

Chemical, Petroleum and Environmental Engineering

**Activated Bentonite for Removal Nickle and Vanadium from
Petroleum Distillates**

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ABSTRACT

The present work is to investigate the feasibility of removal vanadium (V) and nickel (Ni) from Iraqi heavy gas oil using activated bentonite. Different operating parameters such as the degree of bentonite activation, activated bentonite loading, and operating time was investigated on the effect of heavy metal removal efficiency. Experimental results of adsorption test show that Langmuir isotherm predicts well the experimental data and the maximum bentonite uptake of vanadium was 30 mg/g. The bentonite activated with 50 wt% H₂SO₄ shows a (75%) removal for both Ni and V. Results indicated that within approximately 5 hrs, the vanadium removal efficiencies were 33, 45, and 60% at vanadium loadings of 10, 30, and 40 ppm respectively. Further processing of heavy gas oil with 10 ppm vanadium shows a continuous slight increase in metal removal with operating time. At 10, 20, 40, and 50 hrs the removal efficiency was 68, 75, 78 and 78% respectively. Results indicated that an equilibrium concentration of the 10 ppm of vanadium was attained after 30 hrs while for Nickel at a loading of 4 and 7 ppm the equilibrium achieved after 40 hrs. Results depicted that activated bentonite has higher selectivity towards Vanadium. Results depict that activated bentonite (ACB) has a remarkable capacity for removal of (V) and (Ni) from heavy gas oil.

Keywords: Heavy metals, Bentonite, gas oil, acidic activation.

استخدام البنتونايت في ازالة الفناديوم والنيكل من المقطرات النفطية

لمى حسين محمود

مدرس

الجامعة التكنولوجية/قسم الهندسة الكيماوية

الخلاصة

العمل الحالي يهدف الى دراسة امكانية ازالة الفناديوم (V) والنيكل (Ni) من زيت الغاز الثقيل العراقي باستخدام البنتونايت المنشط. تم دراسة ظروف تشغيل مختلفة مثل درجة تنشيط البنتونايت، تحميل البنتونايت المنشط، ووقت التشغيل على تأثير كفاءة ازالة المعادن الثقيلة. أظهرت النتائج التجريبية لاختبار الامتزاز أن (Langmuir isotherm) يتنبأ جيدا بالبيانات التجريبية والحد الأقصى لامتصاص البنتونايت للفناديوم كان 30 ملغ / غم. وقد توضح من النتائج العملية ان البنتونايت المنشط مع 50% وزنا

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H₂SO₄ أعطى إزالة (75٪) لكل من Ni و V. وأشارت النتائج إلى أنه خلال حوالي 5 ساعات، كانت كفاءة إزالة الفناديوم 33 و 45 و 60٪ عند تركيز الفناديوم من 10 و 30 و 40 جزء في المليون على التوالي. معالجة زيت الغاز الثقيل العراقي مع 10 جزء في المليون الفناديوم يظهر زيادة مستمرة في إزالة المعادن مع وقت التشغيل. في 10 و 20 و 40 و 50 ساعة حيث كانت كفاءة الإزالة 68 و 75 و 78 و 78٪. وأشارت النتائج إلى أن تركيز التوازن ل 10 جزء في المليون من الفناديوم قد تحقق بعد 30 ساعة بينما بالنسبة للنكل عند التحميل 4 و 7 جزء في المليون، يتحقق التوازن بعد 40 ساعة. أظهرت النتائج أن البنتونايت النشط له انتقائية أعلى نحو الفناديوم. نتائج البحث أكدت أن البنتونايت العراقي المنشط لديه قدرة ملحوظة لإزالة (V) و (Ni) من زيت الغاز الثقيل العراقي.

الكلمات الرئيسية: معادن ثقيلة، بنتونايت، زيت الغاز، التنشيط باستخدام الحامض.

