Efficient Removal of Heavy Metals from Crude Oil Using High Surface Area Adsorbent Media: Vanadium as a Case Study

Salem J. K. Alhamd a, Mehrdad Manteghian b, Mohammed A. Abdulhameed c, Thekra A. Ibrahim c, Karar D. S. Jarmondi d

a Department of Petroleum Engineering, College of Engineering, Kerbala University, Kerbala, Iraq
b Department of Petroleum Engineering, Faculty of Chemical Engineering, Tarbiat Modares University, Tehran, Iran
c Department of Biology, College of Education for Pure Sciences, Diyala University, Diyala, Iraq
d Environmental Engineering Department, College of Engineering, Mustansiriyah University, Baghdad, Iraq

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Abstract: Vanadium, one of the heavy metals present in crude oil, harmfully affects the equipment of oil refineries and the quality of petroleum products. As a result, it is important to innovate effective methods for reducing or removing its concentration. This paper aims to study removing vanadium metal from Iraqi crude oil using activated carbon as an effective adsorbent material. Different experimental factors, i.e., the activated carbon dose, contact time, and agitation speed, were regulatory varied to evaluate their impact on vanadium adsorption efficiency. The outcomes revealed an exceptionally good efficacy of activated carbon to eliminate vanadium. The results exhibited that the maximum remediation was 86.33%, recorded at optimum factors, i.e., 0.5 g of activated carbon, 400 rpm of agitation speed, 75 °C temperature, and time of 400 minutes. According to these findings, activated carbon has a great ability to adsorb vanadium from crude oil. Thus, it can be considered a sustainable material for treating petroleum. Furthermore, this approach will help the refineries by reducing costs by eliminating the heavy metals that lead to corrosion or poisoning catalysts.
1. INTRODUCTION

