

REMEDICATION OF PETROLEUM CONTAMINATED GROUNDWATER USING SAWDUST AS AN ADSORBENT*

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Abstract– Among the various adsorbents used, sawdust appears to be the most attractive material in terms of cost, versatility and abundance. In the present research, synthetic contaminated water with gasoline was used. Adsorption of petroleum compounds on four types of sawdust (Walnut, Poplar, Beech and Pine) was studied by using batch adsorption techniques. It was found that walnut sawdust has higher adsorption capacity than other types of sawdust. It was also observed that equilibrium adsorption capacity was a function of pH, temperature, and H₂O₂ concentration in solution. Maximum adsorption of petroleum compounds was obtained at pH 8. The adsorption of petroleum compounds was increased by decreasing the temperature and H₂O₂ concentration in the solution. The maximum equilibrium capacity of walnut sawdust was $84.03 \frac{\text{mg COD}}{\text{gr sawdust}}$ and 606.37

$\frac{\text{mg TPH}}{\text{gr sawdust}}$ obtained at pH 8 and+ a temperature of 10°C.

The experimental adsorption data were fitted to a Freundlich and Langmuir adsorption model. Calculated correlation coefficients indicated that the Freundlich model was best suited, indicating that the nature of walnut sawdust is heterogeneous.

In this study, to illustrate the relation between q_e , C_e , pH and temperature, regression analysis was taken into consideration. The obtained model (with $R^2=0.985$) improved the correlation coefficient at least 1.13% compared to the Freundlich model. The maximum and minimum error of the predicted values of q_e to the experimental data was obtained as 14.29% and 0.034% for regression model, while these errors for the Freundlich model were 52.15% and 1.63%.

Keywords– Petroleum compound, sawdust, groundwater remediation, TPH, COD, adsorption, isotherm, regression

1. INTRODUCTION

The penetration of petroleum contaminants into groundwater resources (as the most stable and safe resource of drinking water in Iran) has become a major environmental problem in Iran. Petroleum contamination in groundwater is mainly due to leakage of ground fuel storage tanks, gas stations, oil pipe transmission and the activities of refineries and other petroleum industries [1].

According to studies by W.H.O. (1996), regions whose distance to gas station or industries (which have ground fuel storage tanks with leakage probability) is less than 0.5 miles encounter a greater risk of water contamination compared to other regions [2]. By taking samples from water wells around the oil refineries of Iran, the contamination of groundwater with petroleum compounds has been proven, the contamination of groundwater near the Isfahan, Shiraz and Tehran refineries can be mentioned [1].

The presence of petroleum compounds in water has unfavorable effects on human health. For example, MTBE (Methyl tertiary butyl ether) used as a gasoline additive to increase octane levels is a resistant compound in the environment. MTBE inhalation can cause headaches, nausea, dizziness, irritation of the nose or throat and feelings of confusion [3]. Swallowing Benzene (another important

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gasoline compound) via food or water is a definite cause of cancer. This compound can cause anemia, difficulty in breathing and weakness in the body defense system [4]. For these reasons, investigation on the remediation of petroleum contamination, especially in water resources, is an important issue.

Treatment methods for petroleum contaminated groundwater are classified into physical- chemical and biological methods. Filtration, adsorption, chemical oxidation and air stripping methods are among the most common physical and chemical methods of treatment of petroleum contaminated water. Adsorption technologies are the most effective methods to remove organic matter from water. Adsorption of petroleum compounds by many types of adsorbents such as organo clay [5, 6], activated carbon [7], zeolite [8] and peat [9] has been taken into consideration. In order to select a proper adsorbent to perform treatment, parameters such as the adsorption capacity of contaminants by adsorbents, the decrease of contaminant toxicity, practicality, and the existence of some practical and economic methods for the regeneration of adsorbents must be considered [8].

Recently, the use of low cost agricultural by-products such as pine bark, rice straw, rice hull, rice bran, wool, sawdust, etc. as adsorbents for removing heavy metals from contaminated water has been documented [10–13]. Sawdust is an easily available by-product in the timber and paper industry. It is inexpensive and when saturated with petroleum compounds, can be used as fuel in power plants. It also exhibits good sorbent characteristics for the treatment of wastewater containing heavy metals [10–15], dyes [16–17], or phenolic compounds [18–19], (these results have been mentioned in Table 1)).

Table 1. Some conducted studies by adsorption with low cost agricultural by-products

Adsorbent	Adsorbate	Adsorbent dosage (g/L)	Initial concn. (mg/L)	Temperature (°C)	pH	Time of contact	Adsorption capacity (mg/g)	Reference
Maple sawdust	Cu(II)	40	50	23	7	24 h	1.79	[10]
Maple sawdust	Pb	40	50	23	7	24 h	3.19	[10]
Sawdust of <i>P. sylvestris</i>	Pb	1	5	25	5	1 h	9.78	[12]
Sawdust of <i>P. sylvestris</i>	Cd(II)	1	5	25	5	1h	9.22	[12]
Maple Sawdust	Ni	50	3	23	9	24 h	-	[13]
Teakwood sawdust	Zn(II)	10	3	30	5	3 h	14.10	[14]
Teakwood sawdust	Cd(II)	10	3	30	6	3 h	26.73	[14]
Sugarcane bagasse	Ni (II)	10	140	25	5	2 h	2.1	[15]
Pine sawdust	Acid Blue 256	5	2000	25	3.5	2 h	280.3	[16]
Pine sawdust	Acid Yellow 132	5	2000	25	3.5	2 h	398.8	[16]
Indian Eucalyptus sawdust	Brilliant green dye	4	50	15	2.9	3 h	58.48	[17]
tobacco residues	Phenol	0.5	12	2	8	4 h	45.49	[18]
Coca shell	4-nitrophenol	1.6	100	30	7	-	167.17	[19]

In this laboratory research, first, the ability of four different types of sawdust to adsorb petroleum contaminants is investigated. By selecting the sawdust with the greatest adsorption ability, the effect of

pH, temperature and usage of H_2O_2 on adsorption ability were examined. Then, adsorption isotherm was determined and simulated using Freundlich and Langmuir models. Finally, the relation between pH, temperature, adsorption capacity and concentration in equilibrium state was determined by using regression analysis.

