

Original Article

Direct Blue 71 Removal from Aqueous Solutions by Adsorption on Pistachio Hull Waste: Equilibrium, Kinetic and Thermodynamic Studies

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Abstract

Background and Purpose: Azo dyes including Direct Blue 71 (DB71) are toxic, mutagenic and carcinogenic contaminants in effluents of industries. This study aimed to investigate the adsorption of DB71 from aqueous solution onto pistachio hull waste (PHW) as a low-cost adsorbent.

Materials and Methods: A series of experiments were performed via batch adsorption technique to examine the effect of the process variables such as contact time 0-210 minutes, initial dye concentration 10-100 mg/l, pH 2-12, adsorbent 0.05-1 g/l, and the processing temperature of 25, 40, and 50° C. The concentration changes of DB71 were measured using the colorimetric method by the spectrophotometer T80 ultraviolet/visible at the 587 nm wavelength. Moreover, The PHW was characterized by scanning electron microscopy, Fourier transform infrared spectroscopy, Freundlich and Langmuir isotherm model, pHpzc and Brunauer–Emmett–Teller (BET) surface area analysis.

Results: Maximum adsorption capacity was 90.48 mg DB71 per 1 g adsorbent at pH 2, DB71 100 mg/l, temperature 50° C, and time 210 minutes. In general, by increasing the adsorbent dosage, time, and processing temperature, the removal efficiency was increased; however, incrementing pH and dye concentration had a reverse effect. Maximum BET specific surface and total pore volume on the adsorbent were 1.04 m²/g and 0.0002 cm³/g, respectively. The Freundlich isotherm (R² = 0.9912) model fits the equilibrium data better than the Langmuir isotherm (R² = 0.9024) model. The adsorption kinetic was found to be well described by the pseudo-second-order model. Thermodynamic analysis indicated that the adsorption process is a spontaneous and endothermic process.

Conclusion: PHW can be used well as a low-cost surface adsorbent in the treatment of DB71 from aquatic environments.

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1. Introduction

Water resources, due to anthropogenic activities and natural processes, have been always exposed to various pollutions, which are beyond self-purification (1,2). Pollution phenomenon is largely the result of technological development in the current century, which is inter-twisted with political, economic, and social issues (3). One of the causes of surface water pollution is the discharge and disposal of industrial wastewater containing dye into them (2). Dyes are present in the wastewater of different industries, including printing, wood and paper, leather, hygienic and cosmetics, food, electroplating, and textile industries (4). Annually worldwide, more than one million tons of different dyes are produced and used in various industries, especially in the textile industry (5,6). Estimates indicate that 15-20% of the dyes used in these industries are dumped through wastewaters. Colorfulness, particulate matter, pH, and chemical oxygen demand are the most important characteristics of the textile industry effluent (6,7). Dyes, based on the chemical structure or chromophore, are classified into different groups of which most important ones are: Azo, anthraquinone, phthalocyanine, and ethane, and the most common among these are azo dyes (8). The structure of azo dyes includes azo bond dye agents (-N=N-) and one or more aromatic rings (9,10). Direct Blue 71 (DB71) with the chemical formula ($C_{40}H_{23}N_7Na_4O_{13}S_4$) belongs to the tri-azo group, and its azo form is the dominant type in the aquatic environments (11). In general, dyes, and in particular azo dyes, have complex, toxic, mutagenic, and carcinogenic structure; moreover, these

color substances are also considered as possible carcinogens or mutagens to human (12). Furthermore, some azo dyes are highly stable and are resistant to degradation by chemical and biological processes (5). Discharge of wastewater containing azo dyes not only affects the esthetic aspect of the receiving water but also by preventing transmission of sunlight into the aquatic environments, result in reduced photosynthesis process, and decreases the amount of dissolved oxygen in the river (13). Hence, to prevent health and environmental hazards, before discharging effluents containing such dyes into receiving waters, appropriate action to filter the wastewater must be taken. Various methods have been exploited to remove or reduce the concentration of azo dyes in wastewater of industries of which most important ones include coagulation and flocculation process, biological treatment, chemical oxidation, electrochemical treatment, and ion replacement. Most of these methods have advantages such as high treatment efficiency, short process time and lack of selection of the system, and undoubtedly impose disadvantages such as high cost of treatment, the need for additional treatment, and generation of dangerous side materials (14-16). Another method of applied physical treatment of such contaminants consists of adsorption process, which in case of using cheap and abundant adsorbents in nature, compared to other wastewater treatment processes, for reasons, including lower cost, simpler design, more access, and capability of treatment of dyes in higher concentrations, has more advantages than others (17). In the process of adsorption, different materials