Several fossil fuel types, including crude oil, are considered a very complex blend of hydrocarbon substances and many other materials. Crude oil can be found in subterranean reservoirs; its composition changes based on the petroleum field’s particular geographic location and geological features [1]. Knowledge of the crude oil component is important to improve the refinery’s work and obtain high-quality petroleum fractions and oil products. In general, any kind of petroleum comprises various hydrocarbons, oxygen, nitrogen, and sulfur, in addition to different ratios of heavy metals [2]. Iraqi crude oil is well-known for its relatively superior quality and advantageous attributes. It is generally categorized as a medium to heavy crude oil, distinguished by its relatively higher density and viscosity than lighter crude oils. In general, heavy crude oil is an oil with a relatively high density, close to the density of water, making it difficult to extract [3]. Light crude oil is an oil with a low density relative to the density of water; therefore, it floats on its surface easily. One of the most important characteristics of light oil is that it flows easily and does not contain waxy substances, while heavy oil is viscous and does not flow easily and contains waxy substances, while very heavy oil does not flow at normal temperatures and is very viscous [4]. Iraqi crude oil is characterized by its high density and high viscosity. Given these specifications, this type of crude oil causes many problems and great burdens for refineries. However, these disadvantages are considered advantages of high value on the other hand, as this type of crude contains high quantities of hydrocarbons and organic materials desired in crude oil, making it a preferred raw material for producing petroleum derivatives with high economic returns, such as asphalt and grease oils [5]. On the other hand, heavy crude has a lower cost than lighter crude, making it another benefit due to the increased demand for it by refineries and oil refining stations [6]. One of the most important contributions of the American Petroleum Institute was the establishment of a density standard measured in degrees, starting from zero. Oil with less than 25 degrees density is considered heavy, oil with a range of 25 degrees and 35 degrees is considered medium, and any oil higher than 35 degrees is considered light. Oil above 42 degrees is considered very light, and any oil with a density higher than 10 degrees floats on the surface of the water, and it does not float if it is less than 10. As for Iraqi crude oil of all types, its API value is variable and falls within a range of 25 degrees and 35 degrees, making it a preferred raw material for producing petroleum derivatives with high economic returns, such as asphalt and grease oils [5]. On the other hand, heavy crude has a lower cost than lighter crude, making it another benefit due to the increased demand for it by refineries and oil refining stations [6]. One of the most important contributions of the American Petroleum Institute was the establishment of a density standard measured in degrees, starting from zero. Oil with less than 25 degrees density is considered heavy, oil with a range of 25 degrees and 35 degrees is considered medium, and any oil higher than 35 degrees is considered light. Oil above 42 degrees is considered very light, and any oil with a density higher than 10 degrees floats on the surface of the water, and it does not float if it is less than 10. As for Iraqi crude oil of all types, its API value is variable and falls within a range between greater than or equal to 20 and less than or equal to 40 degrees. According to these values, it is clear that Iraqi oil can be classified as medium-heavy [4]. In addition to the abundant hydrocarbon contents of Iraqi crude oil, which is a significant advantage, it contains other substances that cause problems for oil equipment in refineries [5]. The most important of these problems are equipment corrosion and auxiliary factors poisoning, which are indispensable materials in any transformational process for producing various petroleum profiles, which increase the operational costs and maintenance requirements for the equipment and increase the replaced quantities of auxiliary factors as a result of reducing its operational life [6]. These problems lead to significant environmental impacts due to accumulating residual
materials, which require additional economic resources to treat them [7]. The most important heavy elements that Iraqi crude oil contains are vanadium, nickel, and, to a lesser extent, cadmium, copper, chromium, and others [5]. Catalysts play an effective role in reducing reaction time and increasing the required derivatives’ productivity. Therefore, these materials must work under excellent operating conditions to achieve the desired results [7]. Heavy elements in crude oil hinder these materials from performing as required, making them an additional burden on oil refineries instead of being useful materials [8]. Vanadium, nickel in the first level, and other heavy elements lead to prohibit the function of the catalysts. Over time, the catalyst loses its ability to process crude oil efficiently [6]. Thus, it will be a useless substance - if it does not become a harmful substance to the product - as the poisoning of the catalysts will increase the reaction time interaction and reduce the quality of the petroleum derivatives produced, thus causing countless economic damage [9]. Catalysts containing heavy metals could increase the time interaction and produce more residue from spent catalysts, leading to environmental issues. From an environmental standpoint, heavy metals as a component of crude oil are a real problem [10]. Aside from the economic damage mentioned above, the environmental damage resulting from the presence of these elements will be greater and greater because they will extend for long periods and have their effects on humans and living organisms in the ecosystems adjacent to various oil activities, such as refineries and oil extraction fields [11]. Toxic emissions containing heavy metals resulting from industrial and oil activities pose various environmental and health risks, which contribute to health problems, such as respiratory problems and skin diseases, and their impact may extend to developing various cancers and effects on organisms and biodiversity [12]. According to the environmental legislation and laws, whether local or international, various industrial activities, including oil refineries, must adhere to several conditions to ensure that their wastes and releases, whether gaseous, liquid, or solid, are within the established limits to reduce as much as possible the impact of pollutants released to the environment [13]. Since the topic of the present paper deals with heavy elements, it is necessary to study the methods and techniques used to remove vanadium from crude oil or reduce its percentage to the lowest possible before it enters oil refinery equipment to avoid the costly economic consequences and harmful environmental effects resulting from this element [14]. In addition to general environmental legislation, oil refineries must apply environmental standards and determinants more severe and stringent than other industrial activities to avoid harmful environmental pollution resulting from heavy elements in crude oil, petroleum derivatives, and exhausted auxiliary factors [15]. In addition to the above, various petroleum operations generally include parameters to address fires, spills, or accidental pollution from liquid waste generated due to continuous operation [16]. To reduce the environmentally harmful and economically costly effects resulting from waste disposal from various oil refineries, efficient methods and methods must be adopted to eliminate these effects or at least reduce their effects to the least possible degree. Among the most important techniques currently used by modern oil refineries to treat pollution with heavy metals is the technique of various catalysts, sedimentation, coagulation, sintering, electrolysis, and adsorption, and others [17]. All methods used to get rid of heavy metals have several disadvantages, including the need for large areas and advanced units, requiring high energy, or producing waste that requires costs to be treated and disposed of [18]. On the other hand, the adsorption method is a promising technology for treating pollution with heavy metals because it is characterized by ease and requires small areas and conventional systems [19]. Although they leave behind potentially toxic waste, this obstacle has been addressed through the zero-residue level (ZRL) concept, assuming that these materials can be used before disposal [20]. Activated carbon proves to be an extraordinarily effective method for eliminating any concentrations of heavy metals from soil, water, and crude oil [21]. Its high surface area and great adsorption capacity allow activated carbon to selectively hold heavy metal ions through electrostatic interactions or chemical bonding [20]. Although activated carbon continues to be a common option for crude oil treatment, it has some drawbacks associated with its use. One of the worthy drawbacks is the high cost linked to activated carbon, presenting a financial obstacle for refining operations [1]. Activated carbon incurs a relatively high expense due to the specialized equipment and intricate processes required for production and regeneration [12]. Activated carbon is a popular choice for adsorbing a wide range of contaminants. However, agricultural and industrial wastes are increasingly being used as an alternative to activated carbon due to their unique properties, making them the first option in medical [17] or treatment methods [14]. Many types of these non-valuable materials are used successfully as adsorbents, like rice husk [11], and other agricultural waste. Not only heavy metals but also different toxic pollutants are efficiently remediated by adsorbents, such as dyes and pesticides [12].
Activated carbon adsorption technology has several advantages. However, accumulating toxic substances at the end of the treatment process is a significant obstacle. The concept of zero residue level (ZRL) can be used to convert these harmful residues into economic products, thereby avoiding this obstacle [18], useful materials; however, using these low-cost media may not be highly selective for specific heavy metals in crude oil like vanadium element. Activated carbon is a valuable tool for heavy metal adsorption from crude oil. However, it lacks selectivity and could result in the simultaneous removal of desirable components, potentially losing valuable hydrocarbons during adsorption. Although this result is possible, it has not been proven yet. By considering these drawbacks and continuously improving the performance of activated carbon, the petroleum industry can make convenient decisions regarding its application for vanadium removal from crude oil in petroleum refineries. The essential target of this study is to remove vanadium, one of the famous heavy metals, from Iraqi crude oil by adsorbing activated carbon at different operating parameters.

