Thermodynamics Study of Adsorption of Oil Hydrocarbons from aqueous solutions onto the Porcelanite Surface

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ABSTRACT

This work describes removal of hydrocarbons from aqueous solution using porcelanite as an adsorbent surface with investigation of some factors that affect on adsorption process of the hydrocarbons such as contact time, primary hydrocarbons concentration in the solution, adsorbent particle size and temperature of the solution. Removal of hydrocarbons was conducted using the batch method. From the obtained results, it was found that, the quantity of adsorbed hydrocarbons was increased with increase in adsorption temperature. Equilibrium time was attained at 30min for efficient removal of hydrocarbons. Removal percentage of hydrocarbons over porcelanite powder was found to be 41.61% and the amount of adsorbed hydrocarbons over porcelanite was 83.22(mg/g). The results of adsorption processes were more fitted with Freundlich model rather than Langmuir adsorption model. Thermodynamic study showed that, ΔH was endothermic, ΔG at the values were negative at lower concentrations and then turned positive when concentrations increased and ΔS was found to be positive.

Key words: porcelanite, batch adsorption, Hydrocarbons, Langmuir and Freundlich
INTRODUCTION

Petroleum plays a significant role in daily life. However, there is very great concern with this issue due to ship accidents and oil spills in the waters (e.g., seas, river, ocean, etc.) that may occur as a result of oil extraction, transportation, or during oil storage [1, 2]. It is estimated that the quantities of oil that spill and reach the water globally are about 400,000 tons annually [3]. Moreover, the risk of water contamination with oil has increased due to refining, transportation and the increased use of crude oil in recent years. Oily water causes many problems, including widespread pollution and serious environmental problems, including significant damage to the environmental system, as well as causing a loss of energy resources [4]. Therefore, it is important to develop, find effective and economically feasible techniques to treat spills of petroleum and its products. Currently, several technologies have been developed to treat oil spills including; chemical (e.g., in-situ burning and dispersion) [5], physical (e.g., skimmers and absorption) [6,7] and biological methods [8]. Among the multiple methods, adsorption has attracted the attention of most scientists because of its multiple Features such as; Simplicity of work, environmentally friendly, low cost, the availability of various adsorbents and low energy consumption, etc. [9,10]. The adsorption is the phenomenon of collecting a gaseous or liquid substance in the form of molecules, atoms, or ions on the surface of another solid substance. In recent decades, many materials have been used to treat water pollution, including bentonite, activated carbon, sand, peat, fiberglass, coal, polypropylene and amberlite [11]. The main objective of this work is to eliminate Hydrocarbons from water using porcelainite as the adsorbents. This technology is an environmentally friendly method and it is cost effective. The present work would involve removal of polluted hydrocarbons from aqueous solutions in simulation to that may spillage into sea water or stream water. Hydrocarbons contaminate would be investigated including effect of hydrocarbons concentration, and effect of temperature. Besides that adsorption isotherms and kinetics would be considered.

EXPERIMENTAL SECTION

Preparation of adsorbent

Natural Porcelanite samples were obtained from the Ministry of Industry and Metals / the General Geological Survey and Mining Corporation, Baghdad, Iraq. Samples were washed using distilled water to remove impurities and get rid of water-soluble substances from salts and others. The samples were dried for three hours in an oven at a temperature of (120 °C), grinding. The dried powder for the purpose of obtaining fine particles by means of an electric grinder into fine particles and sifting the ground powder using laboratory sieves of different sizes 75 to 300 µm and preserved in tight-lidded containers for the purpose of using them in the research.

