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Study on Removal of Vanadium from Iraqi Crude Oil by Prepared Nanozeolites

Abstract-The present study has been conducted to investigate the removal of vanadium from Iraqi crude oil by prepared zeolite nanoparticles. Ball milling was used as a top down approach to synthesize zeolite nanoparticles. Different variables such as adsorbent loading, Vanadium loading, and operating time were investigated for their influence on Vanadium removal. Experimental results of adsorption test show that both Langmuir and Freundlich isotherms predict well with the experimental data. Kinetic analysis of the studied system gives the following linear equations, For Langmuir isotherm: $\frac{1}{q_e} = 1.6505 \frac{1}{C_e} - 0.0139$ with $R^2 = 0.9738$, For Freundlich isotherm: $\ln q_e = 1.0848 \frac{1}{C_e} - 0.4412$ with $R^2 = 0.9711$

XRD and EDX analyses reveal 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 6 h, the removal efficiencies of V were 65, 40, and 30% at vanadium loadings of 70, 80, and 90 ppm respectively. Long-time tests revealed the high capability of zeolite A for vanadium removal.

Keywords: Heavy metals; crude oil, zeolite A; mechanical milling, isotherm models.

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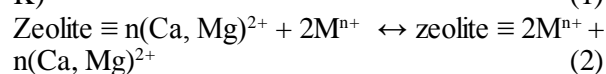
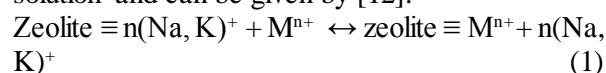
1. Introduction

Iraqi crude oils contain different amounts of heavy metals such as Vanadium, and Nickel (see Table 1). These metals poison the catalysts used in many processes in petroleum refinery leading to environmental threats and low specification of products [1].

In petroleum refinery various methods are used to remove heavy metals from oil fractions but some of these methods required high temperature and pressure such as hydrotreating and hydrocracking which makes these processes considered costly [2]. Other removal processes are adsorption [3], electrolysis [4], acid attack [5], and solvent extraction [6].

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 wastewaters [9], crude oil and as catalyst for the catalytic cracking of heavy oils [10-11]. Ion exchange reaction takes place between exchangeable cations (Na^+ , K^+ , Ca^{2+} and Mg^{2+}) located in zeolite structure and cations (Mn^+) in solution and can be given by [12]:



During ion exchange process, metal ions have to move through the pores and channels of zeolite and they have to replace exchangeable cations (Na^+ , K^+ , Ca^{2+} and Mg^{2+}) [13].

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 zeolite 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 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.

Iraqi crude oil of east Baghdad field contains higher amounts of vanadium (> 75 ppm) than other heavy metals [14]. The main objective of present work was to investigate the ability of zeolite type A to remove vanadium ions to provide a method for the removal of this heavy metal (i.e., V) during hydroprocessing of crude oil, as well as study the kinetics of adsorption process.

2. Materials and Methods

I. Materials

Zeolite A was purchased from Ava Chemicals Private Limited, India. Crude oil was received from Al-Daura Oil Refinery, Baghdad. Vanadium tetrachloride (VCl_4) and EDTA were supplied from GCMIL, India. Table 1 lists the physicochemical properties of crude oil of east Baghdad field. Ball milling was used as a top down approach to Synthesis zeolite nanoparticles. The objective of milling is to reduce the particle size by a simple, low cost and in high yield production. Ball milling is a process involving repeated

deformation, welding and fracture. Many parameters such as miller type, ball to powder weight ratio, characteristics of the balls and their speed, milling atmosphere and temperature, and process control agent influence the stages of milling. In mechanical milling (MM), a suitable powder charge is placed in a high energy mill, along with a suitable milling medium. The starting zeolite particles were in the range of 32-50 μm , where the average particle size for different powders that were used in this work was characterized by using the Nano-Brook 90Plus particle size analyzer. A dilute suspension in the order of 0.0001 to 1.0% v/v was prepared, using suitable wetting and/or dispersing agents, a small ultrasonicator is useful in breaking up loosely-held agglomerates. After the mechanical milling for the zeolite particles for a sufficient period, the new particles have the range of 59-123 nm, where the milled powder was characterized by the particle size analyzer, XRD, and scanning electron microscopy (SEM).

II. Experimental method

A schematic of the experimental setup is shown in Figure 1. Zeolite particles were grounded. Figure 2 shows the Zeolite particles before and after milling. 1 gram of the sieved zeolite was added into 100 mL of the crude oil in a separating flask with 5mL of Ethylenediaminetetraacetic acid (EDTA).