2. MATERIALS AND METHODS

a) Materials and instruments

1. Contaminated water:

- Location of contaminated area

Groundwater samples were collected from an existing well at a distance of 1025 meters from Isfahan refinery (approximately depth of 80 m). The Isfahan refinery lies between latitudes $32^{\circ}46'N$ and $32^{\circ}47'N$ longitudes $51^{\circ}29'E$ and $51^{\circ}30'E$. It's located approximately 10 Km north-west of Isfahan. The climate of the area in which the samples were collected is semiarid with mostly cold winters. Its reception of an annual rainfall is approximately 120 mm and the annual average temperature is $15.6^{\circ}C$ [20].

- Characteristics of contaminated water:

Seventy samples from an existing well over a 2 year period (2006-2007) were collected and analyzed by water laboratory of the Isfahan oil refinery. Hydrocarbons found in water samples (by GC-Mass) were compared with the range of these compounds in gasoline [21]. As an example, aromatic hydrocarbon with 9 carbon atoms measured 6.5%, whereas the range of this compound in gasoline is 1.46- 7.44%. Finally, Leakage history in the Isfahan refinery and GC-Mass analysis on the collected samples revealed that the reason for groundwater contamination in the region is the gasoline leakages from pipes and fuel storage tanks.

In this research, synthetic contaminated water was used because of environmental parameter alterations (such as changes in contaminated concentration). The synthetic contaminated water was produced by adding 2.5 volumetric percent of gasoline to distilled water. The 2.5 volumetric percent of gasoline was selected because statistical distribution of groundwater samples taken from the contaminated site showed that 90% of the samples had gasoline contamination of less than 2.5 volumetric percent. Initial COD and TPH concentrations of synthetic contaminated water were measured to be 1769.25 mg/L (maximum, minimum and variances of measured values are 1825.01, 1715.05 and 38.36, respectively) and 13191.73 mg/L (maximum, minimum and variances of measured values are 13521.16, 13034.12 and 159.63, respectively).

2. Characteristics of adsorbents:

In order to compare the adsorption ability of petroleum compounds by sawdust, four types of sawdust originating from walnut, poplar, beech and pine wood were used in this research. These sawdusts were passed through #35 sieves (0.5 mm in diameter) and then washed three times with distilled water and dried in an oven at $105^{\circ}C$ for 24 hr. Their characteristics were determined by the American Standard Testing Method (ASTM) and are shown in Table 2.

Table 2. Characteristics of adsorbents determined by ASTM

Type of Sawdust	Specific Area (m^2/gr)	Density (Kg/m^3)	Moisture content (%)	Ash content (%)	Volatile matter (%)
	Method # C204-00	Method # D5057-90	Method # E871-82	Method # E1534-93	Method # E872-82
Walnut	1.256	0.239	3.8	1.326	95.37
Poplar	1.05	0.333	3.204	4.803	94.529
Beech	0.911	0.281	5.638	5.815	91.555
Pine	1.084	0.264	3.913	2.584	95.087

3. Instruments and materials:

pH measurements were obtained using pH meter (Hach sens ion^{TM3}), constant temperatures were obtained with an incubator (Mettmert model Bv80RI-Western Germany), and hydrogen peroxide solution 30% (Merck, Germany) was used for the desired concentration of H₂O₂.

Phosphate buffer at 0.05 M was used in the solution to minimize fluctuations. Solutions were adjusted to the desired pH by using HCl (assay 36.5%-38% ACS grade, Merck, Germany) and NaOH (assay 50%, Merck, Germany).

b) Experimental set up and analysis

Adsorption experiments were carried out using the batch technique, and glass bottles were used as contactors. The bottles were pre-rinsed with chromic acid, soap and distilled water three times. In each adsorption experiment, 500 ml aqueous solution of the desired pH and H₂O₂ concentration was added to 10 grams of sawdust at the desired temperature. The range of pH was 5-9 and that of temperature was 10-30°C (the ranges of pH and temperature in groundwater). H₂O₂ was added to the system for testing the effect of the adsorption capacity of sawdust due to the oxidation of the adsorbed contaminants on sawdust (regeneration of sawdust). The range of added H₂O₂ concentration was 0-6.66 mg/L.

For any experimental condition, 3 sets of samples were used as shown in Table 3. One set was a sample containing the adsorbent and petroleum contaminated water (A contactors). The second set contained adsorbent and distilled water that was used for measuring the probable leakages of COD and TPH from the sawdusts (B contactors). The third set contained only petroleum contaminated water that was used for measuring the probable reduction of COD and TPH from the solution (by volatilization and/or adsorption to glass bottle wall and/or oxidation by H₂O₂) (C contactors).

Table 3. Experimental plan

Purpose of experiment	Name of contactor	Volumetric percent of gasoline in water	Mass of sawdust (gr)				pH	Temperature (°C)	Concentration of H ₂ O ₂ (mg/L)
			Walnut	Poplar	Beech	Pine			
Effect of sawdust type	A	2.5	10	10	10	10	8,9	10,15	0
	B	0	10	10	10	10	8,9	10,15	0
	C	2.5	0	0	0	0	8,9	10,15	0
Effect of pH	A	2.5	10	0	0	0	5,6,7,8,9	15	0
	B	0	10	0	0	0	5,6,7,8,9	15	0
	C	2.5	0	0	0	0	5,6,7,8,9	15	0
Effect of temperature	A	2.5	10	0	0	0	8	10,15,20,30	0
	B	0	10	0	0	0	8	10,15,20,30	0
	C	2.5	0	0	0	0	8	10,15,20,30	0
Effect of H ₂ O ₂ concentration	A	2.5	10	0	0	0	8	15	0,3.33,6.66
	B	0	10	0	0	0	8	15	0,3.33,6.66
	C	2.5	0	0	0	0	8	15	0,3.33,6.66

The solution in bottle contactors was mixed slowly by a magnet stirrer. Samples were taken at 5, 15, 30, 45, 60, 120, 240, 300 and 1440 min. The COD of the samples was determined by closed reflux method described by the American Public Health Association (5220 D.) and the TPH of the samples was also undertaken using a procedure described by the American Public Health Association (5520 F.) [22].