1. INTRODUCTION

It is well-known that gas oil contains tiny amounts of heavy metals with (V) and (Ni). However, these metals, in the form of complexes, are usually concentrated in the oil fractions causing corrosion of equipment and permanent deactivation of catalysts due to pore poisoning. Several conventional methods for the elimination of V and Ni from the petroleum fractions like extraction, acid attacking, and oxidation. **Gawel, et al. 2005 and Rana, et al., 2007**, reported that asphaltene contain the most of heavy metals. Thus the process for heavy metals removal from asphaltene such as deasphalting, hydrocracking, and hydrotreating needs sever conditions of temperature and pressure, **Smith and Lai, 2001, Siddiqui, et al., 2006 and Murray, 1999**. These catalytic processes need a pretreatment stage to lower the concentration level of heavy metals in order to prolong the service life of the catalyst. Bentonites have many industrial applications, **Barrer, 1978**, such as synthesis of adsorbents, **Siddiqui, 1968**, agent for bleaching, **Siddiqui, 1968**, beds of catalysts, **Srasra, et al., 1989**, carbon-copying paper, **Pinnavaia, 1983 and Takashima, et al., 1993**, and as binding component in ceramic industries, **Gomizet, et al., 1992**. The above-mentioned applications depend on bentonite properties which may change considerably due to thermally treatment, **Kodiand Jones, 1997**. Recently treatment of natural bentonite by acidification attracts the interest of many authors, **Jacobs, 1984, Tanabe, et al., 1989, Pesquera and Gonzalez, 1992**. This attention is attributed to that a considerable change in porosity of bentonite occurs during the acid treatment process. In addition activity increases due to the replacement of H⁺ ion instead of ferric, aluminum, and calcium ions, **Tiwan, et al., 1996**. The present work aimed to study the feasibility of removal of vanadium and nickel from gas oil using activated bentonite. Different operating parameters such as the degree of bentonite activation activated bentonite loading, and operating times were studied for their effect on removal efficiency

2. EXPERIMENTAL

2.1 Materials

Bentonite samples were gathered from the western region of Iraq. Analysis results for chemical composition were conducted by Iraqi National Company for Geological Survey and Mining Company and are listed in **Table 1**. Concentrated sulfuric acid (98 wt. %) was supplied by Sigma-Aldrich Co. Gas oil was supplied from Al-Daura Refinery. **Table 2** lists the physical properties of Iraqi petroleum fractions (Al-Daura Refinery/Midland Refinery Company, Ministry of oil). Commercial bentonite was obtained from Manek Minerals, India.



2.2 Preparation of Activated Bentonite

The procedure of bentonite activation was cited by **Yildiz, et al., 2004** and **Inaamet, et al., 2008**. Grounded bentonite was de-moisturized at 110 °C for 3 hours. Then, eight samples were taken each having a mass of (5) gm. Eight mixtures of H₂SO₄-water, every sized 100 ml were prepared in 200-ml beakers in such a way to obtain a different concentration of H₂SO₄(0, 10, 20, 30, 40, 50, 60, 70 wt%). Experiments for bentonite acidification were carried out by adding the 5 gm samples to each H₂SO₄-water mixture. The eight bentonite-mixture suspensions were heated in a shaking water bath type (Unmax 1010 DT, Germany) at 85 °C. The solid particles were then separated by filter paper under vacuum and was washed several times with deionized water. Muffle oven at 120 °C was used to dry the washed solids for 6 hrs. Each sample was numbered and stored until the time for the experiments of heavy metals removal. The experiments were carried out using the above-prepared samples with gas oil, supplied by Al-Daura Refinery /Baghdad – Iraq). The removal efficiency (R %), during the time period of each experiment, was determined using the following expression:

$$R\% = \frac{BCO_{untreated} - BCO_{treated}}{BCO_{untreated}} \times 100 \quad (1)$$

Where BCO_{untreated} and BCO_{treated} are the concentrations of heavy metals for untreated and treated samples of gas oil, respectively were measured by atomic absorption type (AA-7000, Shimadzu, Japan) at the Petroleum Research and Development Center, Ministry of Oil, Baghdad/Iraq.

