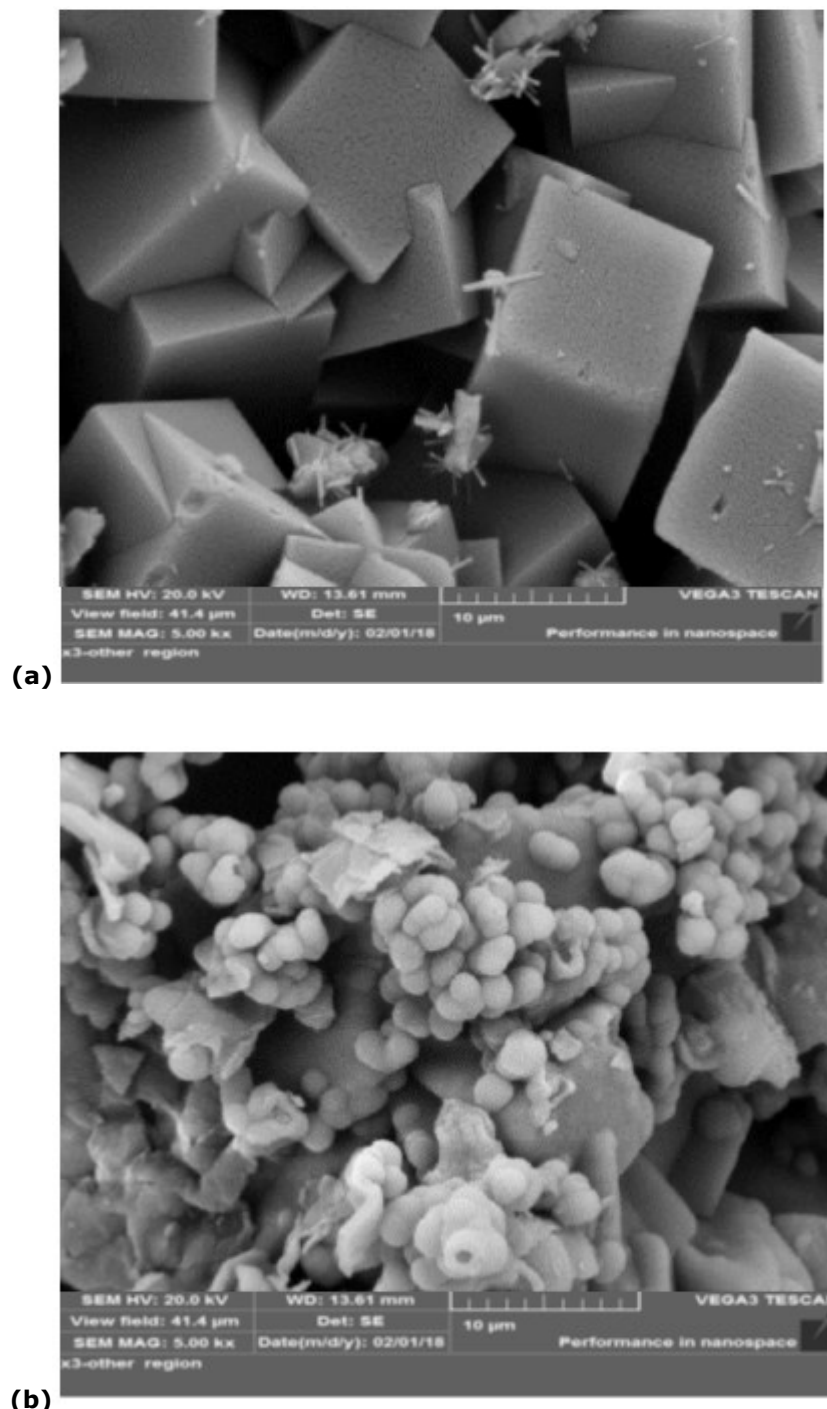
**Figure 4:** XRD images of zeolite A before vanadium uptake (upper) and after vanadium uptake (lower).