are used as adsorbent and activated carbon especially the industrial type is among the most effective and most widely used adsorbent for the removal of various contaminants, especially dyes from liquid environments such as water (18). The relatively high costs of production, usage, and recovery of industrial activated carbon along with output in discussions on the economy and reducing costs as much as possible, and on the other hand, the full consumption and recycling waste and used natural and artificial materials to usable materials, and in general, utilization of materials that are environment friendly and nature oriented, has caused leaders and researchers of treatment practices to use low-cost natural adsorbents in the upcoming years (18-20). Among the affordable adsorbents and with the ability to analyze biological subjects, we can point out waste material from agricultural activities, such as pistachio hull that in addition to large available quantities, they are also from nature and nature friendly (21). There have been studies regarding the adsorption of different contaminants on carbon and raw adsorbent produced from pistachio hull, and its good performance in the removal of various contaminants is acknowledged. Among them, we can point out studies of Moussavi and Khosravi (21) for the usage of pistachio hull wastes (PHWs) to remove cyanide from wastewater in a study conducted, Moussavi and Khosravi (22) for the removal of cationic dyes from aqueous solutions, Moussavi and Khosravi (23) on the catalytic use of pistachio hull coal in process of ozone injection for removal of RR198 dye from aquatic environments, and the study of Moussavi and Barikbin (24), on

the removal of hexavalent chromium from industrial wastewater. This study aimed, designed, and conducted to evaluate the efficiency of adsorptive DB71 from aqueous solutions onto PHW, along with studying parametric experiments, equilibrium, and kinetics.

2. Materials and Methods

This study is an applied research, which is empirical and done on an experimental scale. All chemicals used in this study except DB71, which was the product of Alvan Company, were supplied from Merck Co., Germany. PHW was collected from lands near to Rafsanjan city (30°23' N, 56°00' E) of Kerman province in the south-eastern part of Iran. PHW was ground as much as possible to form a powder using an HR-1727 grinder (Philips, Zhuhai, China) and then sieved through standard sieves to give 20-100 µm mesh particles, 0.15-0.85 mm diameter between two sieves, then they were washed using distilled water for several time to remove impurities, such as sand and leaves as well as soluble and colored components and were kept overnight at room temperature for 24 hours and then dried at 85° C for 72 hours to prepare adsorbent. To prepare the stock solution with a concentration of 1000 mg/l of DB71, 2 g of DB71 dye was solved in distilled water and to do subsequent experiments, and the concentration needed was prepared from dilution of the stock solution. The initial pH of the solution was adjusted by a 0.1 N sodium hydroxide (NaOH) or hydrochloric acid (HCl). A portable Denver Ultra basic-UB10 model pH meter was used for measuring pH values in the aqueous

phase. To prevent changes in concentration, the stock solution was kept in the refrigerator.

Studies of scientific resources revealed that the most important variables affecting the adsorption of solution pH are adsorbent dosage, contact time, initial concentration of dye, and the temperature which in this study the effect of these variables on adsorption of dye using PHW was investigated. To study the effect of each of the parameters, the experiments were performed in a 250 ml Erlenmeyer flask and an incubator shaker model KS 4000i IKA Germany. In each flask, 100 ml solution was put with predetermined concentration, and for each stage, according to its target level, after adjusting the pH (by pH meter model WTW, Germany), a certain dose of adsorbent was added to the samples. Then, samples for appropriate contact were placed on shaker with the speed of 120 rpm, for a determined time. After passing of contact time, the samples refined by Whatman 42 filter paper; and finally, the concentration of dye in the filtrated solution was measured by colorimetric method using a spectrophotometer (ultraviolet/visible Model T80). To do so, first using the spectrophotometer, a wavelength that DB71 had the most adsorption was determined (587 nm). Then, the calibration curve of dye was drawn, equation (1). Next, based on the linear equation obtained and the read adsorption number by spectrophotometer for each test, dye concentration in the samples was measured. Ultimately, the efficiency of removal of dye and its adsorption capacity (mg/g) were calculated by equations (2 and 3), respectively:

$$[\text{DB71}] = 0.2237 * \text{Adsorption} - 0.008, \\ R^2 = 0.9871 \quad (1)$$

$$\% = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (2)$$

In equation (1), C_0 and C_e represent the initial and final concentrations (after adsorption) of dye.

$$q_e = \frac{(C_0 - C_e)V}{M} \quad (3)$$

Where, C_0 and C_e are the initial concentration of the dye and concentration after testing and reaching a stable state. V is the volume of solution (l), and M is the amount of adsorbent used (g). All experiments to determine the optimum value of parameters affecting adsorption (pH, adsorbent dose, contact time) were performed at 25° C, and they have been repeated twice for further insurance. Final results are reported as the average of the two measurements.

The surface morphology and chemical characterization of PHW were carried out using scanning electron microscopy (SEM) (Philips XL-30 SEM). The pH of zero-point charge (pHpzc), of pH was analyzed according to the method proposed by Lim et al. (27), where 50 ml of 0.01 M NaCl solution was placed in a closed Erlenmeyer flask. The pH was studied over a pH range of 2–12 using the pH meter (WTW, Germany). Each PHW sample was then added to the solution, and the final pH was measured after 24 hours agitation at room temperature. The pHpzc is the point where the curve pH final versus pH initial crosses the line pH initial = pH final (27). The surface area of PHW area was calculated by the Brunauer–Emmett–Teller (BET)

equation within the 0.05-0.30 relative pressure range (25). To illustrate the functional groups, present on the surface of the adsorbent, Fourier transform infrared (FTIR) spectra were collected between 450 and 4000/cm using a Nicolet spectrometer. At the end of experiments, to analyze the behavior of the adsorption system, models related to adsorption isotherm (Langmuir and Freundlich), which are the main examples in the application of these techniques in real scale, were used, and thermodynamic parameters such as free energy, enthalpy, and entropy changes were calculated for the adsorption process.