2.3 Experimental Setup

A 250-ml beaker with a thermometer was inserted into the beaker to measure the temperature. A (150) g of gas oil was placed on a magnetically stirred hot plate used to heat the gas oil until 70 °C was attained. The gas oil was heated, with stirring, until its temperature reached 70 °C. Different weights of the ACB were added and maintained at 70 °C for any desired operating time. The mixture was filtered using Whatman filter paper no. 40.

3. RESULTS AND DISCUSSION

3.1 Influence of Acid Treatment on Bentonites Density and surface area

ASTM method D2854- 83 was used to measure the density of bentonite while instrument model Q-surf (9600) was used to estimate the surface area based on the BET technique. **Fig.1** shows the experimental measurements of activated bentonite (ACB) density. As can be seen in **Fig.1**, a noticeable decrease in density occurred as the concentration of acid increased. The density decreased from 1.05, 0.8, and 0.6 g/cm³ as the acid concentration increased from 0, 10, and 40 wt% respectively.

Moreover, acidification affects the surface area (g/m²) of bentonite. As acid concentration increased from 0 to 70%, the surface area increased from 59.9 to 240.03 m²/g. This depicts that the properties of ACB change as acidification process proceeds with a higher concentration of acid. The results obtained for different characterizations of Iraqi bentonites together with



commercial active bentonites for comparison are summarized in **Table 3**. The activated Iraqi bentonites' properties agree well with those of the commercial bentonites'.

3.2 Tests for Capacity of Adsorption

To estimate the capability of ACB for adsorption of utmost capacity, a series of experiments was conducted by applying five samples of prepared ACB each 1.0 g. into five 250 ml beakers where 150 ml of gas oil were poured. Equation 2 was utilized to estimate the quantity of heavy metals adsorbed at equilibrium, (mg/g).

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

Where C_o and C_e : concentrations of vanadium at initial and at equilibrium (mg L^{-1}), respectively, V : volume of the heavy oil used, and W : a mass of ACB used (gm). The Freundlich and Langmuir equations are the most widely used models for isotherm **Sahu, et al., 2008**, the correlation of Freundlich and Langmuir isotherms are represented by eqns. 3 and 4, respectively.

$$q_e = K_F \cdot C_e^{1/n} \quad (3)$$

$$q_e = \frac{q_m \cdot K_L \cdot C_e}{(1 + K_L \cdot C_e)} \quad (4)$$

Where q_m : maxima quantity of metal V adsorbed per unit mass of ACB (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.

Fig. 2 plots the experimental results of vanadium adsorption at equilibrium on ACB sample. 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 1 and respectively. Equations 5 and 6 represent the linearized form for equations 3 and 4 respectively.

$$\frac{1}{q_e} = \frac{1}{q_o} + \frac{1}{b q_m C_e} \quad (5)$$

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

Figure (3a) represents a plot of $\frac{1}{q_e}$ vs $\frac{1}{C_e}$ with a correlation coefficient (R^2) = 0.9738. Meanwhile, Fig. (3b) 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 this 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 bentonite structural frame with high percentage of pore volume.

3.3 Heavy metal removal

Removal efficiency curves of heavy metals (Ni and VI) from gas oil are shown in **Figs. 4 and 6**. As can be seen in **Fig.4**, the weakest removal value (i.e., 10 wt. %) is given by the inactivated bentonites, moreover, the bentonite acidified with different concentration of acid shows values which surpass (75%) for both Ni and V. This confirms the capability of activated bentonite in removing heavy metals from gas oil.



The decrease in metal removal at acidification over 50 wt.% H₂SO₄ may be attributed to the strong demolition of the layer and interlayer space of ACB this may give the image of the decreasing in metal removal trend above 50 wt.% H₂SO₄.