Table1: Physicochemical properties of crude oil of east Baghdad field [14]

Item property	Value
Density @ 15 °C g/cm^3	0.932
Sulfur content %wt	2.834
Vanadium, ppm	70.870
Nickel, ppm	21.440
Aluminum, ppm	2.774
Asphaltenes %wt	6.765

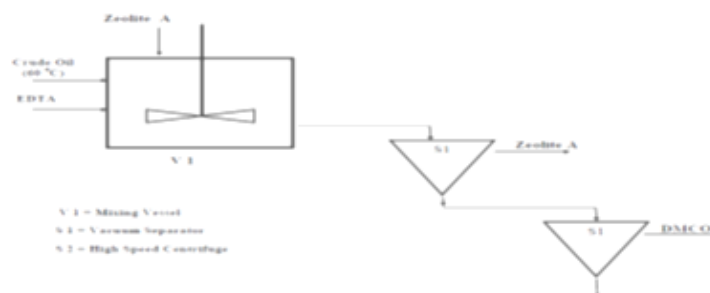


Figure1: Experimental setup

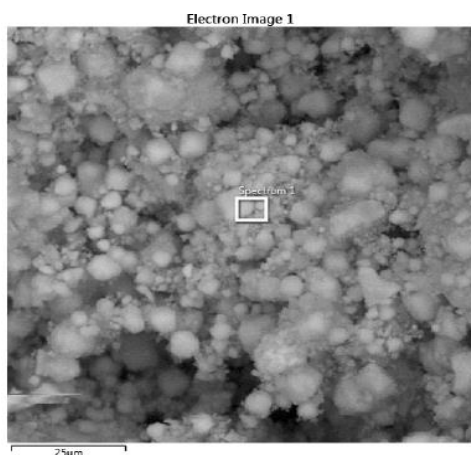


Figure 2: Electron Image of zeolite A particles (left) before grounded and after grounded

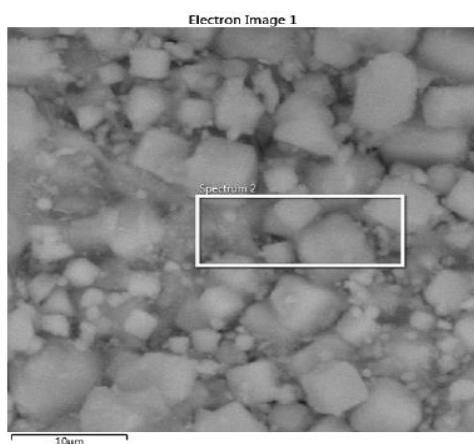


Figure 3: Adsorption of vanadium over zeolite at equilibrium

This mixture was well mixed by a magnetic stirrer at 200 rpm for an hour at room temperature (~25°C). Zeolite 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 EDTA and analyzed for the metal ions.

III. Analysis techniques

XRD-6000 Shimadzu (X-ray diffractometer with incident angle of 0.154 nm using Cu-K α 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 10⁵X. The chemical composition of zeolite 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 flame atomic absorption type

(AA-7000, Shimadzu, Japan) at the Petroleum Research and Development Center, Ministry of Oil, Baghdad/Iraq. The standard addition method (SA) was used to estimate vanadium in the samples of crude oil. The procedure of analysis is cited in [1].

3. Results and Discussion

I. Kinetic study of adsorption

The maximum adsorption capacity of zeolite A was estimated by conducting adsorption experiments for the removal of vanadium (IV) ions from VCl₄ solution and has been evaluated in order to provide a method for the removal of the metal ions during hydro-processing of crude oil. Different concentrations (10, 20, 30, 40, 50, 60, 80 and 100 ppm) of an aqueous solution of VCl₄ in distilled water were prepared. Then 200 ml of each concentration is placed in a 300mL flask separately with 1 g of zeolite. The amount of vanadium adsorbed at equilibrium, (mg/g) was estimated using Eq. 3 [15].

$$q_e = \frac{(C_o - C_e)V}{W} \quad (3)$$

Where C_o and C_e : concentrations of vanadium at initial and at equilibrium (mg/ L), respectively, V : volume of aqueous solution used, and W : mass of zeolite used (gm). The Freundlich and Langmuir equations are the most widely used models for isotherm, the correlation of Freundlich isotherm [18] and Langmuir isotherm [16] are represented by Eqns. 4 and 5, respectively.