2. EXPERIMENTAL PROCEDURE
2.1 Crude Oil
The crude oil samples were obtained from Al-Nasiriyah refinery located at Dhi-Qar Government, about 350 km south of Baghdad. The API gravity and sulfur content were 27.15 API° and 4.03%, respectively. The other compositions of crude oil used in this study are listed in Table 1.

Table 1 Composition of Iraqi Crude Oil.

<table>
<thead>
<tr>
<th>Element</th>
<th>Al</th>
<th>Ca</th>
<th>Cr</th>
<th>Fe</th>
<th>H</th>
<th>K</th>
<th>Li</th>
</tr>
</thead>
<tbody>
<tr>
<td>Con. (ppm)</td>
<td>0.75</td>
<td>11186</td>
<td>0.57</td>
<td>0.33</td>
<td>6.77</td>
<td>4724.99</td>
<td>0.02</td>
</tr>
</tbody>
</table>

Table 3 Chemical Composition of Activated Carbon

<table>
<thead>
<tr>
<th>Element</th>
<th>Wt%</th>
<th>Element</th>
<th>Wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon (C)</td>
<td>90.69</td>
<td>Manganese (Mn)</td>
<td>0.05</td>
</tr>
<tr>
<td>Oxygen (O)</td>
<td>5.38</td>
<td>Zinc (Zn)</td>
<td>0.045</td>
</tr>
<tr>
<td>Silicon (Si)</td>
<td>0.73</td>
<td>Cadmium (Cd)</td>
<td>0.04</td>
</tr>
<tr>
<td>Chloride (Cl)</td>
<td>0.69</td>
<td>Aluminum (Al)</td>
<td>0.033</td>
</tr>
<tr>
<td>Potassium (K)</td>
<td>0.63</td>
<td>Manganese (Mn)</td>
<td>0.023</td>
</tr>
<tr>
<td>Copper (Cu)</td>
<td>0.52</td>
<td>Arsenic (As)</td>
<td>0.017</td>
</tr>
<tr>
<td>Sodium (Na)</td>
<td>0.41</td>
<td>Phosphorus (P)</td>
<td>0.01</td>
</tr>
<tr>
<td>Iron (Fe)</td>
<td>0.39</td>
<td>Bromide (Br)</td>
<td>0.006</td>
</tr>
<tr>
<td>Calcium (Ca)</td>
<td>0.27</td>
<td>Chromium (Cr)</td>
<td>0.0025</td>
</tr>
<tr>
<td>Molybdenum (Mo)</td>
<td>0.062</td>
<td>Lead (Pb)</td>
<td>0.0015</td>
</tr>
</tbody>
</table>