Preparation of oil emulsion

The emulsion is prepared by adding a certain amount of crude oil from West Qurna fields of American density API (19) in (1L) of distilled water and mixed for 20 minutes at 6000 rpm. The pH value of the initial oily solution was about 7. The following chemicals were mixed for the purpose of preparing an brine solution in 1L of deionized water for 6 hours at 200 rpm: 0.044 g of KCl, 0.63 g of NaCl, 0.16 g of NaHCO3, 0.13 g of CaCl2 and 0.026 g of MgCl2 and then mixed at a speed (200 rpm) for a period of (6 h) then left the emulsion for one hour to determine its stability [12].
Adsorption studies

The adsorption of hydrocarbons on the surface of porcelanite is studied using the batch adsorption method. Adsorption of Oil Hydrocarbons was performed in 250ml plug conical flask by totaling 0.5g of porcelanite with a particle size of 75 µm to 100ml of 1000mg/L of Hydrocarbons. All experiments were carried out at 25°C often with shaking for a desired time at 120rpm. The mixture were separated by a centrifuge. concentrations of total petroleum hydrocarbons were measured after dissolving them with pure hexane using a spectrofluorophotometer. The emission intensity was measured at a wavelength of 360 nanometers, for excitation it was measured at a wavelength of 310 nanometers. (RF-5301pc, SHIMADZ). The adsorption percentage (R%) and the adsorption capacity (Qe) values were calculateusing (eq.1) and (eq.2) [13].

\[ Q_e = \frac{V(C_o - C_e)}{m} \] ................................(1)

\[ \text{removal} \% = \left(\frac{C_o - C_e}{C_o}\right) \times 100 \] ............(2)

Where ; Qe is the adsorption capacity (mg/g), m is the amount of the adsorbent (g), V is the volume solution (l), C_o is Initial solution concentration in mg l\(^{-1}\), C_e= Concentration of the solution in mg l\(^{-1}\) after adsorption.

RESULTS AND DISCUSSION

Characterization of the adsorbent

Functional groups in the powder of porcelanite were probed using a device type FT-IR shimadzu (4000-400 cm\(^{-1}\)). The FTIR spectra is shown in Figure (1). These spectra show the emergence of clear and powerful band around (3621-3460 cm\(^{-1}\)) ascribe to stretching vibration of (OH) group , As for the (si = o)group shows the stretching vibration at the site at 1138 cm\(^{-1}\), the band at 476.42 cm\(^{-1}\) can be attributed to the stretching vibration Fe – O group and the band around 792cm\(^{-1}\) vibration is attributed to the stretching of the Al – O group [14].
Effect of contact time

The contact time to reach the equilibrium state of Oil hydrocarbons on the surfaces of the prepared compounds at different time intervals and range has been studied in the range from (5-120min) at 25°C. Figure (2) shows an increment in the percentage of adsorption of Oil hydrocarbons with the passage of time before reaching equilibrium state. Also it can be seen that, the percentages of adsorption was increased dramatically at the beginning of the first minutes of the adsorption, and then the increase was turned slowly until reaching saturation state. This is due to occupancy or filling of the adsorbent molecules of the most effective sites for adsorption on the surfaces of porcelanite [15] [16]. Equilibrium time was attained at 30min for Hydrocarbons adsorption over porcelanite. The removal percentage of Oil hydrocarbons in porcelanite powder for Hydrocarbons was found to be 41.61% and the equilibrium adsorption capacity was found to be (83.22mg/g).
Effect of initial concentration of Oil Hydrocarbons

The effect of Oil Hydrocarbons concentrations on the efficiency of adorption on the surface of porcelanite was investigated by taking different initial concentrations of Hydrocarbons in the range from (50-1500 mg/l) and this is shown in Figure 4. It was found through the results that, the percentage of removal of hydrocarbons was increased with a decrease in the initial concentration of Hydrocarbons. The removal percentage was around (32.92%) when using solutions of Hydrocarbons with a concentration of (1500 mg/L). Percentages of hydrocarbons removal was increased to (57.89%) when using solutions of Hydrocarbons with a concentration of (50 mg/L). The main reason for this increase in the percentage of adsorption with a decrease in concentration is due to the fact that the high values of the initial concentration contain relatively large numbers of ions of the elements under study, and thus occupy the largest number of active sites on the adsorbing surface, which leads to reduce the percentage of adsorbed ions. In case of low-concentration solutions, the number of ions dispersed in the aqueous solution is equivalent or approximately equal to the active groups present on the adsorbing surface, so the percentage of adsorption is higher [17][18].

