

Removal of Methylene Blue Using Fast Sucking Adsorbent

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Received 03 Oct 2016,
Revised 14 Nov 2016,
Accepted 17 Nov 2016

Keywords

- ✓ Walnut shell,
- ✓ activation,
- ✓ sucking
- ✓ adsorbent,
- ✓ methylene blue,
- ✓ isotherm-kinetic

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Abstract

In this study, walnut shells activated with various acids, such as hydrochloric acid (HWS), sulphuric acid (SWS) and phosphoric acid (PWS), were used as an adsorbent to remove Methylene Blue (MB) from aqueous solution. Adsorption studies were carried out with batch method. Effect of different parameters on adsorption, such as pH, initial dye concentration, time and temperature was investigated. Adsorption isotherms and kinetic models were evaluated using different models. From the obtained results, used acid species for activation was observed to be highly effective in surface morphology of adsorbent and added different characteristic to adsorbent surface. Interestingly, the removal of methylene blue was greatly improved and was not affected change by pH range 3-10 and temperature range 25-65 °C after acid activation. Furthermore, developed adsorbent, especially SWS, behaved like a fast sucking adsorbent. Adsorption of MB onto activated WS fit Langmuir adsorption isotherm, pseudo-second-order kinetic model and mechanism of adsorption was found to be as ion exchange mechanism. From adsorption desorption studies repeated five times, the adsorption capacities of the activated walnut shell were not changed much, and it was observed that all of the activated WS were reusable.

1. Introduction

One of the most important problems affecting live life is inorganic or organic pollutants. Discharged pollutants, both inorganic and organic, into the environment have been increasing in recent years due to evolving industry [1-4]. The largest share in these organic pollutants belongs to synthetic dyes because they are indispensable for many industries such as textile and dyeing industry. Methylene blue (MB) is the most common dye used in dyeing, particularly cotton, silk and wood [5]. Dye wastewater discharged in environment form the most amounts of the industrial wastewater, because approximately 10-15% of the produced dyes are discharged as waste [6, 7].

Due to aromatic molecular structure dyes are extremely stable and hence are difficult to biodegrade [8]. As many dye and their degradation products are toxic and carcinogenic, the removal of synthetic dyes from industrial effluents from the aspect of environmental and health safety have been important research topic in recent years. The removal of pollutants such as dyes and heavy metals from industrial waste waters are used many methods [9-15], but it is stated that adsorption method is effective and economical [16]. In the literature, many adsorbent was developed [4,17-21] and lots of studies were performed by using these adsorbents for removal of pollutants. However, regeneration of most of the adsorbent is difficult except for activated carbon and adsorption rate is not fast. But activated carbon used as adsorbent in adsorption treatment is quite expensive. It is desirable to develop a new adsorbent, particularly cost effective, can be regenerated and used in wide pH and temperature range without losing adsorption capacity. Hence recently, studies have concentrated on developing cheaper and more efficient adsorbents including agricultural and industrial waste materials.

In this work, the potential use of walnut shells activated with various acids as alternative adsorbent for cationic dye removal from aqueous solutions was investigated. The adsorption properties in terms of adsorption capacity were described. The influence of several parameters such as initial dye concentration, and pH on the adsorption capacity was evaluated and discussed. The equilibrium data was analyzed using various adsorption isotherms and adsorption kinetic models. Moreover, desorption and reusability of activated walnut shells was examined.

2. Materials and methods

2.1. Material and Reagents

Walnut shells (WS) were supplied from a local farm in Azizli Bağları (Yozgat, Turkey). Cationic dye, methylene blue (MB), was obtained from Merck and used without further purification. All the other chemicals were Merck and used without any purification. pH values of the medium were adjusted by addition of 0.10 M HCl or NaOH.

2.2. Instrument and apparatus

Fourier transform infrared (ATR-TIR), PerkinElmer Spectrum 400, was used for functional group analysis of the unactivated and activated walnut shell over the wave number range of 400–4000 cm^{-1} . The surface morphology of the unactivated and activated walnut shell was examined by a scanning electron microscopy (SEM), (LEO 440 imaging mode). The surface area, pore volume and average pore diameter of the samples were determined by using Micromeritics Gemini VII analyzer. The concentrations of dye were measured with UV–Vis spectrophotometers (Schimadzu UV-1208). The pH measurements were made with Consort C931 model digital pH-meter.

2.3. Preparation of activated walnut shell

Active WS was prepared according to the literature [22]. 2.5 g dried WS, 15 mL of concentrated acid (HCl, or H_2SO_4 , or H_3PO_4) was added in a 100 ml erlenmeyer. Then placed on a magnetic stirrer and stirred for 3 hours. Later, impregnated with concentrated acid was filtered and was heated in a muffle furnace for 8 h at 150° C. WS taken from the furnace washed with 0.01 M sodium bicarbonate solution until the wash water pH becomes 7 and then it was dried in an oven at 80° C. After the dried walnut shells milled, it was passed through 65 meshes and stored in a desiccator. The HCl treated WS, H_2SO_4 treated WS and H_3PO_4 treated WS were abbreviated as HWS, SWS and PWS, respectively.

2.4. Determination of the neutral pH Point (pH_{PZC})

To determine the neutral pH of unactivated and activated WSs, adsorbent (weighed 0.05 g) was shaken for 24 h in 0.1 M KCl solution and initial pHs of the solution over the pH 3–10 were adjusted with 0.1 M NaOH or 0.1 M HCl solution. After shaking, the final pH of the solution was measured by pH meter. Final pH values were placed on the y-axis and the initial pH values were placed on x-axis and a graph was drawn and pH_{PZC} values were determined [23].