![Fig. 1 Particle Size Distribution of Activated Carbon.](image-url)
where $\%E$ is the percentage removal of vanadium from crude oil by adsorption process (-), $C_{in}$ is the initial concentration of vanadium in virgin crude oil, which is equivalent to (43.8 ppm), $C_f$ is the final concentration of vanadium in treated crude oil (ppm), $q$ is the adsorption capacity of activated carbon to recover vanadium element (g/mg), $V$ is the volume of crude oil used in adsorption experiment = 0.1 L, and $m$ is the dose of activated carbon charged in experiment flask, g.

**Fig. 2** The Batch-Type Adsorption Unit LabTech Incubator Shaker.

**Fig. 3** The Benchtop Oil Analysis - SpectrOil 100 Series (RDE-OES) Elemental Analyzer Device.

**Fig. 4** The Experimental Flow Chart of Vanadium Recovery from Iraqi Crude Oil.
3. RESULTS AND DISCUSSION

3.1. Effect of Agitation Speed

The adsorption process efficiency is significantly influenced by the agitation speed, which is a fundamental parameter of a crucial role. The primary goal of agitation speed is to ensure thorough mixing and optimal contact between the adsorbent media and the earmarked adsorbate. In the present study, an investigation was conducted to assess the effect of different agitation speed values, ranging from 100 to 400 rpm, on vanadium adsorption from crude oil using activated carbon. The experimental conditions for the study included the initial vanadium concentration of 43.8 ppm, a dosage of 0.1 g of activated carbon per 100 ml of crude oil, a temperature of 75°C, and a contact time of 420 minutes. Fig. 5 depicts the correlation between agitation speed and the effectiveness of vanadium removal utilizing activated carbon as the adsorbent. The examination of this pivotal factor revealed a notable association between the adsorption efficiency (%E) and agitation speed. Notably, as agitation speed heightened, the vanadium removal efficiency also increased. This trend can be elucidated by disrupting the film boundary layer enveloping the adsorbent particles. Consequently, this disruption accelerates the rate of external film diffusion, thereby expediting vanadium adsorption onto the surface of activated carbon. The minimum and maximum agitation speeds of 100 and 400 rpm resulted in the lowest and highest removal percentage efficiency of 11.93% and 86.33%, respectively. The vanadium removal efficacy is significantly influenced by agitation speed. Thus, optimizing agitation conditions is important in practical applications to achieve higher adsorption efficiencies and improve the overall performance of the adsorption process using activated carbon as an adsorbent to remove heavy metals from crude oil [21].

3.2. Effect of Contact Time

The contact time parameter is of utmost importance in batch-grade adsorption, as it gives the time required to achieve the adsorption process by allowing the adsorbent to move from the bulk solution to the functional groups spread on the surface of the adsorbent. Within the scope of this study, multiple time intervals ranging from 30 to 420 minutes were used to locate the optimal contact time for realizing the maximum removal efficiency in the adsorption process of vanadium from crude oil using activated carbon, as shown in Fig. 6. The results unequivocally demonstrated that an increase in contact time correlates with a proportional increase in the efficiency of vanadium removal. The study found that the removal efficiency increased from 11.819% at half an hour to 86.33% at 400 minutes. Thus, the optimum contact time for activated carbon to adsorb 86.33% of the total vanadium present in crude oil was determined to be 400 minutes while maintaining all other parameters constant at their optimal conditions at 75°C, 400 rpm, and 0.5 g of temperature, agitation speed and adsorbent dose, respectively. Prolonging the retention time of the adsorbent in contact with the crude oil affords an increased opportunity for more particles to access the active sites on the adsorption surface. Enhancing the overall efficiency of the adsorption process. This observation is further supported by the adsorption capacity curve depicted in Fig. 6, which clearly corresponds precisely to the removal curve. Following the results of changing the contact time to remove vanadium ions using activated carbon, it becomes clear that the adsorption medium needs sufficient time to complete the retention of ions on its surface due to its high surface area. The results of this variable confirmed that the time required to reach the maximum efficiency of the activated carbon was 400 minutes. After exceeding this time, no clear adsorption effects by the adsorbent were recorded, indicating reaching a state of saturation and saturating the active sites with vanadium ions according to the operational conditions studied. Therefore, it is clear that the contact time has an important and direct effect on the efficiency of the adsorption of vanadium ions using activated carbon. Despite the ideal specifications and the high surface area of the adsorbent, the contact time factor is an essential parameter to determine the period required to reach the maximum adsorption efficiency. Similar results were recorded by [1].
3.3. Effect of Adsorbent Dose