Figs. 5 and 6 illustrated vanadium and Nickel removal efficiency as a function of operating time at a different loading of vanadium and Nickel, respectively. As can be seen in **Fig. 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 hrs, the vanadium removal efficiencies were 33, 45, and 60% at vanadium loadings of 10, 30, and 40 ppm respectively. Further processing of gas oil with 10 ppm vanadium shows a continuous slight increase in metal removal with operating time. At 10, 20, 40, and 50 hrs the removal efficiency was 68, 75, 78 and 78%. As can be seen, an equilibrium concentration of the vanadium was attained after 40 hrs. For another vanadium loading (i.e., 30 and 40 ppm), the equilibrium concentration of vanadium was attained at approximately 20 hrs. As can be observed in **Fig. 6**, the removal efficiency for Nickel has the same trend of Vanadium, **Fig.5**, but they differ quantitatively. In **Fig.6**, within approximately 10 hrs, the Nickel removal efficiencies were 68% at all Ni loadings of 4, 7, and 10 ppm respectively. After 30 hrs of operation, the % removal of Nickel was 81, 80 and 76% at Nickel loading of 4, 7, and 10 ppm. This depicts that activated bentonite has higher selectivity towards Vanadium.

Fig. 7 shows the effect of activated bentonite loading (g/100g oil) on vanadium removal (%). As can be seen, bentonite loading has a positive impact on removal efficiency. It is interesting to notice that at higher loading of activated bentonite attained a constant value. This may be attributed to that equilibrium is established between the adsorbed ions of vanadium onto bentonite and that still existed into the treated gas oil.

4. CONCLUSIONS

The aim of the present work is to study the feasibility of removal of vanadium and nickel from gas oil using activated bentonite. Different operating parameters such as the degree of bentonite activation, activated bentonite loading, and operating time was investigated to study the effect of heavy metal removal efficiency. Experimental results of adsorption test show that Langmuir isotherm predicts well the experimental data and the maximum vanadium and Ni uptake of heavy metals was 30 mg/g. The bentonite activated with 50 wt% H₂SO₄ shows a (75%) removal for both Ni and V. Within approximately 5 minutes, the vanadium removal efficiencies were 33, 45, and 60% at vanadium loadings of 10, 30, and 40 ppm respectively. Further processing of gas oil with 10 ppm vanadium shows a continuous slight increase in metal removal with operating time. At 10, 20, 40, and 50 hrs the removal efficiency was 68, 75, 78 and 78%. As can be seen, an equilibrium concentration of the vanadium was attained after 40 hrs. For another vanadium loading (i.e., 30 and 40 ppm), the equilibrium concentration of vanadium was attained at approximately 20 hrs.



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NOMENCLATURE

ACB= Activated bentonite

$BCO_{\text{untreated}}$ =the concentration of heavy metals in untreated heavy gas oil

BCO_{treated} = the concentration of heavy metals in treated heavy gas oil.

C_o =initial concentrations of vanadium in gas oil, mg L^{-1} .

C_e =concentrations of vanadium at equilibrium, mg L^{-1} .

K_L = the Langmuir constant, L mg^{-1} .

K_F = Freundlich constant, $(\text{mg gm}^{-1}) (\text{L mg}^{-1})^{-n}$.

q_e = the quantity of heavy metals adsorbed at equilibrium, mg/g .

q_m = maxima quantity of metal V adsorbed per unit mass of ACB, mg gm^{-1} .

q_e =concentricity of V at equilibrium mg L^{-1} .

R%= the percentage removal efficiency.

V=volume of the heavy gasoil, ml.

W= mass of ACB, gm.