2.5. Adsorption Study

30 mL of MB solution, with a certain concentration, was put into 100 ml Erlenmeyer and pH was adjusted with 0.1 M HCl or 0.1 M NaOH. After 0.3 g adsorbent was added to each erlenmeyer it was placed into a shaker adjusted to 25 °C and was stirred for 3 h to reach adsorption equilibrium condition. After centrifugation of the solution, the dye concentration of MB was measured by UV–Vis spectrophotometers (Schimadzu UV-1208) at wavelength 665nm. The removal percentage (R%) and the adsorption amount (Q, mg/g) were calculated as follows:

$$R\% = \frac{(C_1 - C_2) \times 100}{C_1} \quad (1)$$

$$Q = \frac{V(C_1 - C_2)}{W} \quad (2)$$

Where C_1 and C_2 are the concentrations (ppm) of MB before and after adsorption, respectively, W is the weight of the walnut shell (g), V is the volume of solution.

To examine the effect of pH, before adding adsorbent, the solution pHs were adjusted to different values in the range of 3.0–10.0 with 0.1 mol/L HCl or NaOH. The adsorption isotherm studies, batch experiments were carried out at 25° C in duplicate in the initial concentration ranges of 20–600 ppm (MB).

2.7. Desorption Study and Reuse of the Activated WS

Desorption studies of WS adsorbed MB dye was carried out with 1 M HNO_3 in batch experiment. Dye loaded walnut shells were placed in desorption medium and stirred at 25 °C for 1 h. afterward, the adsorbent was

washed with deionized water and dried. The desorbed adsorbent was reused for adsorption processes. The adsorption–desorption procedure was repeated five times, each times with fresh solution.

3. Results and discussion

3.1. FTIR spectrum

The ATR-FTIR spectra of unactivated and activated WS with different acids are given in Figure 1.

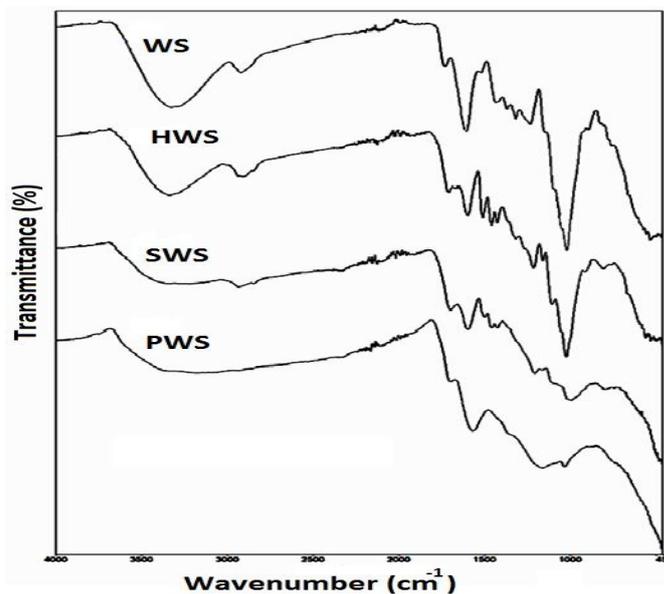


Figure 1: ATR-FTIR spectra of walnut shells.

There are various distinct and sharp absorption bands as well as relatively low intensity peaks for all sample spectra. When these spectrums compared, the spectrum of activated WS with different acids seem to be quite different from that of the original WS. The peaks in 3350 cm^{-1} and 2960 cm^{-1} , which have $-\text{OH}$ and $-\text{CH}$ (aliphatic), much broader but the lower intensity peaks, in 1566 cm^{-1} , 1705 cm^{-1} and 1100 cm^{-1} which have $\text{C}=\text{C}$ stretching vibrations in the aromatic rings bands, carboxylic acid groups and phenolic groups, observed with the increasing influence of acid valence [22-25].

3.2. SEM Results

SEM images of all the WS were shown in Fig. 2. As shown in Figure 2, while unactivated WS has a non-porous, all activated walnut shells have porous structure. Additionally, when surface morphology of SWS is compared with HWS and PWS, it is seen that SWS has much larger and deeper porous structure. Observed fast removal like sucking for removal of MB in this study might be due to these larger and deeper pores that are of important factors for adsorption [26]. As a result, the acid used to activate walnut shell seems to have a significant impact on the microstructure, in other words, the porosity of adsorbent might be adjusted using various acids.

3.3 pH_{PZC} Results

One of the important parameters for the adsorbent is pH_{PZC} that indicate electrical neutrality of adsorbent surface. pH_{PZC} values of adsorbent were given in Figure 3.

From the plot, pH_{PZC} values for WS, HWS, SWS and PWS were determined as 5.95, 4.00, 6.07, and 4.00 respectively. All of activated WSs act as a buffer in a wide pH range from ≈ 4 to ≈ 10 [23,27]. It could mean that all activated WSs can be used with high adsorption capacity in a wide pH range.

3.4. BET Analysis Results

BET analysis results of activated and unactivated WSs were given in Table 1. It is seen that the modified WS surface properties vary with the acid employed. It indicates that the adsorbent surface structures, surface area and pore structure that are crucial for adsorption, can be changed with reagent used for activation [22, 24].