Generally, the adsorption process cannot be completed without a substance representing the adsorption medium. Because the adsorption medium in this study represents a material of important value, determining the amount required to achieve the highest adsorption efficiency is an important requirement that must be determined precisely. The amount of material required for the adsorption of vanadium ions using activated carbon was tested using different masses of activated carbon and observing their effect on changing the adsorption efficiency. Experiments were conducted with all other operational parameters constant at optimal values, as shown in Fig. 7. It is noted that the efficiency of vanadium removal increased with the amount of adsorbent, as the relationship between them is direct, and the best amount of activated carbon was half a gram, which achieved the maximum removal efficiency. It is also noted that increasing the quantity beyond half a gram did not affect the removal efficiency. The reason for this is that the substance has reached the saturation level, after which it can no longer absorb any additional amount of vanadium ions because of the limited surface area that depends on the quantity of the substance. By increasing the mass of the adsorbent dose, the surface area also increased, thereby providing more active sites and an abundance of functional groups, increasing the number of vanadium molecules adsorbed and consequently enhancing the overall adsorption efficiency. At an adsorbent dose of 0.5 g, the maximum efficiency of 86.33% was achieved, with no significant increase in removal observed beyond this dose, as illustrated in Fig. 7. The explanation of this result may be that the adsorbent has reached its maximum capacity for adsorbing vanadium under these specific conditions, which may be attributed to the adsorption saturation state. Thus, the optimal activated carbon dose for recovering the maximum vanadium mass from 43.8 ppm was recorded as 0.5 g [1].

3.4. Effect of Temperature

Temperature fluctuations ranging from 25 to 75°C were investigated to assess their impact on the removal efficiency of vanadium, with an initial concentration of 43.8 ppm. Experiments were conducted to determine the effect of temperature on vanadium adsorption using activated carbon by keeping all other operational variables constant at optimal values. Fig. 8 shows the results reached from studying this variable. It is noted that the increase in temperature was accompanied by an increase in the efficiency of vanadium adsorption and that the lowest efficiency was recorded at 20 °C. In comparison, the adsorption gradually increased until it reached its maximum value at 75 °C. The adsorption process is notably impacted by temperature, influencing the adsorbent and the adsorbate. Nevertheless, the precise influence of temperature varies depending on the specific conditions. In this investigation, the outcomes can be ascribed to a rise in the release of vanadium particles from crude oil due to the heightened energy at elevated temperatures. This augmented energy streamlines the transfer of these released particles, enabling their accumulation on the activated carbon surface [10]. Moreover, temperature can impact the adsorbent media by expanding its pores, allowing it to hold a larger volume of vanadium particles from crude oil [20]. In both scenarios, the vanadium concentration in crude oil diminishes, resulting in a general enhancement in removal efficiency. Temperature is a pivotal factor in vanadium adsorption, influencing the adsorbent’s characteristics and the liberation of vanadium particles from crude oil [21].
4. CONCLUSIONS
Vanadium inhibitors are used to prevent corrosion in high-temperature environments. Removing vanadium from crude oil can reduce the cost of these inhibitors. The crude oil of Al-Nasiriyah refinery contains a high concentration of vanadium at 48.3 ppm. Adsorption is an economic and excellent process to remove or minimize the concentration of vanadium in crude oil. Activated carbon has a very good potential to remove vanadium due to its unique properties, such as high surface area. The optimum operating conditions for the best removal efficiency were 400 rpm, 400 min, 75°C, and 0.5 g of agitation speed, contact time, temperature, and dose of activated carbon, respectively. These operating conditions were directly related to the removal efficiency and resulted in a removal rate of 86.33% from the total concentration of vanadium.

REFERENCES