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

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

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 g⁻¹) (L mg⁻¹)ⁿ. Figure 3 plots the experimental results of vanadium 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 4 and 5, respectively. Equations 6 and 7 represent the linearized form for equations 4 and 5 respectively.

$$\frac{1}{q_e} = \frac{1}{q_o} + \frac{1}{b q_m C_e} \quad (6)$$

$$\ln q_e = \ln K_F + \frac{\ln C_e}{n} \quad (7)$$

Figure (4a) represents a plot of $\frac{1}{q_e}$ vs $\frac{1}{C_e}$ with a correlation coefficient (R^2) = 0.9738. Meanwhile Figure (4b) represents a plot of $\ln q_e$ vs $\ln C_e$ with a correlation coefficient (R^2) = 0.9711. These results assure the viability of Langmuir isotherm in our study.

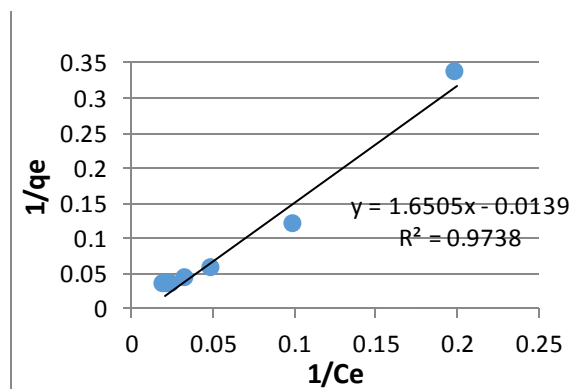


Figure 4a: Linearized plots of Langmuir isotherm model

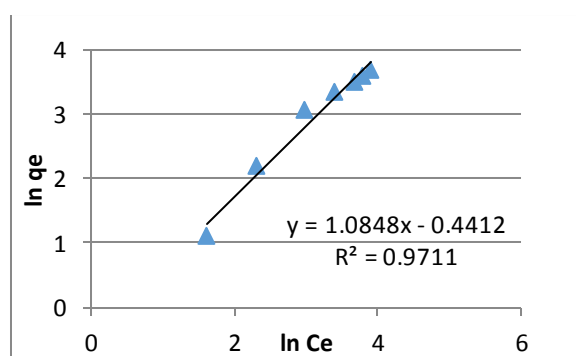


Figure 4b: Linearized plots of Freundlich isotherm model

II. Influence of metal adsorption on zeolite characteristics

1. XRD analysis

Figure 5 shows XRD images of zeolite before and after vanadium adsorption. According to [20], the XRD pattern (Figure 5a) for the zeolite shows excellent match with typical zeolite while the XRD image of the vanadium on zeolite (see fig. 5b) shows a breakdown of structure which indicates an effective exchanger (zeolite). 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 [17]. Gallezot and Leclerc [18] found that vanadium promotes the collapse of zeolite framework because it joins with other ions which stabilize the framework of zeolite.

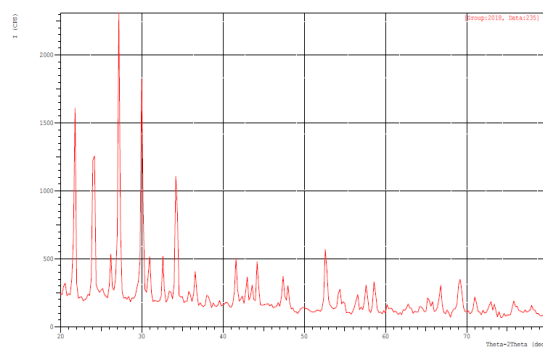


Figure 5a: RDX image of zeolite before uptake.

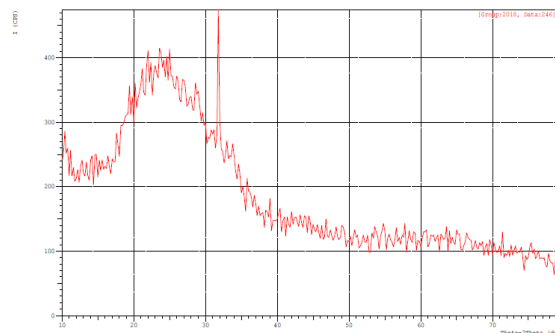


Figure 5b: RDX image of zeolite after uptake .

2. 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 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., [19] stated that ion radius plays an important effect on the ionic exchange. Shannon [20] 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.