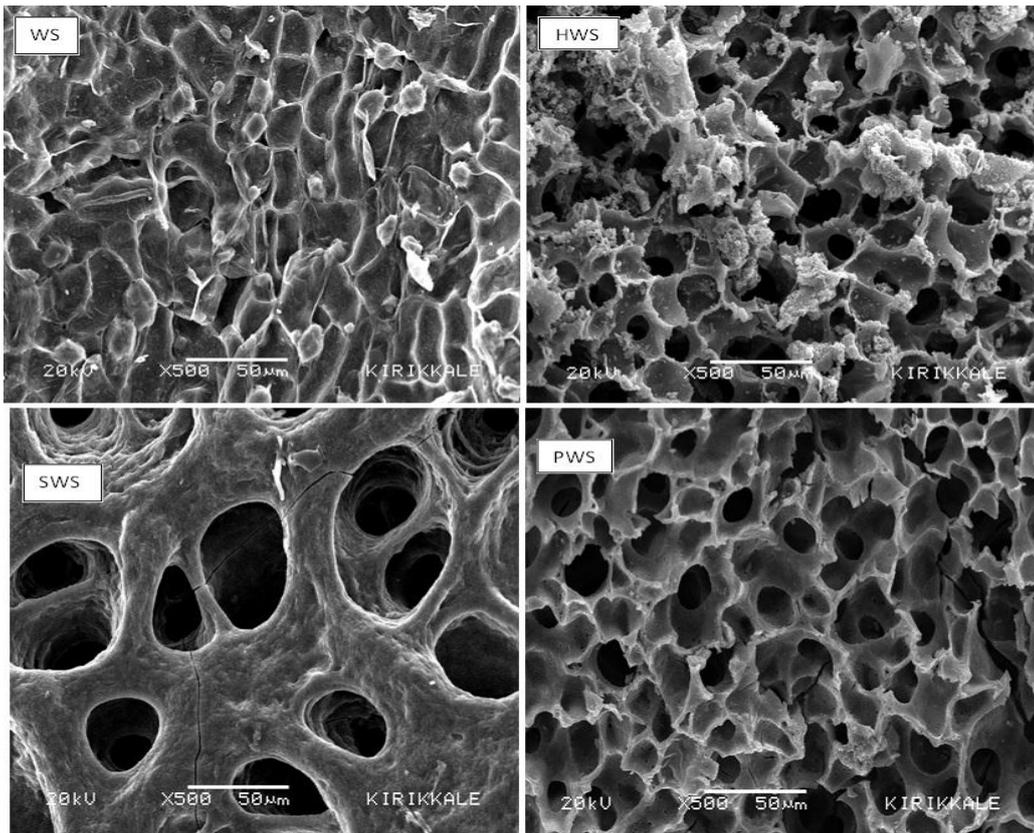


Figure 2: SEM image of walnut shell.

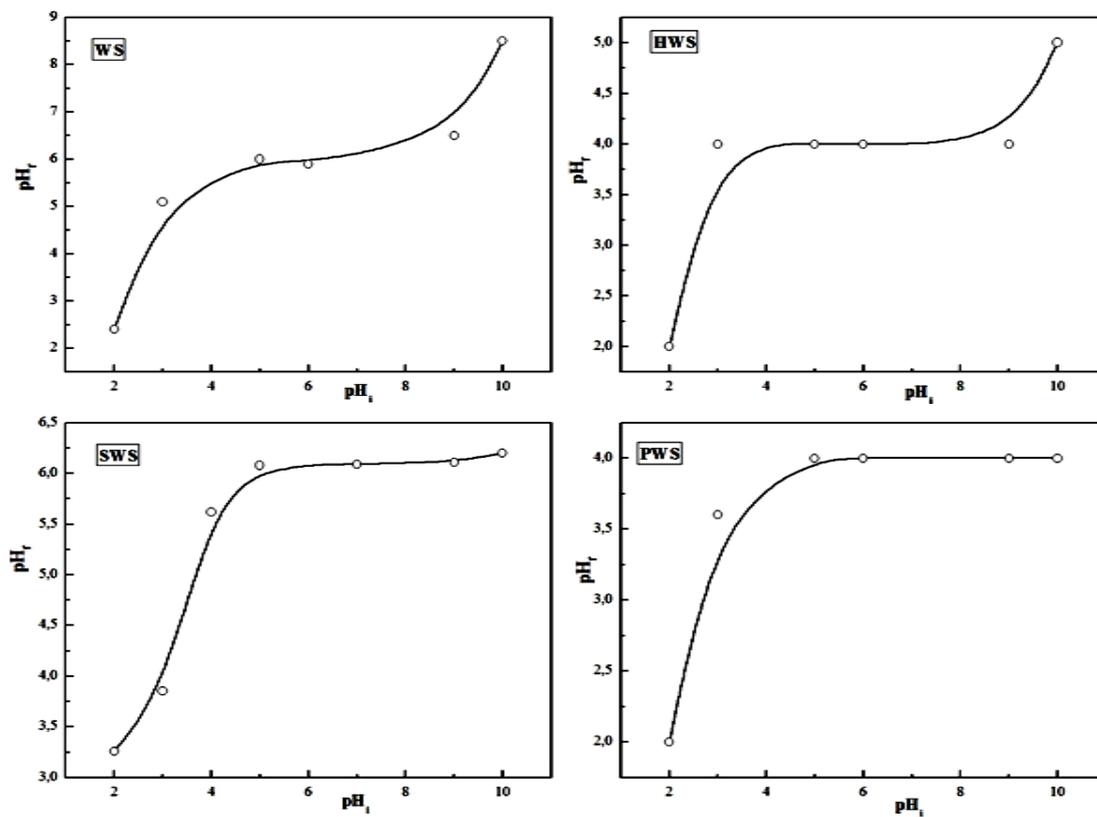


Figure 3: pH_{PZC} of walnut shells.

Table 1: BET Results.

Adsorbent Type	BET Surface Area (m ² /g)	Pore Volume (m ³ /g)	Pore Size (nm)
WS	0.1501	0.002395	63.55729
HWS	0.2964	0.003971	53.59595
SWS	0.0367	0.000654	71.22753
PWS	0.6324	0.003929	24.85221

3.4. Effects of pH on Adsorption

One of the important factors that affect the amount of adsorption is pH of the aqueous solution. At different pH values, the protonation and deprotonation behavior of acidic and basic groups in adsorbent would influence and also the MB dye would exist in different form. The effect of pH on the adsorption of MB dye was carried out pH range of 2 to 10, while keeping all other parameters constant and results were shown in Figure 4.