Determination of concentration

As mentioned in section 2-2, in order to account for the effect of leakage from sawdust, the volatilization of petroleum compounds from the solution, adsorption to the container wall or the petroleum compound oxidation, three sets of contact containers (A, B, C) were used. To consider the mentioned

effect, the actual concentration of contaminant in the solution (C_{actual}) was determined by the following mass balance:

$$\text{Accumulation of contaminant} = \text{input} - \text{output} - \text{decay} + \text{generation}$$

C_0 minus C_A is expressed as the term of accumulation and input concentration in this control volume is zero. The output concentration is determined with contactor C. Adsorbed contaminant to the adsorbent surface is fate terms (C_F), generation is probable leakage from the sawdust particle or container surface which can be determined from contactor B. Therefore the mass balance can be written as:

$$(C_0 - C_A) \cdot (V/t) = (0) \cdot (V/t) - (C_C - C_0) \cdot (V/t) - (C_F) \cdot (V/t) + (C_B) \cdot (V/t) \Rightarrow C_F = C_B + C_C - C_A$$

On the other hand, C_0 minus C_{actual} is expressed as the contaminant absorbed on sawdust (C_F) ($C_F = C_0 - C_{\text{actual}}$). Therefore, the above mass balance can be written as follows:

$$C_{\text{actual}} = C_A - C_B + (C_0 - C_C) \quad (1)$$

q (mg of contaminant per gr of adsorbent) is obtained by a mass balance in the solid phase:

$$q \times M = (C_0 - C_{\text{actual}}) \times V \Rightarrow q = \frac{(C_0 - C_{\text{actual}}) \times V}{M} \quad (2)$$

Equations (1) and (2) were used in this study to determine the concentration of the petroleum compound and the solid phase concentration (q) in the samples during the experiment.

3. RESULTS AND DISCUSSION

a) Effect of sawdust types

Three experimental conditions (pH=8 T=15°C, pH=8 T=10°C and pH=9 T=15°C) were considered to investigate the effect of sawdust types on the adsorption of petroleum compounds. The maximum reduction of COD during the experiments in C contactors (pH=8, T=10°C) was 1.46% due to probable volatilization and probable adsorption on the walls of contactors. Maximum COD leached from sawdust to distilled water in B contactors (pH=9, T=15°C, walnut sawdust) was 582.05 mg/L due to the solution of sawdust organic matter in water.

The variation of actual petroleum concentration (as calculated COD by equation (1)) versus time is shown in Fig. 1 for four types of sawdust. Fig. 1 shows that in all conditions, the rate of adsorption in the first 5 minutes is rapid due to the high concentration gradient between the solution and the solid surface and over 70% of COD removal was obtained during this time period. Fig. 1 also shows that equilibrium was reached in 2 hours for all types of sawdust. In samples with walnut sawdust as the adsorbent, the value of COD is lower than others. It can be concluded that walnut sawdust was more effective in removing petroleum compounds. Other types of sawdust (poplar, beech and pine) had the same adsorption capacity for petroleum compounds.

q_e for all types of sawdust is shown in Fig. 2. Fig. 2 shows that maximum adsorption capacity was obtained in equilibrium state at pH=8 and T=10°C by walnut (84.03 mg/g). While for poplar, beech and pine sawdust, adsorption capacities at pH=8 and T=10°C were 69.63, 67.807 and 70.511 mg/g, respectively. The higher adsorption capacity of walnut sawdust can be related to its relatively higher specific surface area. Therefore, walnut sawdust was considered as the best sawdust among the four types tested, and it was selected for further investigation. Fig. 2 also shows that the difference between maximum and minimum values of q_e was 22.52%.

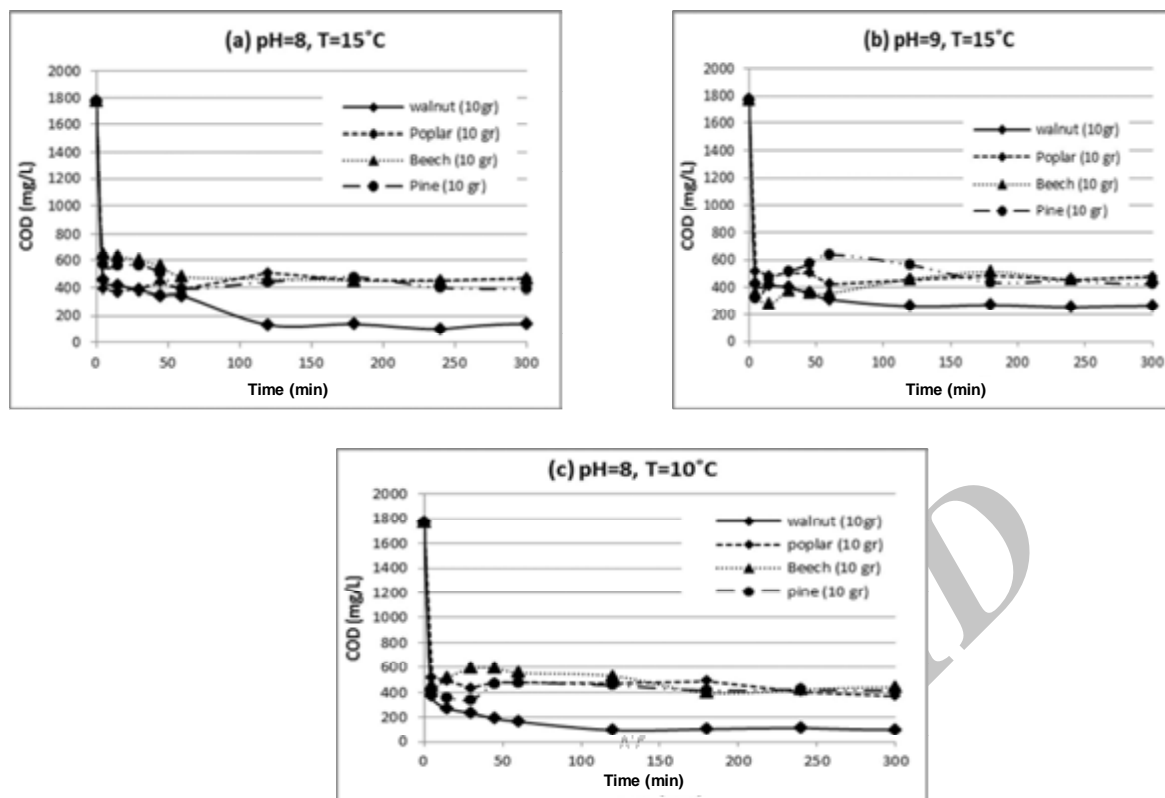


Fig. 1. Actual COD (C_{actual}) in solution versus time (a) pH of solution is 8 and temperature is 15°C (b) pH of solution is 9 and temperature is 15°C (c) pH of solution is 8 and temperature is 10°C