Langmuir isotherm equation is as follows:

$$q_e = \frac{q_m K_1 C_e}{1 + K_1 C_e} \quad (4)$$

Q_e is the adsorbed dye in a specific amount of adsorbent (mg/g), C_e is solution equilibrium concentration (mg/l), and q_m is the maximum amount needed for the formation of a layer (mg/g). Langmuir equation can be linearized for ease of drawing and obtaining Langmuir constant (K_1), and the maximum adsorption of a layer of the ash of *Moringa peregrina* tree (q_m). K_1 and q_m values can be obtained by drawing line $1/q_e$ against $1/C_e$.

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m K_1} + \frac{1}{C_e} \quad (5)$$

Freundlich isotherm is generally and empirically based on the adsorption on heterogeneous surfaces, and therefore, does not guarantee a single-layer capacity. Its equation is in the form of the following:

$$q_e = K_f C_e^{\frac{1}{n}} \quad (6)$$

Where, K_f and $1/n$ are Freundlich

constants, and they are dependent on the adsorption capacity and density. The assessment of Freundlich equation constants is done from contact of the slope of the linear chart, $\log q_e$ against $\log C_e$ on the basis of data obtained from the tests. To determine Freundlich constants, the equation can be written as a linear logarithm like the following equation:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (7)$$

3. Results

3.1. Characterization of PHW

Surface morphology of PHW particles was characterized using SEM micrograph and is shown in figure 1.

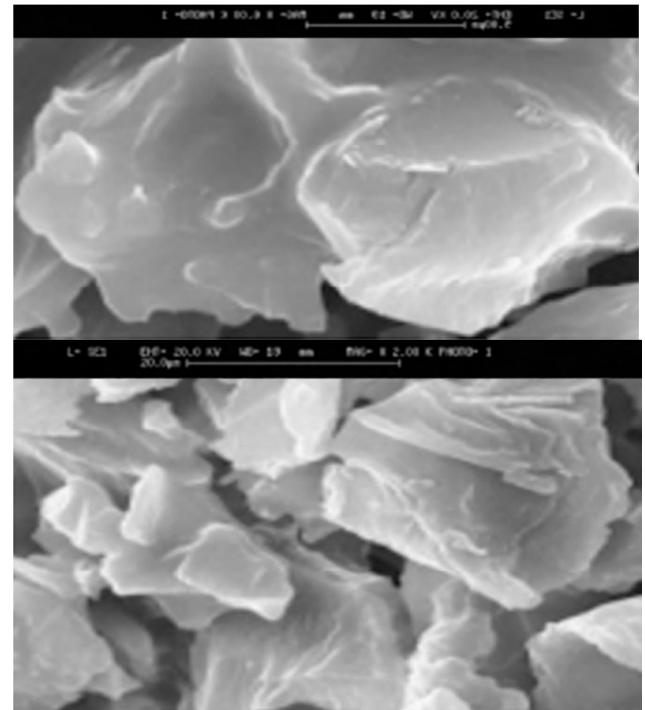


Figure 1. Scanning electron microscopy micrographs of pistachio hull waste

Analysis of the SEM micrograph shows

that it is flask-type amorphous particles with smooth surfaces, uneven and pores that will permit the movement of water and large ions through its crystal structure (21). The BET surface area of PHW was measured using standard BET equation of which its value is $1.04 \text{ m}^2/\text{g}$. Because the specific surface area of PHW is medium, the functional groups likely have an equal pronounced role with particle surface area (24). In adsorbing DB71 from liquid, the pH_{pzc} of PHW was determined to be 7.6, signifying a positive surface charge for a solution pH below 7.6 and a negative surface charge for a solution pH > 7.6. The pH_{pzc} is an important characteristic of any adsorbent as it indicates the net surface charge of the adsorbent in solution. pH_{pzc} is the pH at which the net surface charge on adsorbent is zero. Figure 2 shows the "pH drift" data, from which the pH_{pzc} of PHW can be determined (pH 7.6).

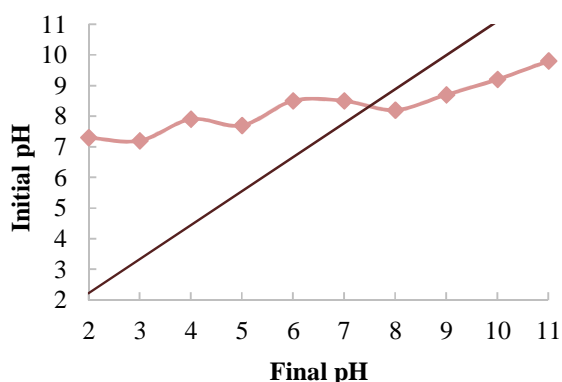


Figure 2. Determination of pH_{pzc}

Figure 3 illustrates the FTIR spectrum of PHW including the peak wave numbers and the corresponding assigned groups. As shown in figure 3, there are hydroxyl, carboxylic, phenolic, and amino groups (–OH, –CH, C=O, and –CO groups) on the surface of the tested adsorbent. This result implies that a

complex PHW particle surface is involved in adsorbing DB71 (24,26).