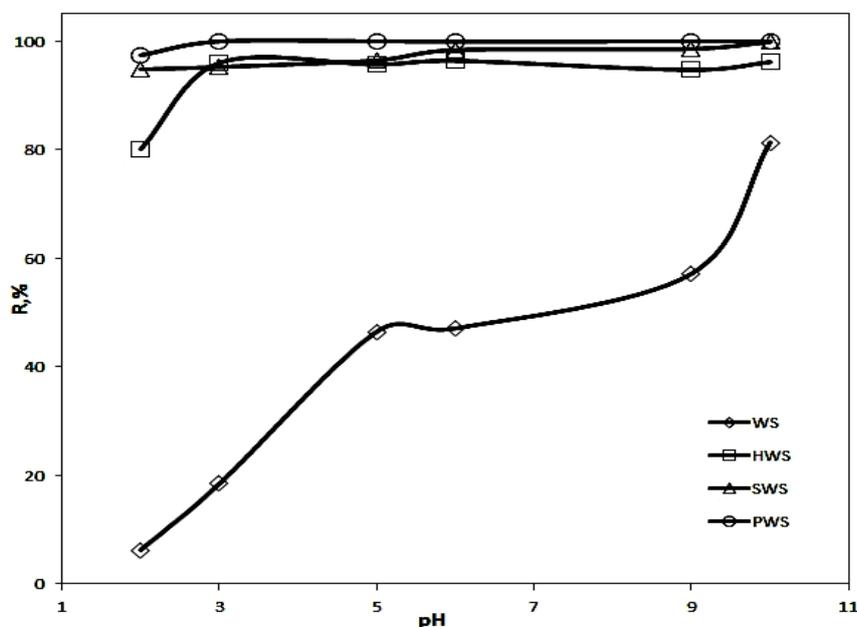


Figure 4: Effect of pH on Removal of MB onto walnut shells. [T = 25°C; t = 3 h; C_i = 50 ppm].

It shows that adsorption of MB onto activated walnut shells was not drastically influenced [22, 28] but adsorption of MB onto unactivated walnut shell was strongly influenced by initial pH. Low adsorption of unactivated WS at low pH, can be attributed to the abundance of hydrogen ions in the solution at low pH, the competition interaction between cationic dye and excess H⁺ in the solution and also the surface of the adsorbent tends to be positive charge at acidic pHs or low pHs (pH < p*H*_{PZC}). As a result, adsorption decreased due to repulsion and competitive adsorption of the same charged species. Increasing the pH causes the negative charge of the adsorbent surface (pH > p*H*_{PZC}). This situation leads to the strong electrostatic attraction between the negatively charged surfaces and positively charged MB dye and increase in the adsorption. However adsorption amount of activated WS was not affected by pH change. It could be attributed to the porous structure and also buffer behavior of activated WSs. In addition, adsorption of MB onto activated walnut shells was seen to be very close to 100% in wide pH range (4-10) but unactivated walnut shell was 80% in only pH=10. It might be considered that activated WSs could be used in a wide pH range effectively for the removal of dyes like MB. To be used in a wide pH range of activated WSs, it is advantageous in applications.

3.5. Effects of Contact Time on Adsorption and Adsorption Kinetic

Experimental data obtained from kinetic studies at different concentrations of MB were shown in Figure 5.

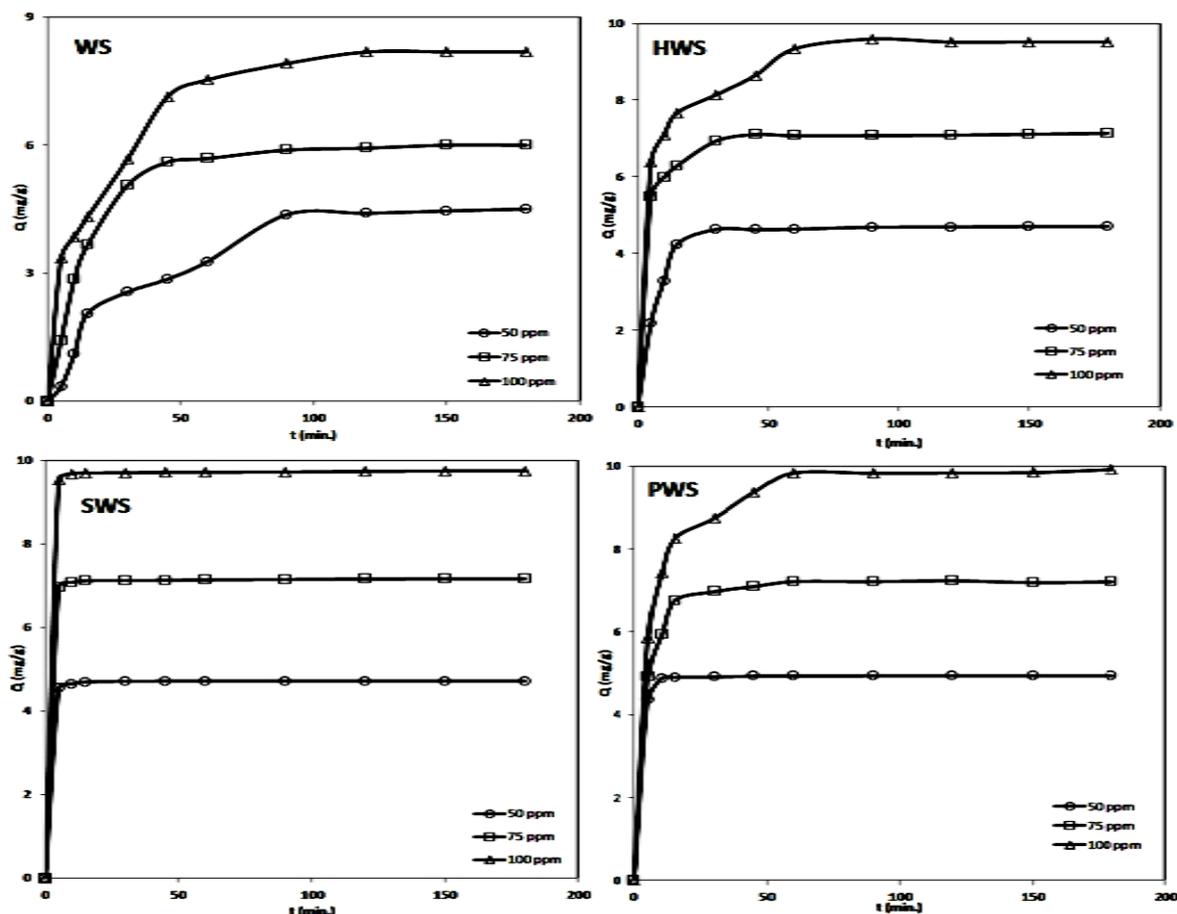


Figure 5: Effect of Time on adsorption of MB on walnut shells [pH = 10; T = 25 °C]