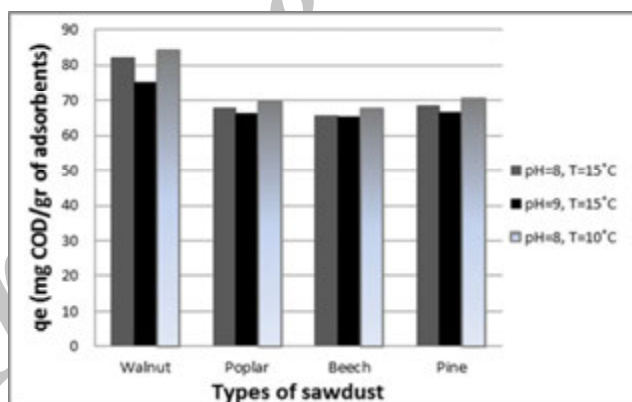


Fig. 2. Solid phase adsorption capacity at equilibrium state for different types of sawdust (adsorbent dosage 20 g/L, initial concentration of COD 1769 mg/L)

b) Effect of pH

pH is one of the most important parameters controlling the adsorption process. The adsorption ability of petroleum compounds by walnut sawdust was studied at pH 5, 6, 7, 8 and 9 all at 15°C. Maximum reduction of COD and TPH during the experiments in C contactors (pH=5) were 1.53% and 8.92%, respectively. This reduction is due to the volatilization and adsorption to the walls of the contactors. TPH concentration in all B contactors was zero and the maximum COD in the B contactors (pH=9) was 582.05 mg/L due to the sawdust leakage in water.

Figures 3a and 3b show actual concentration of COD and TPH at different pH versus time. As these figures indicate, the slope of the curve in the first 5 minutes is sharp due to the high concentration gradient which was available between the solution and the solid surface. The maximum COD and TPH removals in

the first 5 minutes were 79.03% and 42.23%, respectively. These figures also illustrate that the samples were equilibrated after 120 min for COD and 300 min for TPH.

Figures 4a and 4b show q_e expressed as COD and TPH at different pHs for walnut sawdust. These figures show that q_e is maximum (for COD, 82.029 mg/g and for TPH, 589.4326 mg/g) at pH 8. The difference between the maximum and minimum values of q_e as COD and TPH were 18.39% and 3.21%, respectively, for the tested pHs.

The affinity of organic matter for adsorption is an important function of pH. When pH is in a range where the molecule is in the natural form, the adsorption capacity is relatively high. When pH is in a range where species is ionized, the affinity for water is high and adsorbent capacity is accordingly low [23].

The observations from Fig. 4 can also be justified as follows. The petroleum compound (gasoline) investigated is a combination of aromatic and aliphatic compounds [21]. These compounds involve C—H bonds in which H attached to an unsaturated carbon or carbon radical. The phenomenon that occurs about these compounds- especially compounds with more H bonds (most compounds in gasoline) - is Hyperconjugation. Hyperconjugation can cause the ionization of compounds due to the release of H^+ [24].

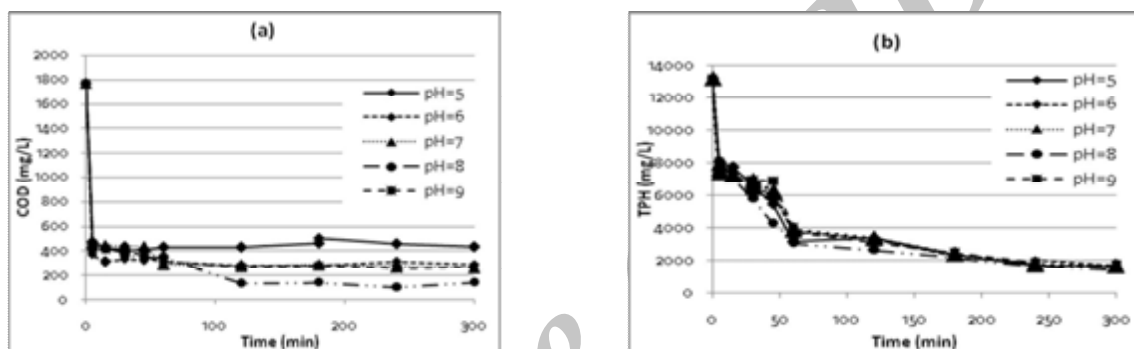


Fig. 3. (a) Actual COD (C_{actual}) in samples versus time at different pH and $T=15^{\circ}C$
(b) Actual TPH (C_{actual}) in samples versus time at different pH and $T=15^{\circ}C$

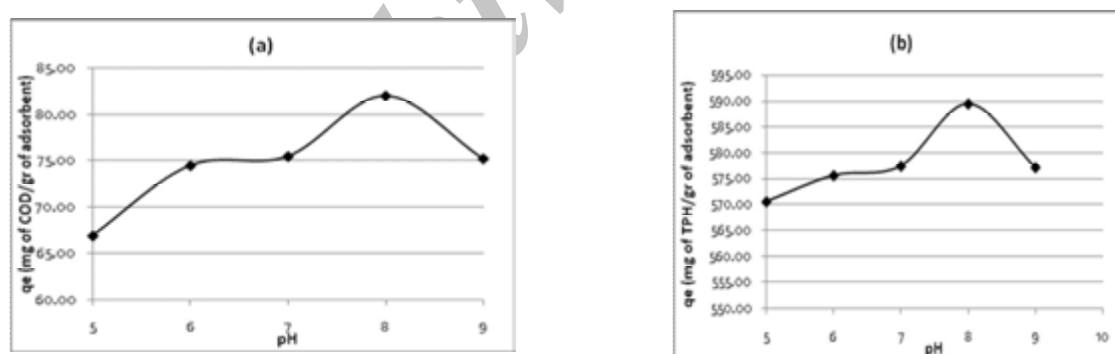


Fig. 4. (a) Adsorption capacity of walnut sawdust in equilibrium state (q_e) as COD at different pHs and $T=15^{\circ}C$ (b) Adsorption capacity of walnut sawdust in equilibrium state (q_e) as TPH at different pHs and $T=15^{\circ}C$

At low pHs, in which the concentration of H^+ is high, the surface attraction between H^+ and the carboxylic groups (with negative charges) on the sawdust surface is more than the surface attraction between the petroleum compounds and the carboxylic groups. Therefore, the adsorbed H^+ on the sawdust surface can probably decrease the adsorption sites for petroleum compounds. The decrease in adsorption sites due to the presence of H^+ ions was responsible for the lower adsorption of metals to the sawdust [13].