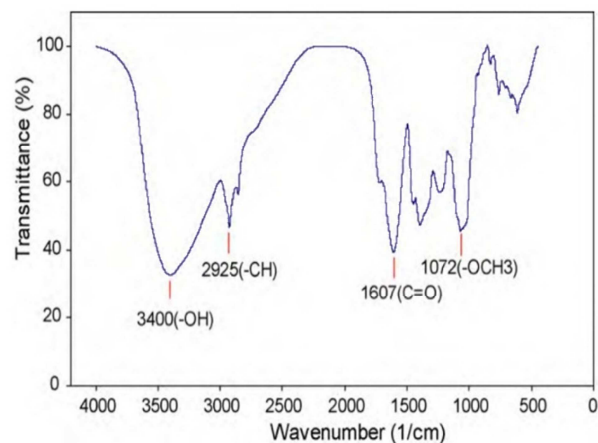


Figure 3. Fourier transform infrared spectrum of pistachio hull waste at wave numbers from 450 to 4000/cm

3.2. Effect of contact time

To evaluate the effect of contact time on the process of adsorption, a survey was conducted on the removal of dye from aqueous solution in time intervals from 0 to 210 minutes with an initial concentration of 10 mg/l DB71 and adsorbent dose of 0.1 g/l. Figure 4 shows the amount of dye adsorbed by PHW by increasing contact time. Studies showed that by increase in contact time, dye removal also increases in a way that the minimum and maximum 0-210 minutes; however, as is clear in figure 4, after 90 minutes, the amount of removal has not changed much over time and has remained almost constant. The removal after 90 minutes contact time was about 97.76%, which is not a significant amount compared to maximum removal rate obtained at 210 minutes. Accordingly, to continue the tests, contact time of 90 minutes was chosen as the equilibrium time of the adsorption process.

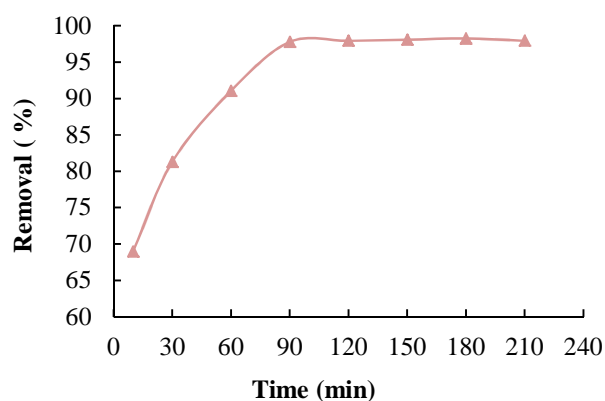


Figure 4. Effect of contact time (dye con 10 mg/l, pH 2, and adsorbent dosage 0.1 g/l)

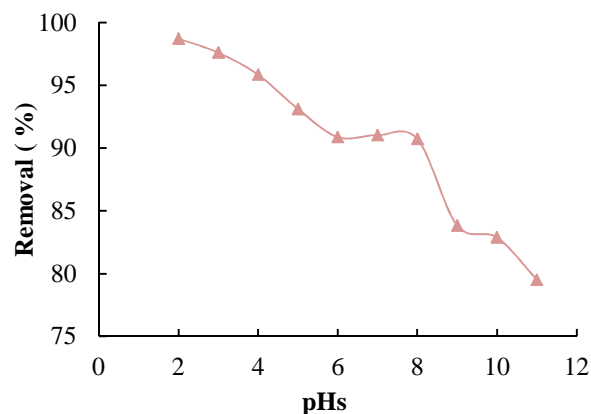


Figure 5. Effect of solution pH (dye con 10 mg/l, adsorbent dosage 0.1 g/l, and time 60 minutes)

3.3. The effect of solution pH

The effect of the initial pH change of samples on the rate of removal of DB71 by pistachio hull was studied. The adsorbent dose was 0.1 g/l of the testing solution, and initial concentration of the dye in all samples was 10 mg/l. Initial pH of samples in each series of tests was determined in the range of 2-11. After 90 minutes of contact time, remaining concentration of dye was determined. Results from effectiveness pH of samples on dye removal efficiency are shown in figure 5. As is clear from the figure 5, the highest removal scale occurred at acidic pHs and by increasing pH from 2 to 11, removal efficiency has declined from 98.72 to 79.52. Therefore, due to this result pH, 2 was chosen as the best solution pH for continuing the adsorption process.

3.4. The effect of adsorbent dosage

Experiments to determine the effect of adsorbent dosage in the removal of dye by PHW were performed within the range of the adsorbent dose 0.05-1 g/l solution containing 10 mg/l DB71, optimal pH 2, and contact time of 90 minutes at $25^{\circ} \pm 2^{\circ} \text{C}$ (Figure 6).