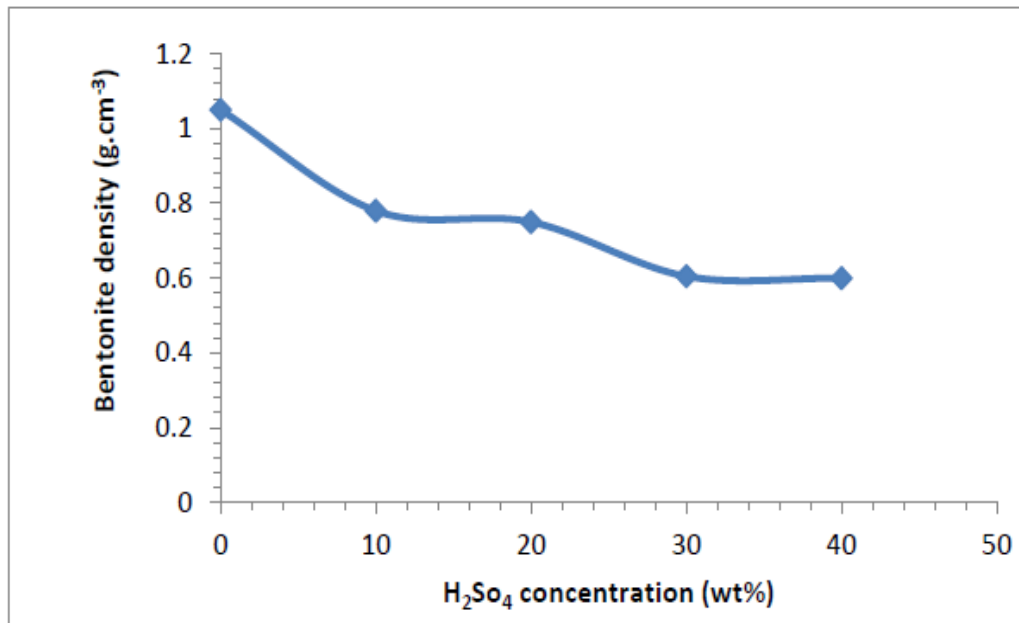


Figure 1. Density of betonite as a function of wt% acid adsorbed.

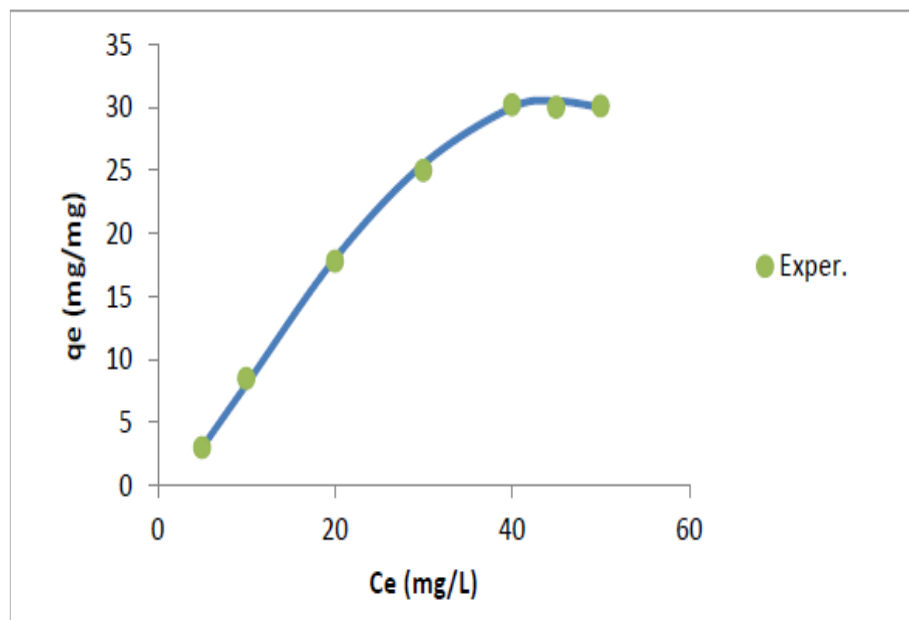
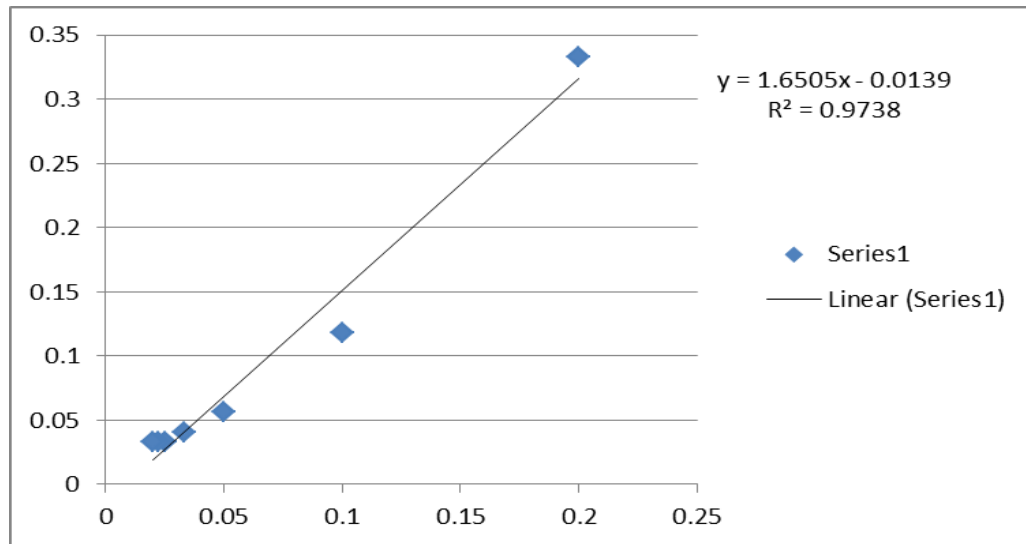