The slight decrease in adsorption capacity at pH 9 compared to pH 8 can be explained as follows. At pHs higher than pK_a , the gasoline compounds are in ionized form [24]. Some factors such as high

solubility of the dissociated form of the compounds, the repulsive force between the anionic species and the competition of OH^- for active sites, may have caused such a result. As the OH^- ion is more mobile than the ionized petroleum compounds, it can easily get to adsorption sites. Therefore, at high pHs where the concentration of OH^- is high, the OH^- can compete with ionized petroleum compounds and decrease the adsorption of petroleum compounds on the sawdust surface.

For the above-mentioned reasons, the maximum adsorption capacity for petroleum compounds by sawdust was obtained at pH 8. Similar results were obtained for the adsorption of organic matters such as 2,4-dichlorophenol and phenylalanine to activated carbon [13, 25].

c) Effect of temperature

In order to determine the adsorption ability of sawdust at different temperatures, experiments were conducted at 10, 15, 20 and 30 °C. The pH was kept constant at 8. Maximum reduction of COD and TPH during the experiments in C contactors ($T=30^\circ\text{C}$) were 1.46% and 8.61%, respectively. This reduction is probably due to volatilization and adsorption to the contactor wall. TPH concentration in all B contactors was zero and the maximum COD in B contactors ($T=10^\circ\text{C}$) was 582.02 mg/L due to sawdust leakage into water.

Variation of petroleum concentration expressed as COD and TPH versus time at different temperatures is shown in Figs. 5a and 5b. As these figures show, in all temperatures, the rate of adsorption in the first 5 minutes is rapid and 78.88% of maximum COD removal and 38.1% of maximum TPH removal were obtained during this time period. The higher removal rate in this time period is due to the high concentration gradient between the solution and the solid surface. These figures also illustrate that all samples were equilibrated after 3 h for COD and 5 h for TPH.

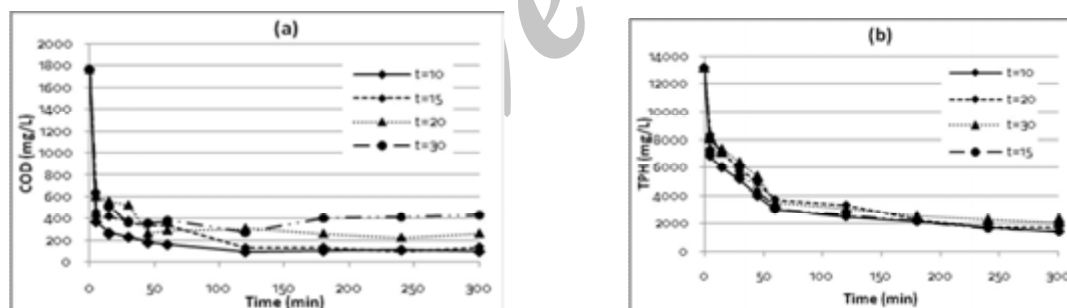


Fig. 5. (a) Actual COD (C_{actual}) in samples versus time at different temperature and pH 8 (b) Actual TPH (C_{actual}) in samples versus time at different temperature and pH8

Values of q_e expressed as COD and TPH at different temperatures are presented in Figs. 6a and 6b. It can be seen from these figures that walnut sawdust has the greatest adsorption ability of the petroleum compounds from contaminated water at 10°C . In these conditions, the adsorption capacity for COD and TPH from contaminated water by walnut sawdust at equilibrium state was calculated to be 84.03 and 606.3665 mg/g, respectively. Minimum adsorption capacity was obtained at 30°C . The differences between the maximum and minimum values of q_e as COD and TPH were 23.55% and 8.19%, respectively.

As the temperature increases the kinetic motion of molecules increases and the lower adsorption capacity at higher temperature is due to breaking of weak adsorption bonds between the contaminants and the adsorbent surface [26]. The findings of the present study are in agreement with previous researches [13, 27].

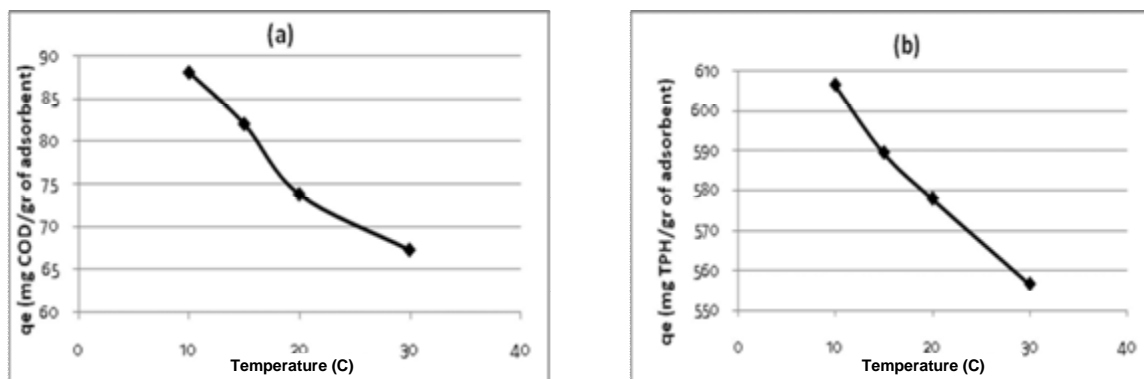


Fig. 6. (a) Adsorption capacity of walnut sawdust in equilibrium state (q_e) as COD at different temperature and pH 8 (b) Adsorption capacity of walnut sawdust in equilibrium state (q_e) as TPH at different temperature and pH 8

d) Effect of hydrogen peroxide concentration

In order to investigate the effect of Hydrogen peroxide on the adsorption ability of petroleum compounds by walnut sawdust, H_2O_2 at concentrations of 0, 3.33 and 6.66 mg/L was added to the contactors. In these experiments, pH and temperature were kept constant at 8 and 15°C , respectively. TPH concentration in all B contactors was zero and the maximum COD in the B contactors ($C_{H_2O_2}=6.66$ mg/L) was 552.3 mg/L due to sawdust leakage into water.