**Table 2:** Details of peaks in XRD of zeolite A (before vanadium adsorption).

Peaks	$2\theta^\circ$	Intensity (counts)
1	21.385	1600
2	24.211	1250
3	27.493	2550
4	29.554	1750
5	34.440	1100

*SEM analysis:* Figure 5a and Figure 5b show the SEM image of zeolite A at 200 nm before and after vanadium ions uptake respectively. As can be seen in Fig. 6b that the particles be dissimilar in

dimensions after the exchange, which revealed that the vanadium ion uptake had a significant effect on the structural framework of zeolite A.



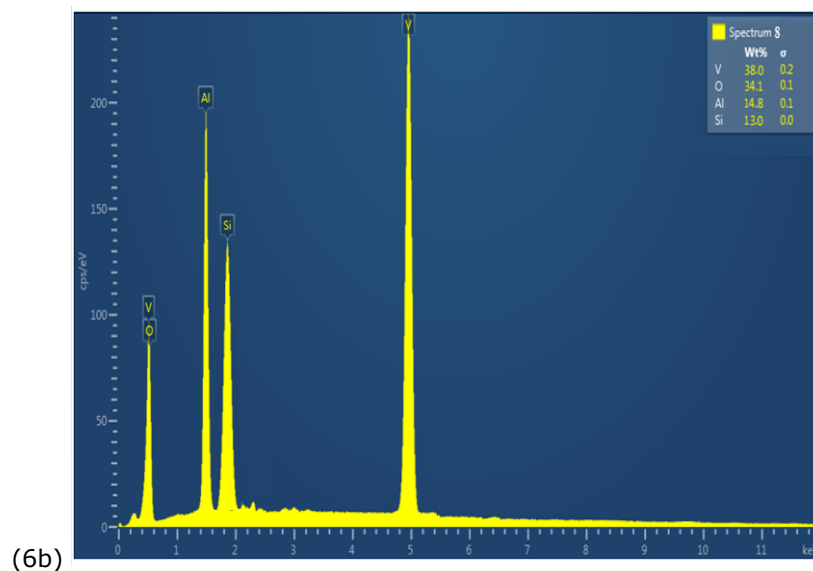
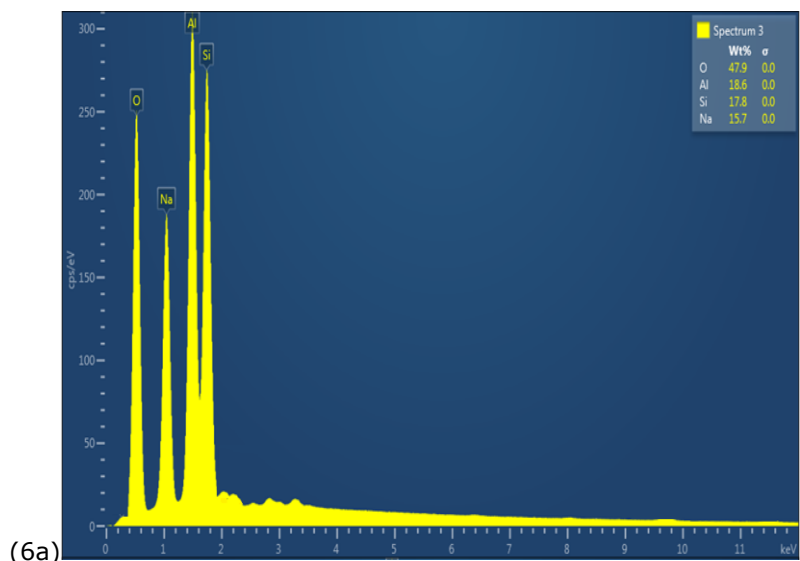
**Fig.5** SEM images before vanadium adsorption (a) and after adsorption (b).