As seen from Figure 5, the adsorption of MB on activated WSs is faster than on unactivated WS for studied all different initial concentrations. Also, increased concentration enhances the rate of adsorption in all walnut shells because of increasing driving force between the dye molecules and the adsorbents [29]. Moreover, reaching saturation time of activated WSs is shorter than that of unactivated WS. Particularly reaching saturation time of SWS is very short for studied all different initial concentrations and not depend on initial dye concentration. This improvement can be attributed to the pores which are formed as a result of activation on the adsorbent surface. Very short adsorption time for SWS, it might be attributed to effortless diffusion into the adsorbent due to large and deeper pores. Three different kinetic models, pseudo-first-order, pseudo-second-order and intraparticle diffusion models, were used to determine rate of adsorption process. Pseudo-first-order kinetic model of Lagergren [30] and pseudo-second-order kinetic model of Ho [31] are given below respectively

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t, \quad (3)$$

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{1}{Q_e} t, \quad (4)$$

Intraparticle diffusion model is expressed with the equation given by Weber and Morris [32];

$$Q_t = k_{id} \cdot t^{1/2} \quad (5)$$

Where, Q_t and Q_e (mg g^{-1}) are the amount of adsorption on the unactivated or activated WS at time t and equilibrium, k_1 (min^{-1}), k_2 ($\text{g mg}^{-1} \text{min}^{-1}$) and k_{id} ($\text{mg g}^{-1} \text{min}^{-1/2}$) are the rate constant for the pseudo-first-order, the pseudo-second-order and the intraparticle diffusion models respectively.

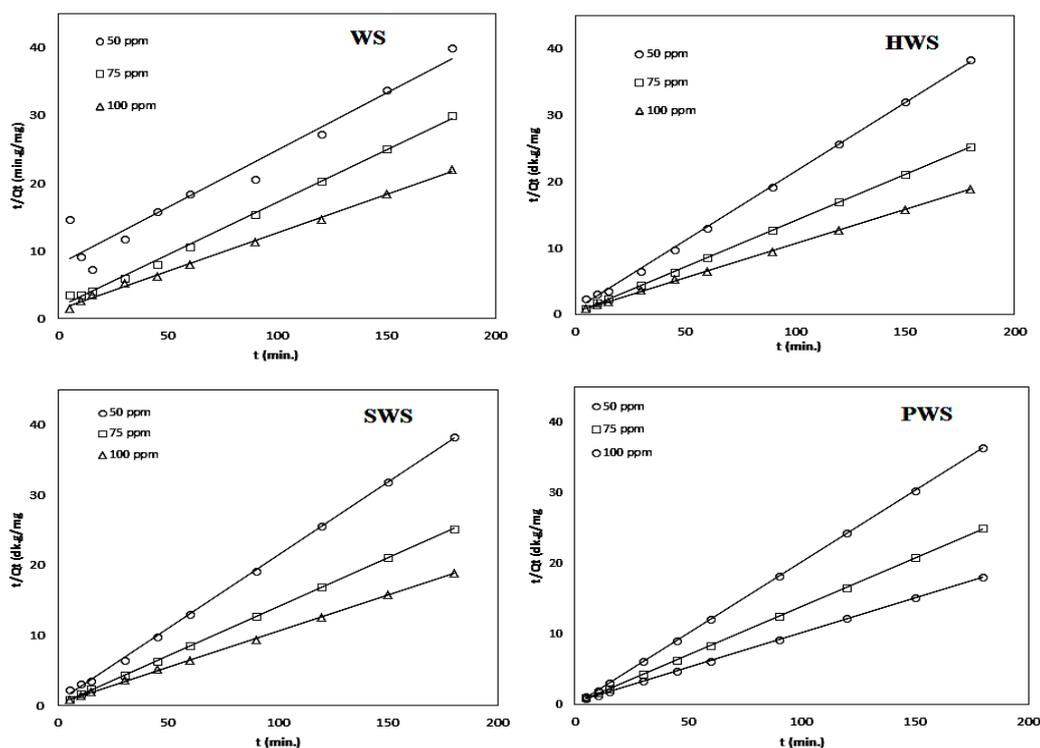


Figure 6: Pseudo-second-order plots for MB on walnut shells. [pH = 10; T = 25 °C]

The values of k_1 , k_2 and k_{id} at 25°C were calculated from the slopes of the linear plot of $\ln(Q_e - Q_t)$ vs t (not given), $\frac{t}{Q_t}$ vs t (Fig.6) and Q_t vs $t^{1/2}$ (not given) and the kinetic parameters obtained for adsorption of MB dye

onto unactivated or activated WS were listed in Table 2. As it can be seen from Table 2, for all initial concentrations 2nd order kinetic model fitted better with high correlation coefficient [33] and resulted in reasonable theoretical and experimental q_e values.

Table 2: Comparison of the pseudo-first- and second-order and intraparticle diffusion adsorption constants at different initial concentrations of MB

[MB] (ppm)	Pseudo-first-order		Pseudo-second-order			Intraparticle diffusion	
	Q_e (exp.) (mg g ⁻¹)	R ²	Q_e (theo) (mg g ⁻¹)	$k_2 \times 10^6$ (min ⁻¹)	R ²	k_{id} (mg g ⁻¹ min ^{1/2})	R ²
WS							
50	4.744	0.7227	5.93	0.125	0.946	0.465	0.866
75	6.090	0.5549	6.40	0.581	0.997	0.350	0.724
100	8.186	0.7893	8.84	0.724	0.998	0.363	0.906
HWS							
50	4.905	0.3586	4.80	1.58	0.999	0.272	0.834
75	7.137	0.4813	7.19	5.00	0.999	0.122	0.655
100	9.518	0.6781	9.80	2.50	0.999	0.154	0.514
SWS							
50	4.72	0.2999	4.73	50	1	0.012	0.540
75	7.408	0.4874	7.19	50	1	0.011	0.629
100	9.905	0.4177	9.80	100	1	0.009	0.445
PWS							
50	4.917	0.1977	4.95	20.0	1	0.294	0.714
75	7.413	0.388	7.29	5.00	0.999	0.144	0.549
100	9.915	0.5481	10.2	2.94	0.999	0.025	0.304

3.6. Effect of concentration and adsorption isotherms

As seen from Figure 7, the adsorption amount of MB increased with increasing dye concentration and reached a plateau value and then it remained unchanged for all walnut shells. Reaching a plateau value at higher concentration may also be attributed to the adsorption sites of the WS become saturated. After activation, the adsorption capacity of walnut shells, particularly PWS, has significantly increased. This increase can be explained by the increase in surface area after activation, except SWS.