Variations of the petroleum concentration (as COD and TPH) versus time for different H_2O_2 concentrations are shown in Figs. 7a and 7b. As these figures indicate, the slope of concentration reduction is sharp in the first 5 minutes due to the high concentration gradient which is available between the solution and the solid surface during this time period, and 73.99% of the maximum COD removal and 42.57% of the maximum TPH removal was reached in this time period. These figures illustrate that samples were equilibrated after 3 h for COD and 5 h for TPH.

Values of solid phase concentration (q_e) expressed as COD and TPH for different concentrations of H_2O_2 are presented in Figs. 8a and 8b. As these figures show, the adsorption capacity of the walnut sawdust was at maximum (82.029 mg/g and 589.4326 mg/g for COD and TPH, respectively) when the H_2O_2 concentration was minimum ($C_{H_2O_2}=0$ mg/L). Minimum sawdust adsorption capacity was observed at high H_2O_2 concentration ($C_{H_2O_2}=6.66$ mg/L). The difference between the maximum and minimum values of q_e as COD and TPH were 37.49% and 26.22%, respectively. The reason for such observation is discussed in the next paragraph.

The above experimental observation can be related to H_2O_2 oxidant power. It can be hypothesized that the H_2O_2 can decrease the adsorption driving force by changing the initial concentration of the petroleum compounds in the solution. To prove this hypothesis, different H_2O_2 concentrations were added to contaminated water samples with no adsorbent. Figures 9a and 9b illustrate the COD and TPH reduction in these samples. These figures show that the maximum reduction of COD and TPH at $C_{H_2O_2}=0$ are 1.44% and 8.54%, respectively. The slight changes are due to the volatilization and adsorption of the petroleum compounds to the contactor wall. These figures also show that the maximum reduction of the initial concentration of COD and TPH (12.56% for COD and 29.41% for TPH) was obtained at maximum H_2O_2 concentration ($C_{H_2O_2}=6.66$ mg/L). Because H_2O_2 is a strong oxidant, it oxidizes the petroleum compounds. As Fig.9 shows, the higher reduction of petroleum compounds concentration was obtained at the higher H_2O_2 concentration. Therefore, the initial concentration reduction of petroleum compounds is greater at the higher H_2O_2 concentration. This phenomenon will decrease the driving force for the adsorption of the contaminant to sawdust, and this is the reason for the lower adsorption capacity at the higher H_2O_2 concentration.

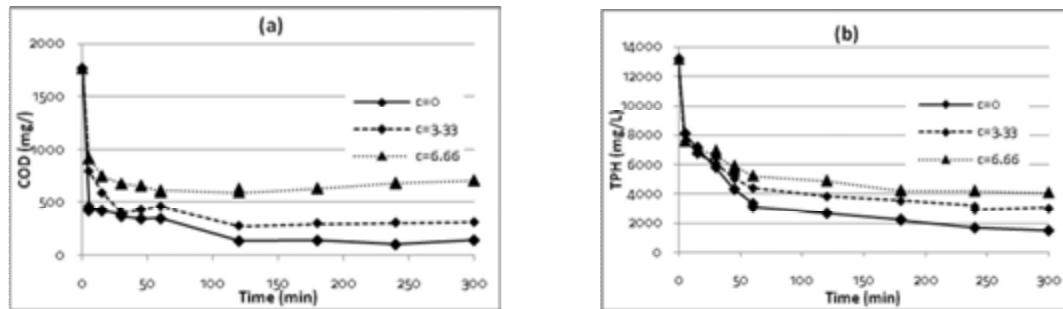


Fig. 7. (a) Actual COD (C_{actual}) in samples versus time at different H_2O_2 concentration in solution (pH 8 and $T=15^\circ C$) (b) Actual TPH (C_{actual}) in samples versus time at different H_2O_2 concentration in solution (pH 8 and $T=15^\circ C$)

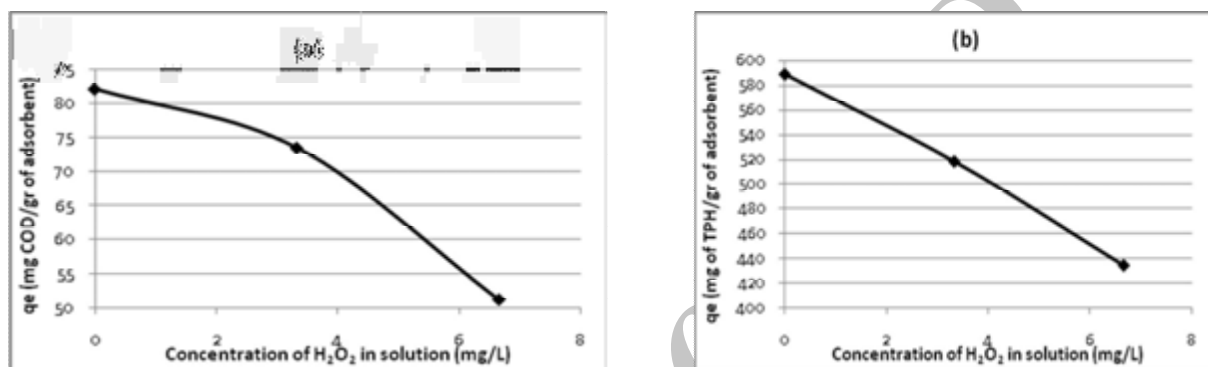


Fig. 8. (a) Adsorption capacity of walnut sawdust in equilibrium state (q_e) as COD at different H_2O_2 concentration in solution (pH 8 and $T=15^\circ C$) (b) Adsorption capacity of walnut sawdust in equilibrium state (q_e) as TPH at different H_2O_2 concentration in solution (pH 8 and $T=15^\circ C$)