Figure 2. Experimental results of vanadium adsorption at equilibrium on ACB sample.



(3a)



(3b)

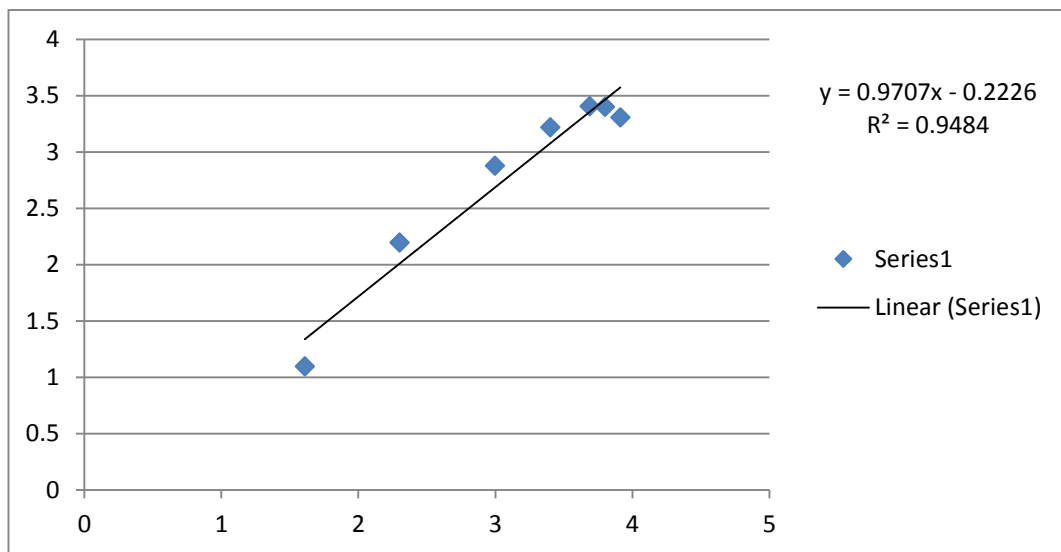


Figure 3. Linearization plots of Langmuir isotherm model (3a) and Freundlich isotherm model (3b).