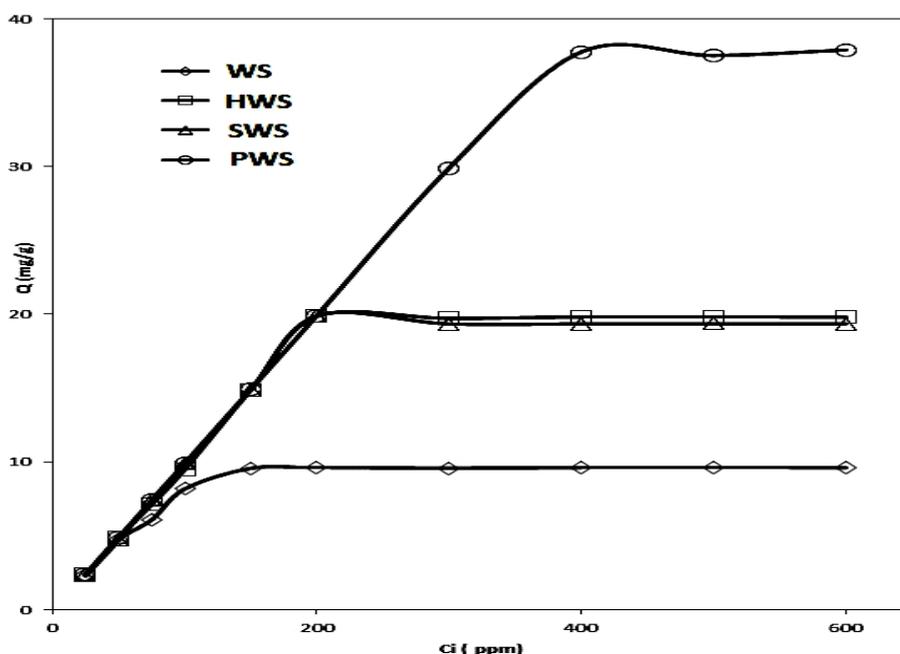


Figure 7: Effect of initial dye concentration on the adsorption amount of MB onto walnut shells [pH = 10; T = 25 °C; t = 3 h].

To explain the adsorption equilibria, many adsorption isotherm models such as Langmuir, Freundlich and D-R are used. The Langmuir isotherm which assumes that the adsorbent surface is homogeneous and the adsorption sites are energetically identical and the Freundlich isotherm, the multilayer adsorption and for the adsorption on heterogeneous surfaces, equations were given below respectively [34, 35]:

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_0} + \frac{1}{Q_0 b} \quad (6)$$

$$Q_e = K_f C_e^{1/n} \quad (7)$$

A linear form of the Freundlich equation can be obtained by taking logarithms of the equation 7.

$$\log Q_e = \log K_f + \frac{1}{n} \log C_e \quad (8)$$

The parameters in the equations are C_e (mg/L) and Q_e (g/mg) the amount of dye remained in the solution and adsorbed onto the resin at equilibrium respectively, Q_0 (mg/g) is the saturated adsorption capacity and b is the Langmuir isotherm constant (L/mg), related to the affinity of the adsorption sites. Freundlich constant K_f (mg g^{-1}) indicates the adsorption capacity also represents the strength of the adsorptive bond and n is the heterogeneity factor which also represents the bond distribution. The plot of C_e/Q_e vs. C_e for Langmuir equation (Fig.8) and $\log Q_e$ vs $\log C_e$ for Freundlich (not given) were drawn from the experimental data given in Figure 7.