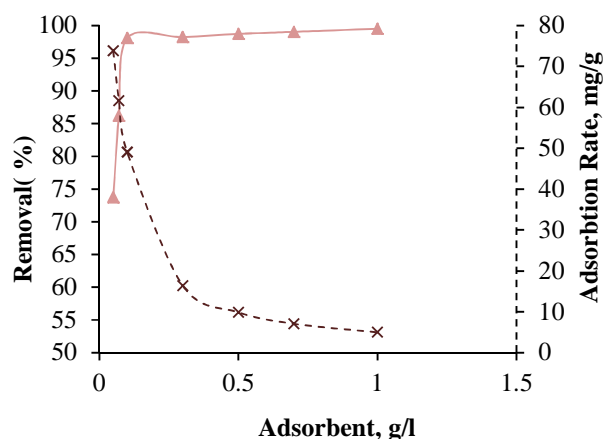


Figure 6. The effect of the adsorbent dosage (dye con 10 mg/l, pH 2, time 90 minutes)

The results showed that removal efficiency increased by increasing doses of adsorbent, to the extent that when the adsorption dose increased from 0.05 to 1 g/l, removal efficiency reached from 73% to 99%. According to the results obtained in figure 6, although with increasing dose of adsorbent, the residual dye in the solution is reduced, the amount of pollutant absorbed per unit mass of adsorbent is reduced from 73.76 to 4.98 mg/g, by which the optimal dose of adsorbent was set at 0.1 g/l, and then was used for other tests.

3.5. The effect of initial dye concentration and temperature

To evaluate the effect of initial concentration of DB71 and temperature increase on the removal efficiency, dye solutions with concentration of 10-100 mg/l were prepared from stock solution, and tests were performed in the optimal pH 2, adsorbent dose 0.1 g/l, contact time of 90 min, and three temperatures of 25, 40, 50° C. The results of the initial concentration of dye in three aforementioned temperatures are shown in figures 6 and 7. Furthermore, in figure 8, the adsorption rate is shown. Figure 8 is a different kind displayed of figure 7. Figure 8 showed that the amount of dye adsorbed per g of adsorbent enhanced with the increasing temperature, slightly. As can be seen in figure 6, with the increase in dye concentration, the removal efficiency decreases and viz. in a way that the highest removal rate occurs at temperature of 50° C and initial concentration of 10 mg/l, which was equal to 99.36%, respectively.

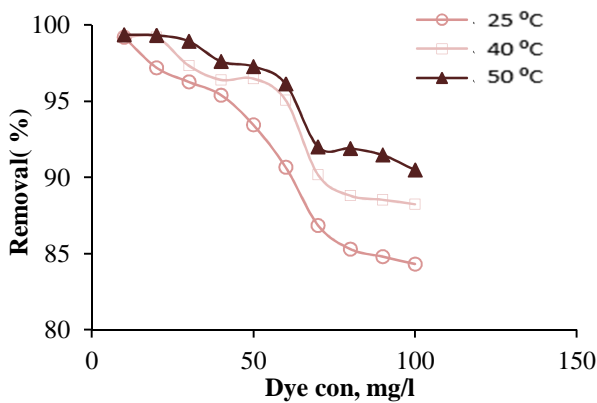


Figure 7. Effect of initial concentration of dye (dye con 10 mg/l, pH 2, time 90 minutes, and adsorbent dosage 0.1 g/l)

3.6. Adsorption thermodynamics

The high correlation coefficient of the

tangent over the curve of free energy and temperature changes show that the data change linearly and with well approximation ($R^2 = 0.9996$). The results of thermodynamic parameters, presented in table 1, indicate that Gibbs free energy of the adsorption reaction is negative showing that the dye adsorption process on adsorbent is carried out spontaneously, and its degree increases with increasing temperature. Furthermore, the positive changes in the value of the enthalpy (+11.054 KJ/mol) indicate that the adsorption process is an endothermic process.

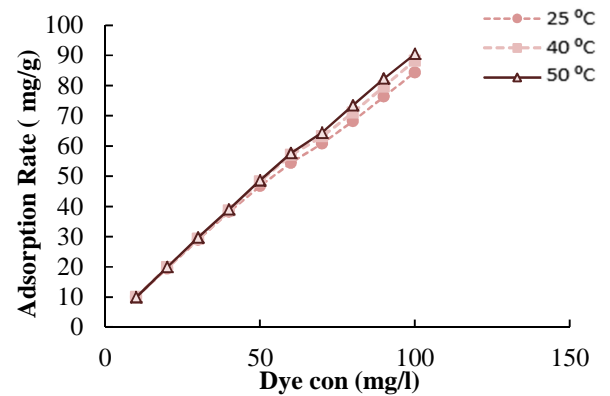


Figure 8. The effect of initial concentration of dye and temperature on the adsorption rate (dye con 10 mg/l, pH 2, time 90 minutes, and adsorbent dosage 0.1 g/l)

Then in Figures 9 to 11 Freundlich and Langmuir isotherm at different temperatures and Gibbs free energy changes in different temperature are shown, respectively. This figures shows the better correlation in occur in Freundlich isotherm and in Langmuir isotherm is in 25 and 50 °C about 0.99 and 0.98, respectively. The amount of Gibbs free energy also decreased with increase temperature from -8.17 to -9.79. the parameters that used with its description has been shown in table 2 and 3.

