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Adsorption of Methylene Blue from aqueous solution by raw and NaOH-modified date fruit waste

Sakineh Khorshidi^a, Heshmatollah Nourmoradi^{b,c}, Omid Rahmanian^d,
Fazel Mohammadi Moghadam^e, Samira Norouzi^d and Mohsen Heidari^{d*}

^aMSc in Environmental Engineering, Islamic Azad University, Bandar Abbas Branch, Bandar Abbas, Iran

^bDepartment of Environmental Health Engineering, Faculty of Health, Ilam University of Medical Sciences, Ilam, Iran

^cBiotechnology and Medical Plants Research Center, Ilam University of Medical Sciences, Ilam, Iran

^dDepartment of Environmental Health Engineering, Faculty of Health, Hormozgan University of Medical Sciences, Bandar Abbas, Iran

^eDepartment of Environmental Health Engineering, School of Health, Shahrekord University of Medical Sciences, Shahrekord, Iran

ABSTRACT

This study examined the adsorption of methylene blue onto raw date fruit waste (DFW) and NaOH-modified date fruit waste (N-DFW). Experiments were done as function of contact time, initial pH (2-12), adsorbent dose (0.5-8 g/L) and initial dye concentration (20-200 mg/L). The solution pH had strong effect on the adsorption capacity of both adsorbents and the extent of the dye removal increased with increasing pH. The experimental data were fitted to different kinetic and isotherm models. The adsorption of methylene blue on both sorbents followed well the pseudo-second-order model. According to Langmuir isotherm model, the maximum monolayer adsorption capacities of DFW and N-DFW were 165.3 and 215.4 mg/g, respectively. Therefore, date fruit waste could be considered as an efficient adsorbent for the removal of MB from aqueous solutions and its adsorption properties were improved through modification with NaOH.

Keywords: Adsorption, Methylene Blue, Date fruit waste, NaOH

INTRODUCTION

Methylene blue (MB) is a common industrial cationic dye which is widely used in dyeing paper, cotton, wood and silk [1, 2]. MB can cause eye burns in humans and animals, cyanosis, methemoglobinemia, convulsions, tachycardia, dyspnea, irritation to the skin, and if ingested, irritation to the gastrointestinal tract, vomiting, nausea, and diarrhea [3]. Therefore, removing this pollutant from waste streams is an urgent task due to its harmful impacts on receiving waters.

The problems associated with dye pollution could be reduced or minimized by physical, chemical, and biological decolorization processes, for example, by microbial degradation, chemical oxidation, coagulation and membrane separation [2]. However, these processes have their disadvantages and limitations, such as poor removal efficiency, high cost and generation of secondary pollutants. Adsorption is an efficient and preferred method in the removal of dye substances from aqueous solutions due to its simplicity of design, ease of operation and insensitivity to toxic

pollutants [4]. Activated carbon is the most widely used material for the adsorption of dyes from water and wastewater, but its cost is quite high and needs a costly regeneration system [5]. The main criteria for choosing a material as adsorbent are availability, cost effectiveness, and adsorptive properties [6]. In this regards, agricultural wastes have been considered for the adsorption of dyes because of low cost, good adsorption capacity, little processing requirement, and high availability [7]. Recently a number of agricultural material such as tea wastes [8], Eucalyptus sheathiana bark [9], Cashew nut shell [10], Stipa tenassicima fibers [11], peanut [12], and Aloe Vera leaves wastes [13] have found to be efficient low cost adsorbents for the removal of dyes from aqueous solutions. In date processing industries, filter press is used to separate date juice from fibrous material. Therefore, a pressurized fibrous cake, here named date fruit waste (DFW), is a main by-product of such industries [14]. According to Food and Agriculture Organization of the United Nations (FAO), around 1066000 tons of date fruit was produced in Iran in 2012 [15]. In hormozgan region, which is the largest date producer in Iran, date processing industries produce huge amounts of DFW. This by-product is mainly dumped into mountains of waste and may pose environmental problems. Hence, DFW could be considered as a low-cost, abundant and renewable adsorbent. To the best of knowledge, no work has been done on the adsorption of dyes onto this agricultural by-product. Therefore, the objective of this work was to study the adsorption of MB onto raw and NaOH-modified date fruit waste.