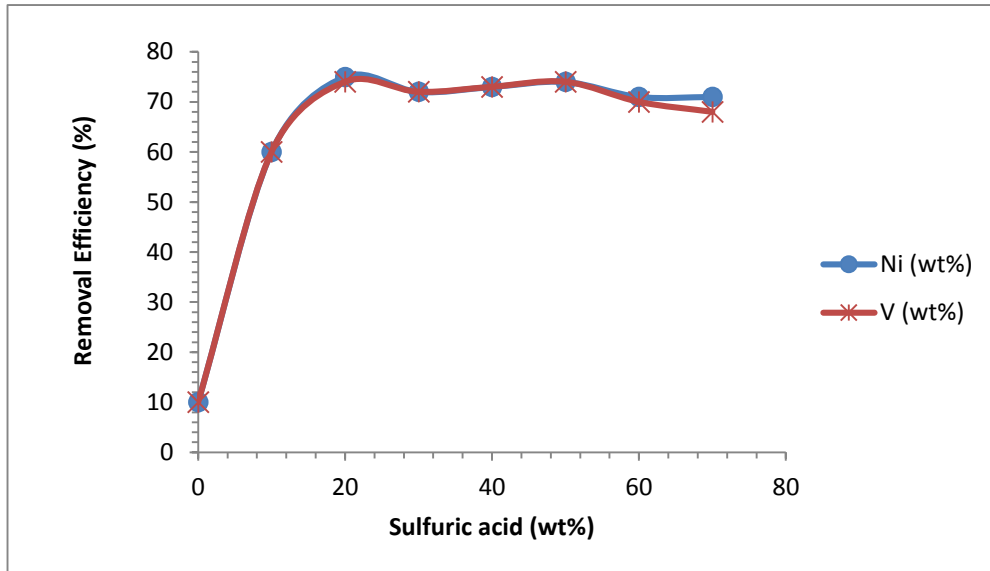


Figure 4. Removal efficiencies of heavy metals at different percentages of acid.

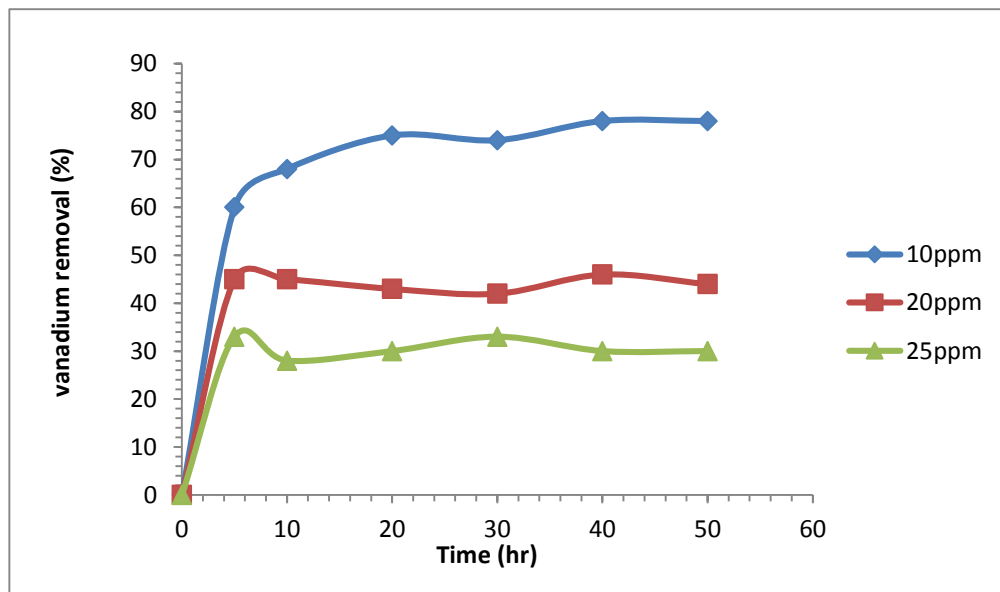


Figure5. Vanadium removal efficiency as a function of operating time.