Table 1. Isotherm parameters in different temperatures

Temperature (° C)	Langmuir isotherm			Freundlich isotherm		
	qm	KL	R ²	kf	n	R ²
25	50.76	2.83	0.9024	27.09	2.51	0.9912
40	63.69	2.38	0.9657	33.19	2.57	0.9648
50	96.93	2.60	0.9857	38.31	2.59	0.9594

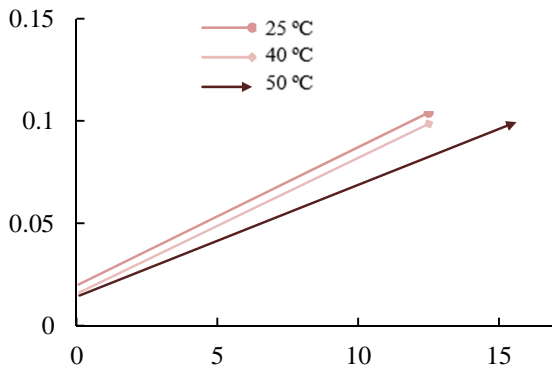


Figure 9. Langmuir isotherm

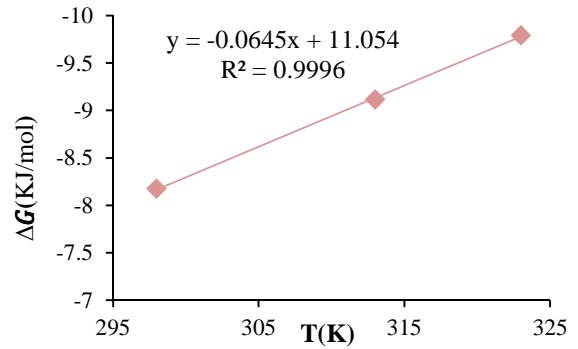


Figure 11. Gibbs free energy changes with temperature

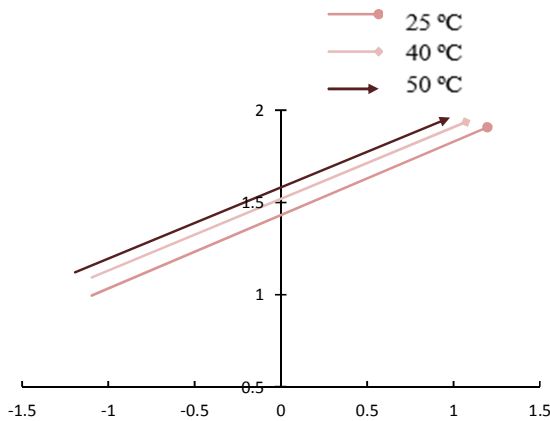


Figure 10. Freundlich isotherm

4. Discussion

4.1. The effect of contact time

There are many factors, which can contribute to the adsorbate concentration effect. The first and important one is that contact time between the pollutant and the adsorbent. Because these important parameters are effected on the practical application of adsorption process (27). Testing the effect of contact time on the removal rate was performed to achieve the adsorption process equilibrium time at intervals 0-210 minutes.

Table 2. Relations for calculating thermodynamic parameters

parameters	Description
1 $\Delta G^0 = -RTL \ln K^0$	ΔG^0 = Gibbs free energy, R = Gas constant (8.314 J/mol/K), T = Temperature in Kelvin degrees, K^0 = Thermodynamic equilibrium constant
2 K^0	K^0 = Thermodynamic equilibrium constant, C = Adsorbed substance mass onto adsorbent per liter of solution (mg), C = Residual concentration of the adsorbed substance in solution (mg per liter), V = Volume
3 $\Delta G^0 = \Delta H^0 - T\Delta S^0$	Solution in mm, and m is the mass of adsorbent used in mg ΔG^0 = Gibbs free energy, ΔH^0 (enthalpy changes), and ΔS^0 = entropy changes

Table 3. Calculation of enthalpy and entropy

Thermodynamic parameters			Temperature
$\Delta S(\text{KJ/mol})$	$\Delta H(\text{KJ/mol})$	$\Delta G(\text{KJ/mol})$	(K)
-0.0645	11.054	-8.17	298
		-9.11	313
		-9.79	323