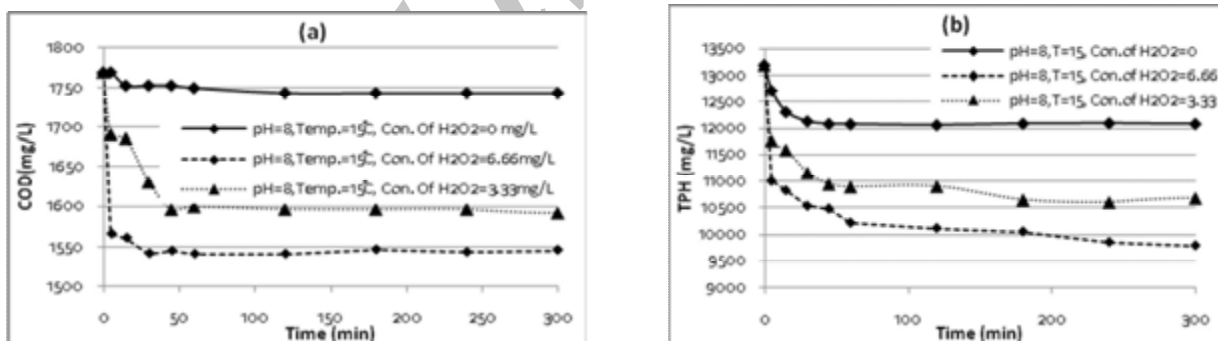


Fig. 9. (a) COD reduction in samples with no adsorbate (pH 8 and $T=15^\circ C$) (b) TPH reduction in samples with no adsorbate (pH 8 and $T=15^\circ C$)

e) Adsorption isotherms modeling

The equilibrium adsorption isotherm is fundamentally important in the design of adsorption systems. Equilibrium studies in adsorption show the capacity of the adsorbent. It is described by the adsorption isotherm characterized by certain constants whose values express the surface properties and affinity of the adsorbent [23].

Two well-known equilibrium models (linear form of Freundlich and Langmuier) were used in order to model the adsorption isotherms (Eq. (3) and (4), respectively) [24]:

$$\log q_e = \log K_f + \left(\frac{1}{n}\right) \log C_e \quad (3)$$

$$\frac{C_e}{(x/m)} = \frac{1}{(b \cdot q_{\max})} + \frac{1}{(q_{\max})} C_e \quad (4)$$

Where q_e (mg/g) is the adsorption capacity in equilibrium state, C_e (mg/L) is the unadsorbed petroleum compound concentration in the solution at equilibrium (as COD or TPH), q_{\max} is the maximum amount of the petroleum compound bound per unit weight of adsorbent to form a complete monolayer on the surface (mg/g), b is a Langmuir constant related to the energy of adsorption (L/mg), and K_f and n are the Freundlich constants.

Figures 10a and 10b show the variation of q_e versus C_e as COD and TPH, respectively (at pH 8, $T=10^\circ\text{C}$ and $C_{\text{H}_2\text{O}_2}=0$). The values of the Langmuir constants (q_{\max} and b) and Freundlich constants (K_f and n) with the correlation coefficients are presented in Table 3 for COD and TPH at different experimental conditions.

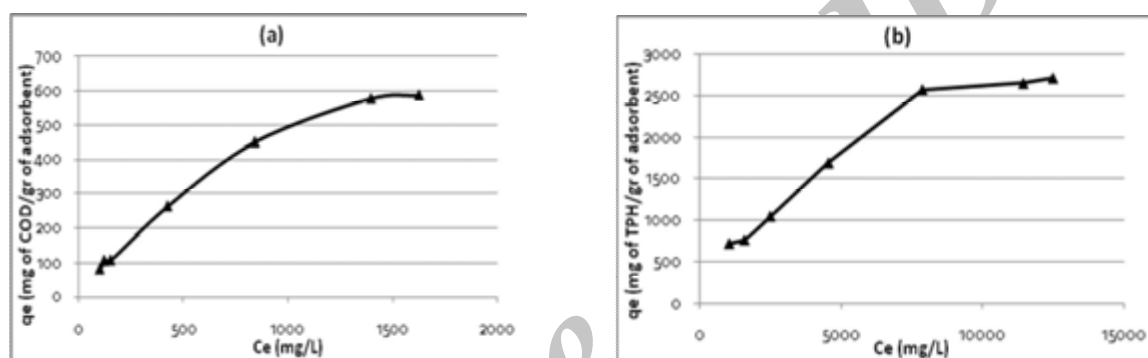


Fig. 10. (a) The q_e values: experimental for COD adsorption on walnut sawdust (at pH 8 and $T=10^\circ\text{C}$), (b) The q_e values: experimental for TPH adsorption on walnut sawdust (at pH 8 and $T=10^\circ\text{C}$)

The values of the correlation coefficient (R^2) in Table 4 indicate that the Freundlich isotherm is best suited for the adsorption of petroleum compounds on walnut sawdust. The Freundlich type adsorption isotherm is an indication of the surface heterogeneity of the adsorbent while the Langmuir model shows the surface homogeneity of the adsorbent. The experimental results best suited the Freundlich model, leading to the conclusion that the nature of the walnut sawdust surface is heterogeneous.

Table 5 shows the value of n , K_f and R^2 for the Freundlich model at the tested conditions.

Table 4. The comparison of the individual constants obtained from Langmuir and Freundlich adsorption isotherms for COD and TPH parameters (at pH 8 and $T=10^\circ\text{C}$)

Experimental parameter	Langmuir isotherm			Freundlich isotherm		
	q_{\max} (mg/g)	b (L/mg)	R^2	K_f [(mg/g)(L/mg) ^(1/n)]	n	R^2
COD	1000	0.00088	0.6789	1.020	0.519	0.954
TPH	5000	0.00012	0.930	8.184	1.626	0.970

Table 5. Constants obtained from Freundlich model

Experimental conditions	pH	5	6	7	8	9	8	8	8
	Temperature ($^\circ\text{C}$)	15	15	15	15	15	10	20	30
Freundlich isotherm	K_f [(mg/g)(L/mg) ^(1/n)]	0.025	0.031	0.076	0.218	0.041	0.519	0.052	0.017
	n	0.719	0.743	0.806	0.922	0.758	1.020	0.774	0.703
	r^2	0.879	0.890	0.900	0.974	0.922	0.954	0.924	0.930

f) Modeling effect of pH and temperature on equilibrium adsorption

To illustrate the relation between q_e , C_e , pH and T, 2823 models (from Table Curve software) such as:

- 1) $q_e = a \log c_e + b \log \text{pH} / \log T$ $R^2 = 0.939$
- 2) $q_e = a \log c_e + b \log (\text{pH} + T)$ $R^2 = 0.909$
- 3) $q_e = a \log c_e + b \text{pH} \cdot T$ $R^2 = 0.903$
- 4) $q_e = a \log c_e + b \text{pH} + c \log T$ $R^2 = 0.929$
- 5) $q_e = a \log c_e + b \log \text{pH} + c T$ $R^2 = 0.927$

were considered. Regression analysis showed that the effect of pH and temperature on equilibrium adsorption can be best described by Eq. (5).

$$q_e = 1.015C_e + 34.281.T - 0.00033C_e^2 - 6.156T^2 - 0.807 \text{pH}^2.T + 0.806T^2 \text{pH} - 11.435 \quad (5)$$

The correlation coefficient of this model which was obtained by regression was $R^2 = 0.985$. Two different experimental conditions, values of predicted q_e by the Freundlich model and the Regression model (Eq. (7)) and calculated q_e from the experimental data are shown in Fig. 11. The values of R^2 and Fig. 11 indicate that the Regression model for all conditions was better suited than the Freundlich model. The obtained model improved the correlation coefficient at least 1.13% compared to Freundlich model. These figures also show that the Regression and Freundlich models had no significant differences at low value of C_e , whereas at a higher value of C_e these models showed significant differences. The maximum and minimum error of the predicted values of q_e to the experimental data was obtained 14.29%, 0.034% for Regression model, while for the Freundlich model the errors were 52.15% and 1.63%.

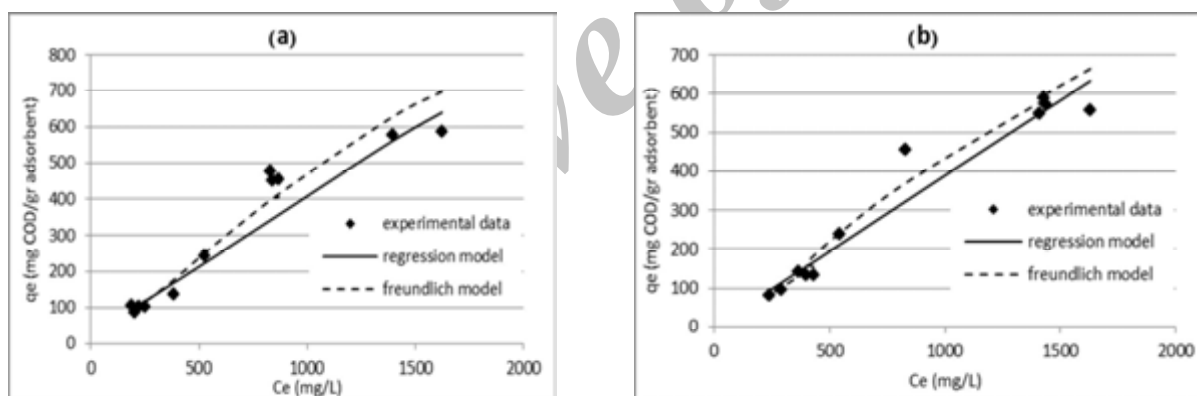


Fig. 11. The experimental, Freundlich and regression model values of q_e versus C_e
(a) pH 8 and T=10°C, (b) pH 8 and T=15°C

4. CONCLUSION

The performances of four types of sawdust as adsorbents (Walnut, Poplar, Beech and Pine) to remove petroleum compounds from aqueous solution have been investigated. It was found that the adsorption ability of walnut sawdust to remove petroleum compounds from water was more than the other types of studied sawdust.

Experimental results showed that the adsorption of petroleum compounds was dependent on the pH, temperature and H_2O_2 concentration in the solution. Maximum adsorption capacity was obtained at pH 8. Adsorption of petroleum compounds was increased by decreasing the temperature, and maximum adsorption occurred at T=10°C. Addition of H_2O_2 decreases the adsorption capacity of the sawdust due to lowering the initial petroleum compounds concentration in the solution, which decreases the driving force.

In this experiment, the maximum equilibrium capacity of walnut sawdust for COD and TPH were 84.03 mg COD/g adsorbent and 606.37 mg TPH/ g adsorbent (at pH 8, 10°C and $C_{H_2O_2}=0$).

Equilibrium isotherms were measured experimentally and simulated by two well-known models (Freundlich and Langmuir). The Freundlich model was found to describe the data best. This leads to the conclusion that walnut sawdust is more heterogeneous. According to the Freundlich isotherm, the constants (K_f and n) of the walnut sawdust were 3.076 [(mg/g).(L/mg)^(1/n)] and 1.381 for COD measuring, respectively, while they were 10.739 [(mg/g).(L/mg)^(1/n)] and 1.709 for TPH measuring, respectively.

In this study, to illustrate the relation between q_e , C_e , pH and temperature, Regression analysis was considered. The obtained model (with $R^2=0.985$) improved the correlation coefficient at least 1.13% compared to the Freundlich model. The Regression and Freundlich models had no significant differences at low value of liquid phase concentration (C_e), but by increasing the value of C_e these models showed significant differences. The maximum and minimum errors of the predicted values of q_e to the experimental data were obtained as 14.29% and 0.034% for the Regression model, 52.15% and 1.63% for the Freundlich model.

NOMENCLATURE

Initial concentration	C_0
Concentration in contactor A	C_A
Concentration in contactor B	C_B
Concentration in contactor C	C_C
Adsorbed contaminant to adsorbent surface	C_F
Volume of contactor	V
Time	t
Actual concentration in solution	C_{actual}
Solid phase concentration (mg of contaminant per gr of adsorbent)	q
Mass of the adsorbent	M
Solid phase concentration at equilibrium	q_e
Acid-ionization constants	pK_a
Unadsorbed concentration in solution at equilibrium (mg/L)	C_e
Monolayer maximum adsorption capacity (mg/g)	q_{max}
Langmuir constant (L/mg)	b
Freundlich constants	K_f and n
Correlation coefficient	R^2
Temperature	T

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