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

% Weight	O	Na	Al	Si	Si/Al	V
before -	before -	before -	before -	before -	before -	before -
after	after	after	after	after	after	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

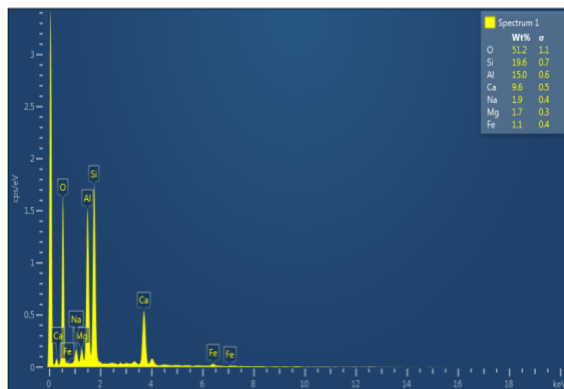


Figure 6a: EDX image of zeolite A before vanadium uptake

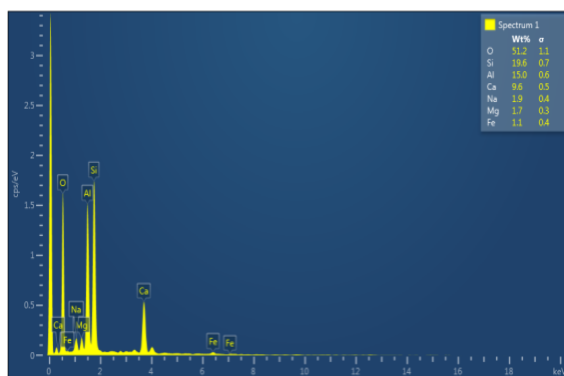


Figure 6b: EDX image of zeolite A after vanadium uptake

3. Removal of Vanadium from crude oil

A series of experiments were conducted to test the capability of zeolite to remove vanadium ions from crude oil. Figure 6 shows 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 6 h, the vanadium removal efficiencies were 30, 40, and 65% 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 ~ 8, 18, 38, and 50 h the removal efficiency was 65, 75, 80 and 80%. 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 [21].

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 [22]. Thus, high selectivity of zeolite for vanadium was due to electrostatic attraction between high valent vanadium cations and cations of solid adsorbent [23].

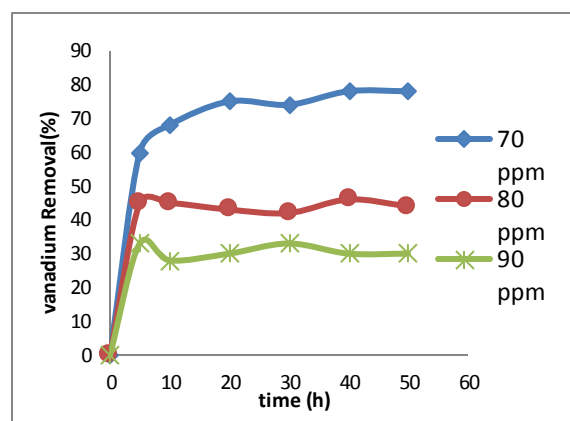


Figure 7: Removal efficiency as a function of operating time

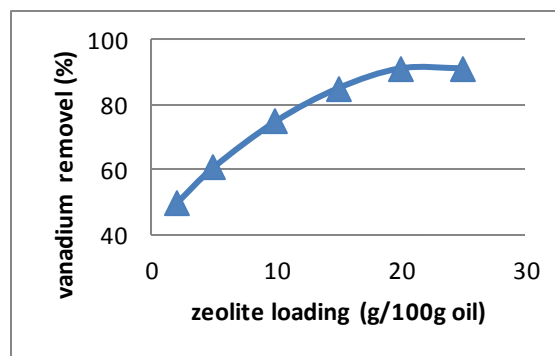


Figure 8: Removal efficiency as a function of zeolite loading

4. Conclusion

In this work the feasibility of zeolite nanoparticles to remove vanadium ions from crude oil was investigate.

* The results suggested 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.

* Experimental results of adsorption test also show that Langmuir isotherm predicts well the experimental data.

* XRD and EDX analyses reveal 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 6 h, the removal efficiencies of V were 65, 40, and 30% at vanadium loadings of 70, 80, and 90 ppm respectively.

* Long-time tests revealed the high capability of zeolite A for vanadium removal.

Acknowledgements

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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 **aqueous solution** used, (ml)

W: mass of zeolite A used, (g)

q_m : maxima quantity of metal V adsorbed per unit mass of zeolite, (mg/ gm)

q_e : concentration of V at equilibrium, (mg/ L)

K_L : Langmuir constant, (L/ mg)

K_F : Freundlich constant (mg/ g) (L/ mg)⁻ⁿ

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