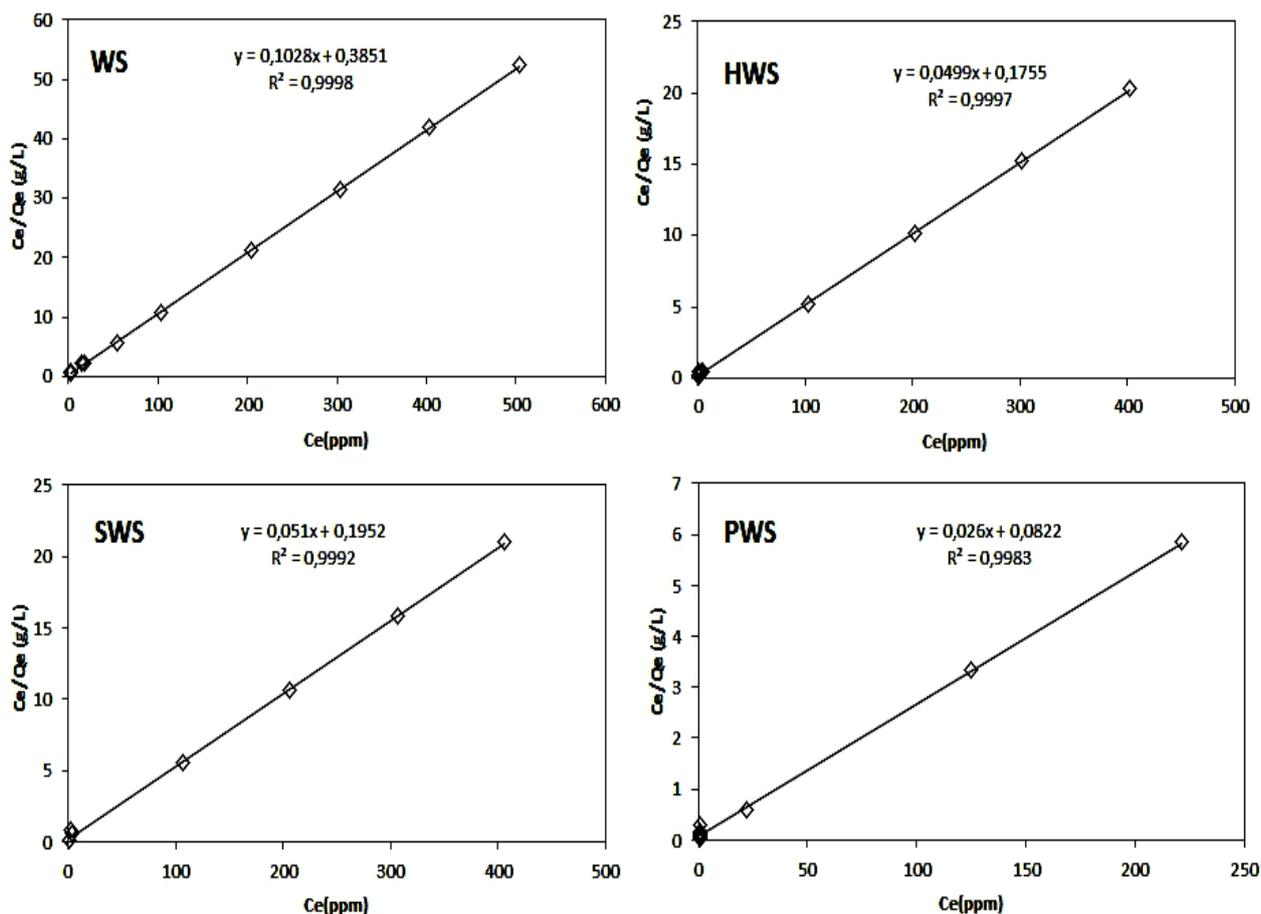


Figure 8: Langmuir isotherm plot of walnut shell

For the explanation of the adsorption mechanism, D-R isotherm given in equation 9 was used [36]:

$$\log Q_e = \log Q_m - k\varepsilon^2 \quad (9)$$

Where Q_m , Q , k and ε show D–R monolayer capacity (mg g^{-1}), the amount of solute adsorbed per unit weight of adsorbent (mg g^{-1}), a constant related with sorption energy ($(\text{mol J}^{-1})^2$), and the Polanyi potential related to the equilibrium concentration (J mol^{-1}), respectively. ε values were calculated using equation given below:

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \quad (10)$$

where R is the universal gas constant ($8,314 \text{ J}/(\text{mol K})$) and T is the absolute temperature (K). The graph, $\log Q_e$ vs ε , was drawn and value of k was found from the slope. The equation given below was used to calculate the mean free energy (E) which is useful for estimating the type of adsorption process:

$$E = (2k)^{-0,5} \quad (11)$$

If E value is below 8 kJ mol^{-1} or between 8 and 16 kJ mol^{-1} or above 16 kJ mol^{-1} adsorption process can be explained by physical adsorption, ion exchange and chemisorption, respectively [37]. The parameters, calculated from the Langmuir and D–R equations mentioned above, were given in Table 3.

Table 3: Isotherm Results.

Adsorbent Type	Langmuir Model			D-R Model		
	Q ₀ (mg/g)	b(L/mg)	R ²	Q _m (mg/g)	β (mol ² /kJ ²)	E (kJ/mol)
WS	9.73	0.26	0.9998	44.8	75 x 10 ⁻⁴	8.16
HWS	20.04	0.28	0.9997	9.6	52x 10 ⁻⁴	9.80
SWS	19.61	0.26	0.9992	19.2	38x 10 ⁻⁴	11.47
PWS	38.46	0.31	0.9983	16.0	71x 10 ⁻⁴	8.39

As can be seen from Table 3, the Langmuir model for each adsorbent, with a high correlation coefficient, is more suitable. The adsorption capacity (Q₀), of SW, HWS, SWS and PWS, was found as 9.75, 20.04, 19.61 and 38.46 mg/g adsorbent respectively. The adsorption capacity of activated WS is high in comparison with the values in literature (see Table 4.).

Table 4: Adsorption capacity of MB onto different adsorbent

Adsorbent	Capacity (mg g ⁻¹)	Reference
Act. date pits (500 °C)	12.94	[38]
Act. date pits (900 °C)	17.27	[38]
Act. olive stones (600 °C)	16.10	[39]
Act. almond shell (750 °C)	1.33	[40]
Act. hazelnut shell (750 °C)	8.82	[40]
Act. walnut shell (750 °C)	3.53	[40]
Act. apricot stones (750 °C)	4.11	[40]
Banana peel	20.80	[41]
Orange peel	18.60	[41]
Act. desert leaves (650 °C)	130	[42]
Act. desert leaves (pyrolysis-650 °C)	53.00	[42]
HWS (150 °C)	20.04	This study
SWS (150 °C)	19.61	This study
PWS (150 °C)	38.46	This study

It seems that the activated WS could be an alternative adsorbent for the removal of dyes like MB. E value calculated for each adsorbent (Table 3) is between 8 and 12 kJ / mol. Therefore it is possible to say that adsorption mechanism of MB on unactivated and activated WS can be explained with an ion-exchange process [35, 43]. Also, after adsorption, another supporting factor for the ion exchange mechanism is decreasing pH of solution [27].

3.7. Effects of Temperature on Adsorption

To investigate temperature effect onto adsorption, the adsorption amount of MB on unactivated and activated WS for different dye concentration was studied by performing adsorption experiment in a temperature between 25 and 60 °C. The found results were shown in Figure 9.

The adsorption amount of WS increases for 200 ppm but HWS, SWS and PWS are not change with increasing temperature. The adsorption amount of HWS, SWS and PWS was not changed too much with increasing temperature could be explained by the deep and large pores.