Equilibrium time is the time, in which the contaminant removal over time is < 5-10% of the amount of the initial removal values. Thus, in the present study, the reason for increased contact time to 210 minutes is to achieve contact time to calculate equilibrium constants. As can be seen in figure 4, by the increase in contact time of samples with adsorbent, the rate of dye removal increases. This is due to the increased possibility of dye molecules collision to the surface of the adsorbent. In addition, the adsorption speed is higher in the initial contact times, and the slope is steeper because at the beginning, most active adsorption places are available and also dye concentration in the solution is at its maximum amount, and this causes the adsorption rate to be high in the beginning. If in during the adsorption reaction duration, the contact time would be sufficient the adsorption sites of adsorbent remain unsaturated (28). In the short contact time, the chemical binding to exist between the adsorbate and adsorbent will be weak and to achieve equilibrium state a longer contact time is required. Furthermore, the long contact time can be cause to agglomeration of adsorbent and would lead to a decrease in the total surface area of the sorbent particles available for pollution adsorption and an increase in the diffusional path length (29). To evaluate the effect of contact time on the process of adsorption, a

survey was conducted on the removal of dye from aqueous solution in time intervals from 0 to 210 minutes. The effect of contact time on the extent of removal of DB71 is presented in figure 7, at a fixed concentration of 10 mg/l DB71 and adsorbent dose of 1 g/l at 25° C. As can be seen in figure 7, the time to reach equilibrium for pistachio hull adsorbent is 90 min. This occurs since the chart comes close to the horizontal line. After 90 minutes, dye removal with the passage of time has not changed much, and it almost has remained constant (30,31). Zazouli et al. (32) in the own study were reported that adsorption rate of 198 reactive red dye from aqueous solutions using activated red mud enhanced with increasing contact time from 0 to 120 minutes. Zazouli and Moradi (33) in the own study were reported that adsorption Acid Red 18 dye using Sargassum Glaucescens biomass from aqueous solutions enhanced with increasing contact time until 120 minutes and after that reach the equilibrium.

4.2. Effect of solution pH

The pH of dye solution plays an important role in the whole adsorption process and particularly on the adsorption capacity (34). Solution pH can change the adsorbent surface charge, the degree of ionization adsorbable substance and ionization of adsorbent active groups. Therefore, the pH changes can play an important role in the process of dye removal. Effect of solution pH on the removal efficiency of DB71 is shown in figure 5. As shown in figure 5, the highest rate of dye removal occurred in pH 2. A high level of removal in pH 2 can be due to a positive surface charge and

protonation of active sites because of the increasing effects of H^+ ions concentration in solution, which triggers high electrostatic gravity force between positive charges of adsorbent surface anionic dye. When pH increases, the electrostatic repulsion force increases, and the removal rate decreases as well (35,36). Raffiea Baseri et al. (35) and Rasoulifard et al. (36) studies are noted that when pH increases, the electrostatic repulsion force increases, and the removal rate decreases as well. Kousha et al. (37) believe when solution pH is lower than pH_{pzc} (pH 7.6), the adsorbent surface will become positively charged, thus favoring the adsorption of anionic dye DB71, which is negatively charged, and vice versa when the solution pH is beyond pH_{pzc} , the adsorbent surface will possess negative charge, which will hinder the adsorption of dye onto PHW.

4.3. The effect of adsorbent dosage

Adsorbent dose is one of the economically important parameters that have a significant impact on adsorption capacity. The effect of the consumed adsorbent on removal of DB71 is shown in figure 6. By increasing the adsorption dose from 0.05 to 1 g/l, the removing rate increased from 73.6% to 99.52%. This increase occurs due to the increased number of adsorption active sites available, as opposed to a fixed amount of dye concentration. The increase in the adsorbent dose leads to an increased probability of interaction between adsorbent particles, reduction of surface area, increase in the length of influence path, and to a decrease in adsorption density (38). It was also observed, when adsorbent dose reaches over 0.1 g/l, the rate of dye removal would

not increase dramatically in the case of dosage increment. It seems that after increasing the adsorbent dose to a certain amount, the highest adsorption rate is achieved, and therefore, from now on, the residual contaminant will remain constant even with the addition of the adsorbent dosage (31). Although by increasing in adsorbent dose, the removal rate of dye increases as well, the amount of adsorbed dye decreases per gram of adsorbent. This happens since the solution dye concentration (10 mg/l) is reduced due to being adsorbed by unsaturated active sites of the adsorbent surface. On the other hand, the increase in the rate of adsorbent causes the accumulation of particles and makes them stick together (39).

4.4. The effect of initial dye concentration and temperature

A given mass of adsorbent can only adsorb up to a fixed amount of adsorbate. Therefore, the initial concentration of adsorbate solution is very important in the adsorption process (27). As figure 7 show, by increasing dye concentration, the removal efficiency of PHW is reduced. This is due to limited number of active sites for adsorbents, which are saturated at high concentrations (40), whereas the amount of contaminants adsorbed per unit mass of adsorbent (Figure 8) in the same conditions shows a reverse process. When the initial concentration of dye increases from 10 to 100 mg/l, the capacity of adsorbent increases from 9.92 to 84.32 mg/g. This fact can be interpreted so that by increasing the concentration of the dye, flow rate of mass transfer and as a result, driving force of dye molecules from solution to the adsorbent surrounding liquid layer, and

finally to the adsorbent particle surface increase (41,42). In other words, increasing the absorption capacity is attributed to the increased collision between dye molecules and adsorbent, as well as the increase of concentration gradient and the acceleration of the mass transfer. This increases the uptake of dye molecules by adsorbent particles, and ultimately increase the adsorption capacity (41,43). The results of the adsorption tests in three temperatures 25, 40, and 50 showed that the increase in temperature increments the rate of removal of DB71 (Figures 7 and 8). Increase in adsorption rate by increase in temperature shows the endothermic nature of the process, which indicates the increased pore size of the adsorbent, as well as the increase in effective collisions between adsorbent molecules and adsorbable substance (44).