Figure (4) The effect of hydrocarbons concentrations on the efficiency of adsorption over porcelanite

Effect of Adsorbent Particle Size

The impact of adsorbent particle size (surface area) on adsorption was studied by using three different sizes of sieves, these were (75, 120, 300μm). These experiment were performed by using a concentration of (1000mg/L) of Hydrocarbons of the weight 0.5g of the porcelanite at temperature (50 C).

The obtained results are shown in the Figure (5), from these results it is clear that, there was an increase in the quantity of Hydrocarbons adsorbed on porcelanite with a decrease in particle size. Such decrease of particle size of porcelanite causes an increase in the active sites on which the adsorbent is adsorbed, and an increase in the adsorption extent[19].
Figure (5) Effect of adsorbent particle Size (µm) on removal of hydrocarbons by adsorption over porcelanite

Adsorption isotherm

The effect of variation in temperature on adsorption of Hydrocarbons from aqueous solution over porcelanite was investigated at the range of temperatures, (25, 37.5, 50°C). According to the obtained results in this part, adsorption isotherms for adsorption of Hydrocarbons are shown in Figure (6). These results are presented in terms of the amount of adsorbent (Qe) on the vertical axis versus equilibrium concentration (Ce) on the horizontal axis at three different temperatures as mentioned above.

Figure (6) Adsorption isotherm of Hydrocarbons on porcelanite surface at different temperatures

From Figure (6), it is clear that, adsorption isotherms for adsorption of hydrocarbons on
porcelanite at different temperatures are of class (L-type) according to the (Giles) classification.
[20]. An isotherm equation model for Langmuir and Freundlich were applied to adsorption hydrocarbons from aqueous solutions on porcelanite. The consequences of applying Freundlich (eq.3) and Langmuir (eq. 4). The obtained results of adsorption isotherms are summarized in Table (1).

\[ \log Q_e = \log K_f + \frac{1}{n} \log C_e \] 

Where \( K_f \), \( n \) is the Freindlich constants represent the adsorption capacity and adsorption density, respectively.

\[ \frac{C_e}{Q_e} = \frac{1}{Qmb} + \frac{C_e}{Qm} \] 

Where \( Q_m \) is the maximum adsorption capacity when the adsorption surface is completely saturated in units (mg/g) Where \( b \) is the Lankmeier constant is related to the adsorption energy or equilibrium constant in units (L/mg).

Table (1) Results of Freundlich and Langmuir adsorption isotherms

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Freundlich constants</th>
<th></th>
<th>Langmuir constants</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( n )</td>
<td>Kf</td>
<td>( R^2 )</td>
</tr>
<tr>
<td>25.0</td>
<td>1.244</td>
<td>0.510</td>
<td>0.9996</td>
</tr>
<tr>
<td>37.5</td>
<td>1.241</td>
<td>0.536</td>
<td>0.9995</td>
</tr>
<tr>
<td>50.0</td>
<td>1.242</td>
<td>0.579</td>
<td>0.9997</td>
</tr>
</tbody>
</table>

The obtained results of adsorption isotherms were utilized in application of the mathematical equations for Freundlich and Langmuir adsorption isotherms by drawing the relationship between \( \log Q_e \) versus \( \log C_e \) and \( C_e /Q_e \) versus \( C_e \) respectively as shown in Figures (7) and (8). From the results listed in Table 1 above, it can be seen that, \( R^2 \) values for the Freundlich model greater than for Langmuir for adsorption process onto porcelanite. So that, Freundlich model is most applicable to process of adsorption of petroleum hydrocarbons on porcelanite and for all temperatures used in the study. This indicates that the adsorption process occurred on heterogeneous surfaces, that is, they have different sites in terms of adsorption energies, and here the adsorption is more than one layer, that is, it is multi layers adsorption. [21].
Figure (7) Freundlich adsorption isotherms for adsorption of hydrocarbons over porcelanite at different temperatures

Figure (8) Langmuir adsorption isotherms for adsorption of hydrocarbons over porcelanite at different temperatures

**Thermodynamic studies**

The effect of temperature on adsorption of hydrocarbons on the porcelanite surface was investigated at different temperatures in the range (25 - 50°C) using different concentrations of the adsorbate. The obtained results were utilized in calculation of thermodynamic values of Gibbs energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS) Using the following equation.