3.9. Desorption Study and Reusability

To investigate the reusability of activated walnut shell, the results obtained from the studies shown in Figure 10. As shown in Figure10, if reuse of the activated walnut shell desorbed, adsorption capacity of activated walnut shell was not observed to change so much for methylene blue. Activated walnut shell could be used as an adsorbent for the removal of dyes like methylene blue from aqueous solutions.

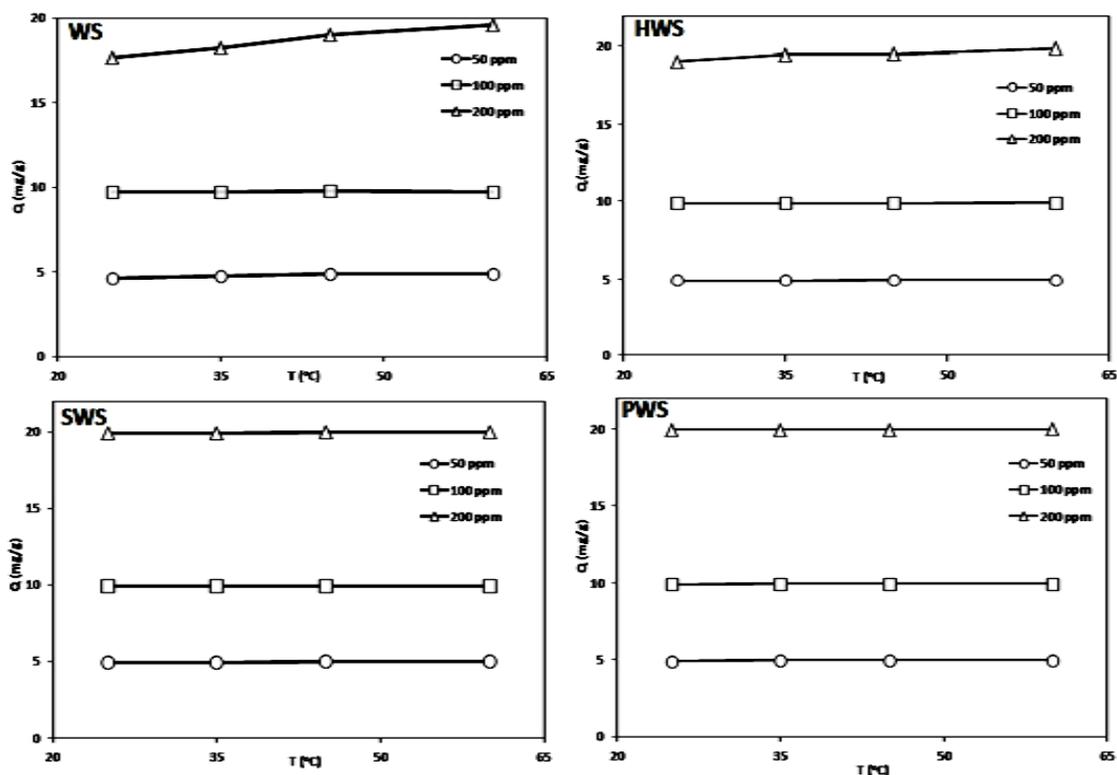


Figure 9: Effect of Temperature on Adsorption amount of MB onto walnut shells, [pH = 10; t = 3 h;].

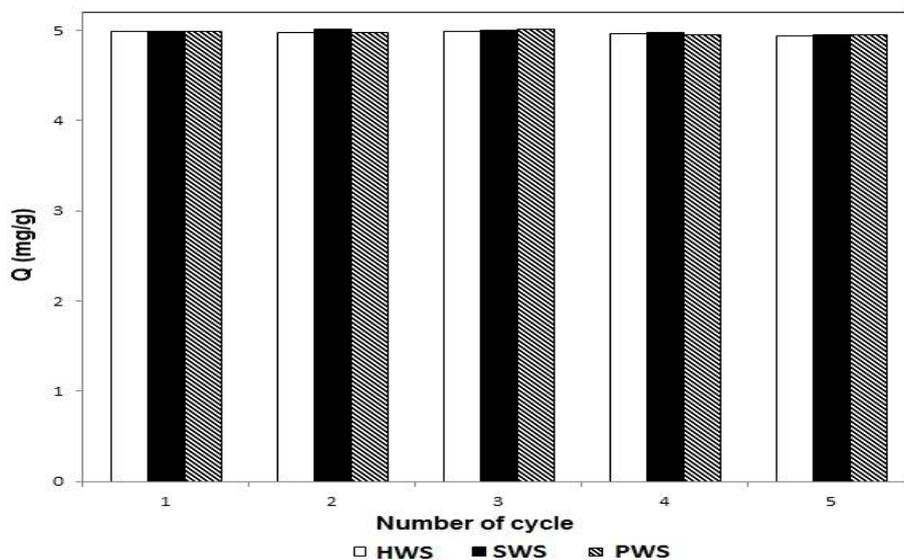


Figure 10: MB adsorption capacity of activated walnut shell after adsorption/desorption cycle [pH = 10; $C_i = 50$ ppm; t = 3 h; T = 25 °C]

Conclusion

In this work, walnut shell activated with an easy method was used as adsorbent for removal of MB. It was observed that used activation agent was very important for adsorbent surface morphology such as surface area, pore structure. In other words, it could be adjusted with used activation agent. Activated WSs behaved like a buffer in a wide pH range (4-10). Fast removal of MB was exhibited by activated walnut shell in broad pH and temperature range. Adsorption of MB onto activated walnut shell fitted Langmuir isotherm model and second order type kinetic model and occur with an ion-exchange mechanism. It was observed that adsorption was very fast especially for SWS. SWS behaved like a sucking adsorbent for MB removal. Activated walnut shells could be regenerated with 1 M HNO₃ and reusable at least five times without losing their adsorption capacity.

Acknowledgements-The authors wish to thank the financial support provided by the Bozok University Research Fund (Project No. I.F.E.F/2011-53).

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