MATERIALS AND METHODS

2.1 Materials

Methylene blue (MB), $C_{16}H_{18}ClN_3S \cdot 3H_2O$ supplied by Sigma Aldrich. Date fruit waste was kindly supplied by Khorma Bon Jonub Co. (Bandar Abbas). The dye stock solution of 1000 mg/L was prepared and diluted by double distilled water to obtain working solutions (20 to 200 mg/L). NaOH and other chemicals were purchased from Merck Co. (Germany).

2.2 Preparation of adsorbent

Date fruit waste (DFW) was washed repeatedly with double-distilled water to remove dust and soluble impurities, and this was followed by drying at 103 °C for 24 h and was ground. The dried DFW was then suspended in alkali solution (5% sodium hydroxide) and stirred for 4 h. The alkali solution was filtered off, and the sample was washed thoroughly with distilled water until the pH of the wash was neutralized. The treated date fruit waste was then dried at 103 °C for 24 h. After drying, the NaOH-modified DFW (N-DFW) was stored in sealed glass container for further use to adsorption experiments.

2.3 Adsorption studies

The adsorption of MB onto raw and alkali-modified DFW was investigated in batch mode experiments. All batch adsorption experiments were carried out in Erlenmeyer flask (250 mL) containing 100 mL dye solution. The flask with solution was wrapped, sealed and mixed by an orbital shaker (180 rpm). The effects of pH (2, 4, 6, 8, 10, 12), adsorbent concentration (0.5, 1, 2, 4, 8 g/L), contact time (0, 10, 20, 50, 90, 180 min) and dye concentration (20, 50, 100, 200 mg/L) were determined on the adsorption of MB. The room temperature during all experiment was 25 ± 1 °C. For pH effect experiments, 0.1 N NaOH and 0.1 N HCl were used to adjust the solution pH to the desired value. The sorption capacities of the sorbents were obtained by Eq. (1):

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

where q_e is the sorption capacity (mg/g) of the sorbents, C_0 and C_e are the initial and the equilibrium concentrations of MB in the solution (mg/L), respectively, m is the dry weight of the added adsorbents (g) and V is the volume of solution (L). The percentage removal of dye ($R(\%)$) was calculated using the following equation, Eq. (2):

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

All the adsorption experiments were duplicated and the average values are presented.

2.4 Analysis

At predetermined time intervals, the dye solution was filtered and the residual dye concentration was determined using a spectrophotometer (Hach Lange DR5000) at 668 nm. Fourier transform infrared (FTIR) analysis of the adsorbents was done by using a Fourier transform infrared spectrophotometer (FTIR, Bruker, Germany), where the spectra were recorded from 400 to 4000 cm^{-1} .

RESULTS AND DISCUSSION**3.1. FTIR characterization**

The FTIR spectra of DFW and N-DFW are presented in Fig. 1. As shown in the figure, after alkali modification of DFW, a large decrease in the intensity of some absorption bands were occurred, which indicates a change in the functionality of the raw material. The band at 3295 cm^{-1} is common to both spectra and is assigned to O–H stretching vibration. The bands at 2916 and 2849 cm^{-1} are attributed to C–H stretching vibration. The decreased intensity of these bands in N-DFW spectrum indicates that hydrogen was broadly removed during the modification process. The bands at 1733 cm^{-1} and 1626 cm^{-1} are assigned to C=O axial deformation of aldehyde, lactone, ketone, and carboxyl groups [16]. The remained absorption peak at these bands for N-DFW is an indication of the presence of a carboxylic acid group. This means that there are still carboxylic groups or C=O groups which are not reacted by NaOH solution. The band at 1031 cm^{-1} is assigned to C-O stretching vibration.