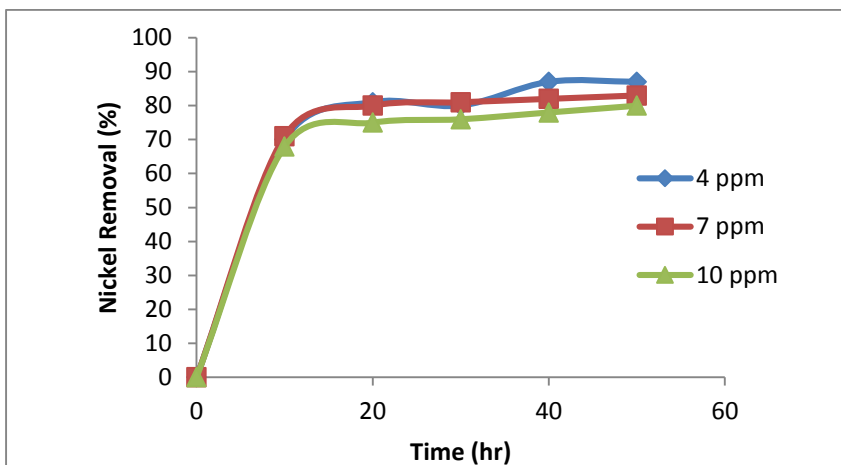


Figure 6. Nickel removal efficiency as a function of operating time.

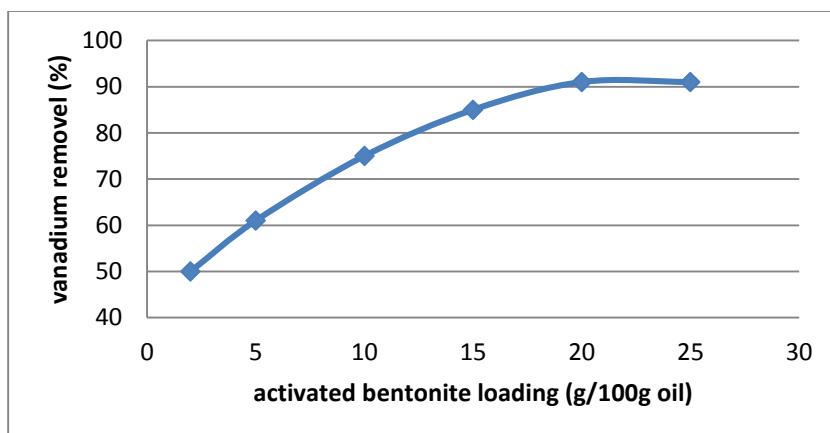


Figure 7. Vanadium removal (%) as a function of activated bentonite loading (g/100g oil).

Table 1. Chemical composition of Iraqi bentonites **Fadhil, and Entesar, 2013.**

Material oxide	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	Na ₂ O	MgO	SO ₃	L.O.I
Bentonite (wt %)	58.58	15.8	2.5	2.77	0.7	6.1	0.1	12.48

**Table 2.**Physical properties of Iraqi petroleum fractions (Al-Daura Refinery/Midland Refinery Company, Ministry of oil).

petroleum fractions	Light naphtha	Heavy naphtha	kerosene	gas oil
API gravity at 15.6 °C	83.7	60.2	47.6	40.1
Sulphur (weight %)	0.01854	0.05101	0.225	0.4945
Boiling range (°C)	(32-122)	(80-180)	(147-242)	(192-322)
Vanadium (ppm)	1.5	2.6	4.3	14
Nickel (ppm)	0.5	1.1	3.2	6

Table 3. Physical properties of raw, activated and commercial bentonite.

Bentonite Type	BET Surface area (m²/g)	Density (kg/m³)	Oil Retention (%)	pH
Raw bentonite	59.9	1105	21	8.1
Activated Bentonite	240.03	740	49.7	3
Commercial bentonite	220	750	35	3.1