*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 3 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 can 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  $\text{Na}^+$  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. (22) stated that ion radius plays an important effect on the ionic exchange. Shannon (23) published a revised

crystallographic data on ionic radii. He estimated the effective ionic radii of  $\text{Na}^+$ ,  $\text{Al}^{3+}$ ,  $\text{Si}^{4+}$ , and  $\text{V}^{4+}$  as equal to 102, 48, 40, and 35.5 picometers, respectively (see also [www.abulafia.mt.ic.ac.uk/shannon](http://www.abulafia.mt.ic.ac.uk/shannon)). 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 with the framework and breakdown of zeolite structure noticed after vanadium uptake.



**Fig. 6:** EDX images of zeolite A before vanadium uptake (6a) and after vanadium uptake (6b).

**Table 2.** Percentage weight of elements before and after vanadium uptake.

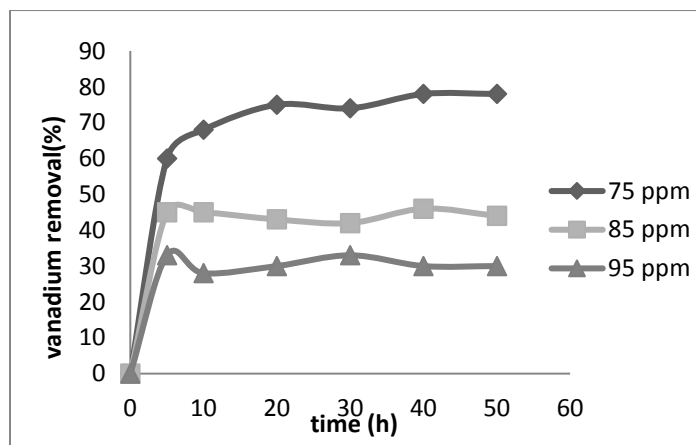
	O	Na	Al	Si	Si/Al	V
%weight	Before/after	Before/after	Before/after	Before/after	Before/after	Before/after
	47.9 / 38.2	15.7 / 0.0	18.6 / 14.8	17.8 / 13.0	1.045 / 1.138	0.0 / 38.2



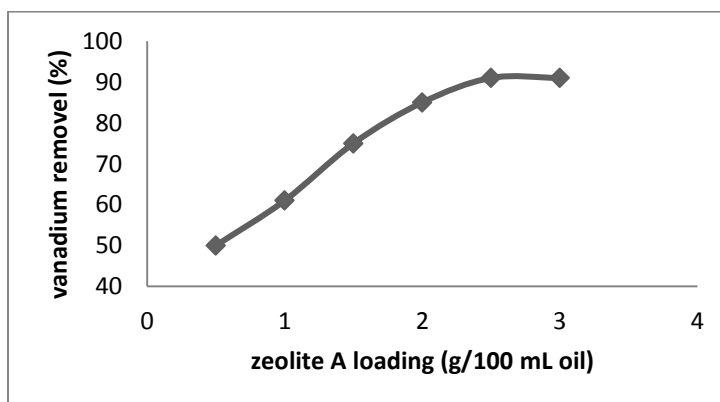
**Removal of vanadium from crude oil**

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 7, 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 75, 85, and 95 ppm respectively. Further processing of crude oil with 75 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 loadings (i.e., 85 and 95 ppm), the equilibrium concentration of vanadium was attained at approximately 20 h. Salman et al. (16)

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 (24). Thus high selectivity of zeolite for vanadium was due to electrostatic attraction between high valent vanadium cations and cations of the solid adsorbent. Figure 8 plots the effect of zeolite loading (g /100 mL 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 (25). It is interesting to note 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.



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



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

**CONCLUSION**

In the 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 a positive impact on removal efficiency while vanadium loading showed a 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.

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**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, (g)  
 $q_m$ : maximum quantity of metal V adsorbed per unit mass of zeolite, (mg/ g)  
 $q_e$ : concentration of V at equilibrium, (mg/ L)  
 $K_L$ : Langmuir constant, (L/ mg)  
 $K_F$ : Freundlich constant (mg/ gm) (L/ mg)<sup>-n</sup>

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