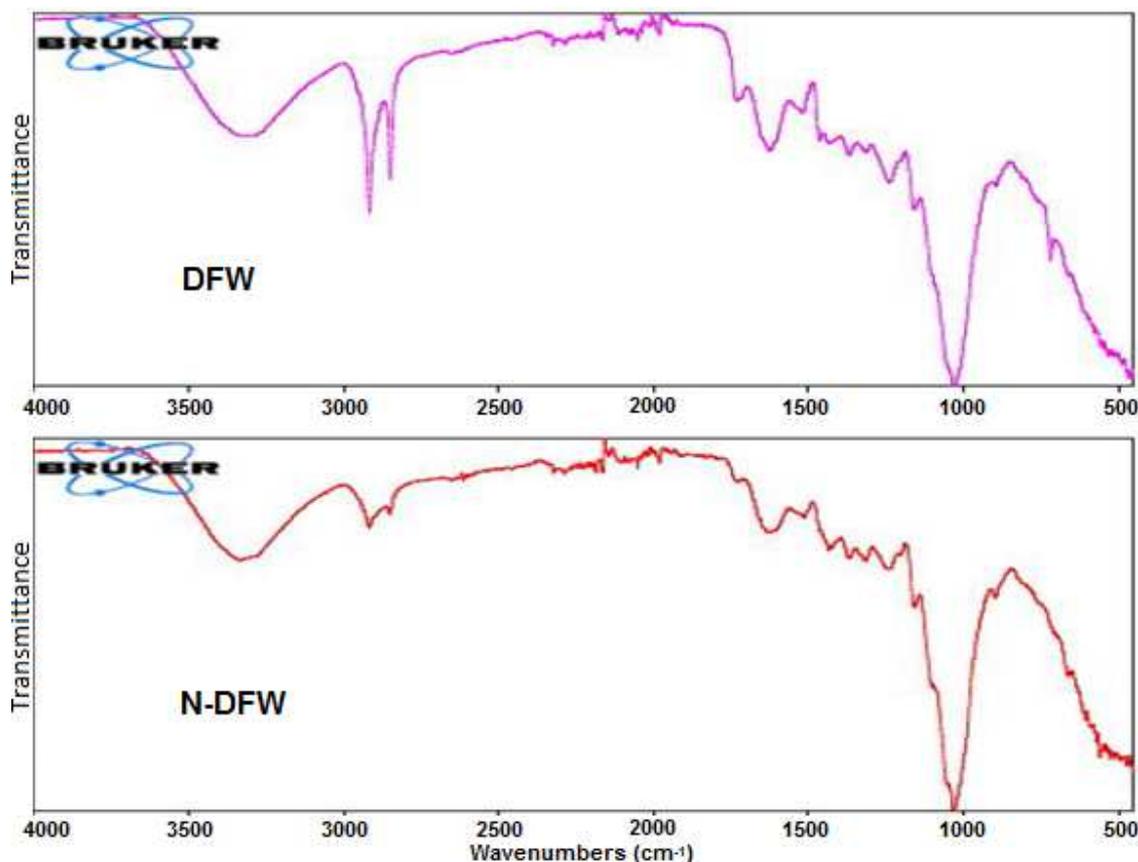


Fig. 1. FTIR spectra of DFW and N-DFW

3.2 Influence of pH on MB adsorption

Solution pH affects both the surface binding sites of the adsorbent and aqueous chemistry [17]; therefore it was presumed that the sorption of methylene blue was mainly affected by solution pH. In the pH effect experiments, 0.05 g of DFW and N-DFW were added to 100 ml of 50 mg/L MB and the initial pH was adjusted from 2 to 12. Fig. 2 shows the dye adsorption efficiency of DFW and N-DFW as a function of pH. Accordingly, the percentage removal of MB by DFW and N-DFW increases with the increase in pH of the dye solution. MB is a cationic dye; therefore it exists in aqueous solution in the form of positively charged ions. At low pH values, the functional groups present on the adsorbent surface are easily protonated. Under this condition, the surface of the adsorbent becomes positively charged, and this decreases the adsorption of the dye cationic species through electrostatic repulsion [18]. When pH is increased, the surface of the adsorbents is more negatively charged and electrostatic repulsion between MB and surface is decreased. In this condition the interaction between the negatively charged sorbent and the cationic dye molecules is improved and the percentage removal of MB would increased [19]. Several studies carried out on

adsorption of MB from aqueous solutions by various adsorbents have also shown that the adsorption this dye preferred higher solution pH values [19, 20 and 21]. Since the difference in the percentage increase was not very significant for pH values ranged from 8 to 12, all further experiments were carried out at pH 8.0.