\[ \Delta G = -RT \ln K \] \hspace{1cm} \text{...................(5)}

\[ K = \frac{C_{\text{solid}}}{C_{\text{liquid}}} \] \hspace{1cm} \text{.............(6)}

\[ \ln K = \Delta S / R - \Delta H / RT \] \hspace{1cm} \text{.........(7)}

Where \( \Delta G \) is the change in free energy (KJ.mol\(^{-1}\)), \( K \) is the thermodynamic equilibrium constant for the adsorption process, \( C_{\text{solid}} \) is the Solid phase concentration (mg/L), \( C_{\text{liquid}} \) is the liquid phase concentration (mg/L), \( R \) is the general gases constant and \( T \) is absolute temperature in Kelvin (0.0083 KJ.mol\(^{-1}\) K\(^{-1}\)).
The values of ΔH (KJ.mol-1) and ΔS (KJ.mol-1.k-1) were calculated using equation (7) So we get a straight line relationship whose slope represents (-ΔH / R) and the cutoff represents (ΔS/R) [22]. The thermodynamic functions of the various studied temperatures are included in the table (2).

Table (2) Thermodynamic functions for adsorption of Hydrocarbons

<table>
<thead>
<tr>
<th>Co (mg/L)</th>
<th>298</th>
<th>310.5</th>
<th>323</th>
<th>ΔG</th>
<th>ΔH</th>
<th>ΔS</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>1.375</td>
<td>1.457</td>
<td>1.627</td>
<td></td>
<td>5.372</td>
<td>0.020</td>
</tr>
<tr>
<td>100</td>
<td>1.221</td>
<td>1.311</td>
<td>1.384</td>
<td></td>
<td>3.965</td>
<td>0.015</td>
</tr>
<tr>
<td>250</td>
<td>1.012</td>
<td>1.097</td>
<td>1.185</td>
<td>0.007</td>
<td>4.924</td>
<td>0.016</td>
</tr>
<tr>
<td>500</td>
<td>0.860</td>
<td>0.891</td>
<td>0.977</td>
<td>0.041</td>
<td>3.837</td>
<td>0.011</td>
</tr>
<tr>
<td>1000</td>
<td>0.712</td>
<td>0.776</td>
<td>0.844</td>
<td>0.853</td>
<td>5.276</td>
<td>0.014</td>
</tr>
</tbody>
</table>

Figure (9) shows the linear relationships of lnK values versus 1/(T) The correlation coefficient was (R² = 0.941– 0.9998) for adsorption of hydrocarbons on the surface of porcelain.

As seen from table (2), in terms of ΔG, it showed negative values at lower concentrations of adsorbate and then turned positive when concentrations were increased [23]. The results indicate that the ΔH values are positive, meaning that the adsorption process is endothermic, the results also showed that the values of (ΔH) for l ranged between (3.837) - (5.372) kJ. mol⁻¹, the (ΔH) values were all less than (40KJ.mol-1), and this indicates that it is a physical adsorption process [24], while the values of the entropy change (ΔS) for the adsorption process of
hydrocarbons on the surface under study were all positive values, which indicates that the adsorbed hydrocarbons are less uniform on the surface than in the solution [25].

Conclusion

The current study showed that porcellanite powder has a good efficiency for adsorption of hydrocarbons from its aqueous solutions. Some factors affecting the adsorption capacity were studied, such as contact time, initial concentration, Particle Size and temperature. The results of this study showed that the studied adsorption process reaches the contact time in a time of (30 min), The optimum of removal of hydrocarbons was (41.61%). and as for the adsorption capacity at equilibrium, its value was (83.22mg/g). According to the isothermal adsorption using Freundlich and Langmer model, the results showed that the adsorption isotherms of hydrocarbons obey the Freundlich equation. As the adsorption reaction was ΔG at the values were negative at lower concentrations and then turned positive when concentrations increased and the adsorption process was endothermic, From adsorption results, it is clear that it is possible to use the powder of porcellanite as an adsorbent surface to remove hydrocarbon pollution from its aqueous solutions.

References