4.5. Adsorption isotherm

Adsorption isotherm is one of the important parameters to optimize the design of an adsorption system. Adsorption isotherm models are widely used for adapting experimental data and determining the most appropriate correlation for the equilibrium curves between the mass of adsorbate adsorbed per unit mass of adsorbent and liquid phase adsorbate concentration at equilibrium state. Adsorption isotherms provide many important practical implications such as efficiency of the adsorbent and how adsorption system proceeds (27). Several isotherm equations have been used to describe the adsorption equilibrium among which Langmuir and Freundlich models are of higher importance. These models have been used to model the adsorption of DB71. Langmuir isotherm

implies that the adsorption takes place in quite homogeneous places, and it can well be used for many adsorption processes.

To draw Langmuir and Freundlich isotherms, dye solutions with concentration of 10-100 mg/l were prepared, and adsorption tests were performed in optimal pH, adsorbent dose, and predetermined contact time, and at three temperatures of 25, 40, and 50° C. Finally, the equilibrium data were fitted to Langmuir and Freundlich isotherm, respectively.

Figures 9 and 10 show the Langmuir and Freundlich plots for the removal of DB71 at pH 2 and three temperatures 25, 40, and 50° C with optimum contact time of 90 minutes. Table 2 summarizes the values of q_m and K_L (Langmuir isotherm), K_f and n (Freundlich isotherm and the correlation coefficients for these two isotherms. From the results obtained, Freundlich isotherm is well fitted to this adsorption process as evident by the high correlation coefficients ($R^2 = 0.9912$) rather than Langmuir isotherm ($R^2 = 0.9024$) at 25°C.

Furthermore, n coefficient in Freundlich isotherm indicates the intensity of the adsorption. The higher n value is the more suitable the adsorbent is to adsorb the contaminant. n values above 1 indicate that the adsorbent is appropriate for the contaminant which in this study was as follows ($n > 2.5$).

4.6. Adsorption thermodynamics

By investigating the changes in adsorption in terms of temperature, we can comment on the nature of the reaction (endothermic or exothermic). Through examining the effects of temperature, we can achieve the optimal temperature to reach the

maximum adsorption and recovery and then calculate adsorption and equilibrium from the slope of the curve in different concentrations. The lower the temperature in which an adsorption process occurs, the more cost effective it would be. If the amount of ΔG^0 of the reaction in a thermodynamic study is negative, it indicates that the adsorption reaction is spontaneous. If ΔG^0 decreases by increasing temperature, it shows that the adsorption process is more desirable at a higher temperature. From positivity of enthalpy, endothermic or exothermic nature of the reactions can be realized. Moreover, the amount of ΔH^0 represents the adsorbent tendency to the absorbable substance. Because of thermodynamic investigation of the adsorption of DB71, adsorption tests were performed at 25, 40, and 50° C for different concentrations of dye (10-100 mg/l) and by maintaining optimum conditions for other parameters. Using relations listed in table 1, equilibrium constants (K) and Gibbs free energy (ΔG^0) were calculated for the studied temperatures (24), and dye concentration of 100 mg/l, respectively. Then, the curve of Gibbs free energy was drawn according to the temperature and from the tangent line on the curve, the enthalpy changes (ΔH), and entropy (ΔS), which are the intercept and the slope of the tangent line, respectively, were obtained (Figure 11). Thermodynamic parameters are presented in table 3.

5. Conclusions

The results of the investigations showed

that the adsorption from the hull of pistachio with high efficiency and output, minimal use of amount of it, and with little time has the ability to adsorb the maximum DB71. The amount of dye adsorbed by the adsorbent type is under the influence of various parameters such as pH, initial dye concentration, contact time, temperature, and the amount of the adsorbent. Studies conducted on the adsorption processes showed that removal efficiency has a direct relationship with the increase in the adsorbent dose, contact time, and temperature, an inverse relationship with increased pH, and concentration of the dye. Maximum adsorption capacity was 90.48 mg DB71 per 1 g adsorbent at pH 2, dye concentration of 100 mg/l, temperature 50° C, and contact time 210 minutes. Adsorption equilibrium data obtained in this study revealed that the Freundlich isotherm ($R^2 = 0.9912$) model fits the equilibrium data better than the Langmuir isotherm ($R^2 = 0.9024$) model at 25° C. The adsorption kinetic was found to be well described by the pseudo-second-order model. Thermodynamic analysis indicated that the adsorption process is a spontaneous and endothermic process. Therefore, PHW can be used well as a low-cost surface adsorbent in the treatment of DB71 from aquatic environments.

Conflict of Interests

The Authors have no conflict of interest.

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