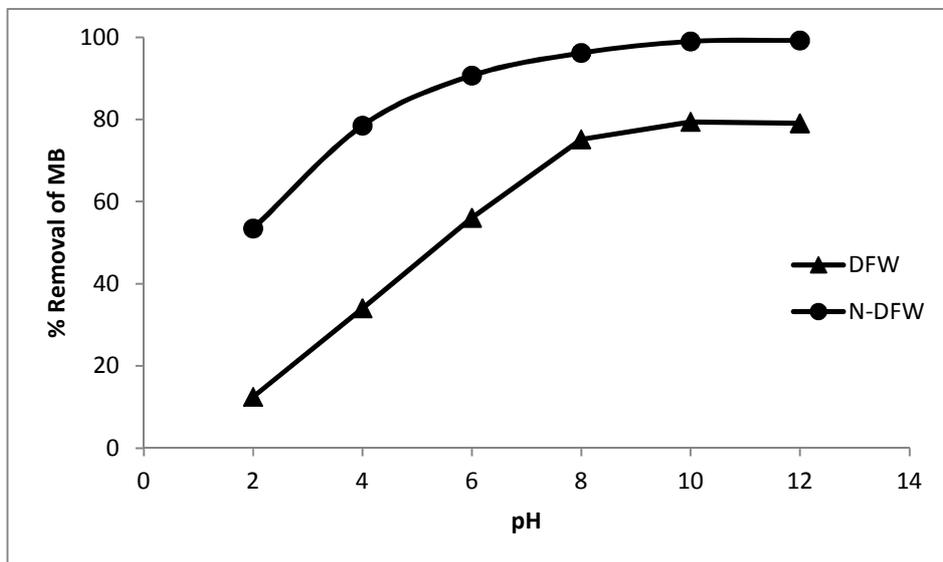


Fig. 2. Effect of initial pH on the adsorption of MB on DFW and N-DFW (Adsorbent dose=1 g/L, initial MB concentration=50 mg/L, solution volume=100 mL, temperature=25 °C, contact time=180 min)

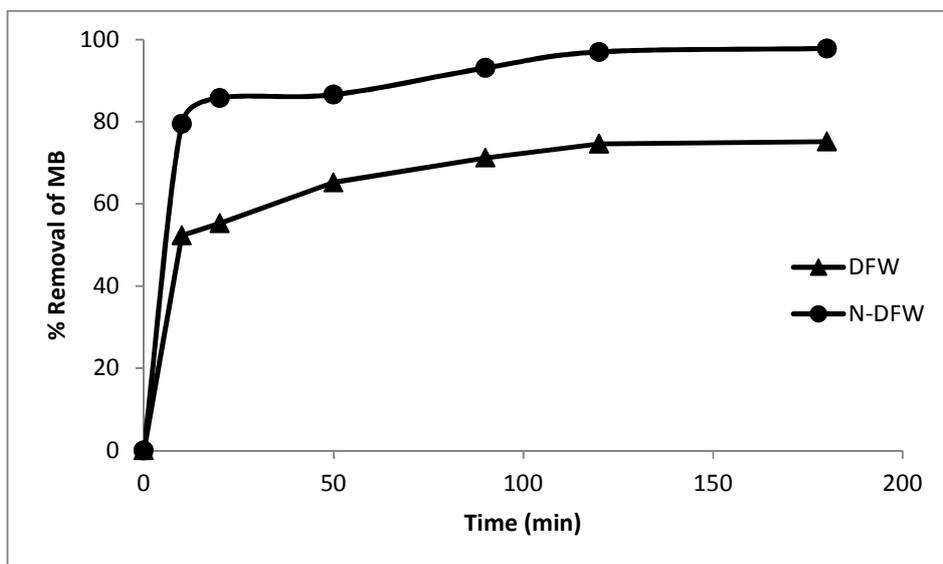


Fig. 3. Effect of contact time on the adsorption of MB on DFW and N-DFW (Adsorbent dose=1 g/L, initial MB concentration=50 mg/L, solution volume=100 mL, temperature=25 °C, pH=8)

3.3 Effect of contact time

In order to evaluate the effect of contact time on dye adsorption process, the experiments were performed at 100 ml of 50 mg/L MB solution. The initial pH for each dye solution was set at 8. Fig. 3 shows the adsorption of MB by DFW and N-DFW as a function of contact time. As seen from the figure, the percentage removal of MB increased with rise in contact time and reached to 75.19 and 96.19% for DFW and N-DFW, respectively, after 180 min contact time. The initial rapid adsorption may be attributed to the presence of more binding sites for adsorption and the slower adsorption rates at the end is due to the saturation of the binding sites and attainment of equilibrium.

Moreover, the adsorption of dye molecules onto the exterior surface may be a reason for rapid dye adsorption rate at initial contact times [22]. Chowdhury *et al.* (2011) have been proposed similar conclusions for adsorption of MG by alkali-modified rice husk [17]. Since the improvement in the percentage removal of MB between 120 and 180 min contact times were less than 1%, all the following experiments were done at 120 min contact time.

3.4 Adsorption kinetics

Kinetic studies provide valuable information regarding the limiting stage of the adsorption process [16, 23]. Adsorption kinetics of MB onto DFW and N-DFW were fitted to pseudo-first order and pseudo-second order kinetic models. The linear form of pseudo-first order kinetic can be presented by Eq. (3):

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{3}$$

where q_t (mg/g) is the dye adsorption capacity of adsorbents at time (t). k_1 (1/min) is the sorption rate constant. k_1 and q_e could be obtained from the slope and intercept of the plot of $\ln(q_e - q_t)$ versus t, respectively [24].

On the other hand, the linear form of pseudo-second order kinetic model is expressed as follow:

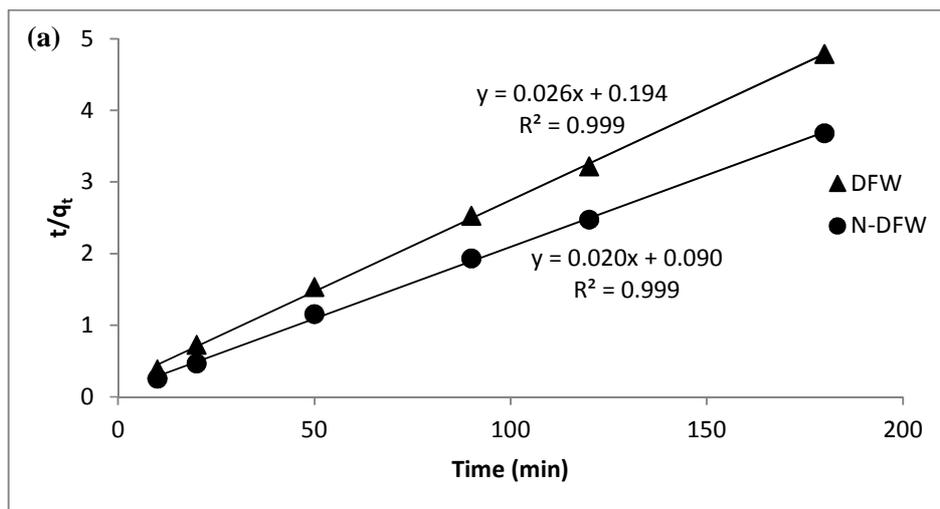
$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{4}$$

where k_2 (the pseudo-second order rate constant, g/mg.min) and q_e can be calculated from slopes and intercepts of the plots of t/q_t against t, respectively [24].

As shown in Fig. 4 (a), pseudo-second order model better described the adsorption kinetics, presenting R^2 values of 0.999 for MB sorption onto both sorbents. Additionally, the q_e values calculated by the model are more comparable to those experimentally obtained (Table 1). Therefore, the adsorption of MB on DFW and N-DFW followed second-order kinetics, indicating that chemical sorption involving valency forces through exchange or sharing of electrons between adsorbate and adsorbent might be significant [17].

Table 1. Parameters of pseudo-first and pseudo-second order kinetics for the adsorption of MB onto DFW and N-DFW

Sorbent	Pseudo-first order			Pseudo second order		
	Q_e (mg/g)	K (1/min)	R^2	q_e	K (g/mg.min)	R^2
DFW	21.91	0.029	0.732	39.15	0.0034	0.999
N-DFW	18.67	0.029	0.904	49.04	0.0054	0.999



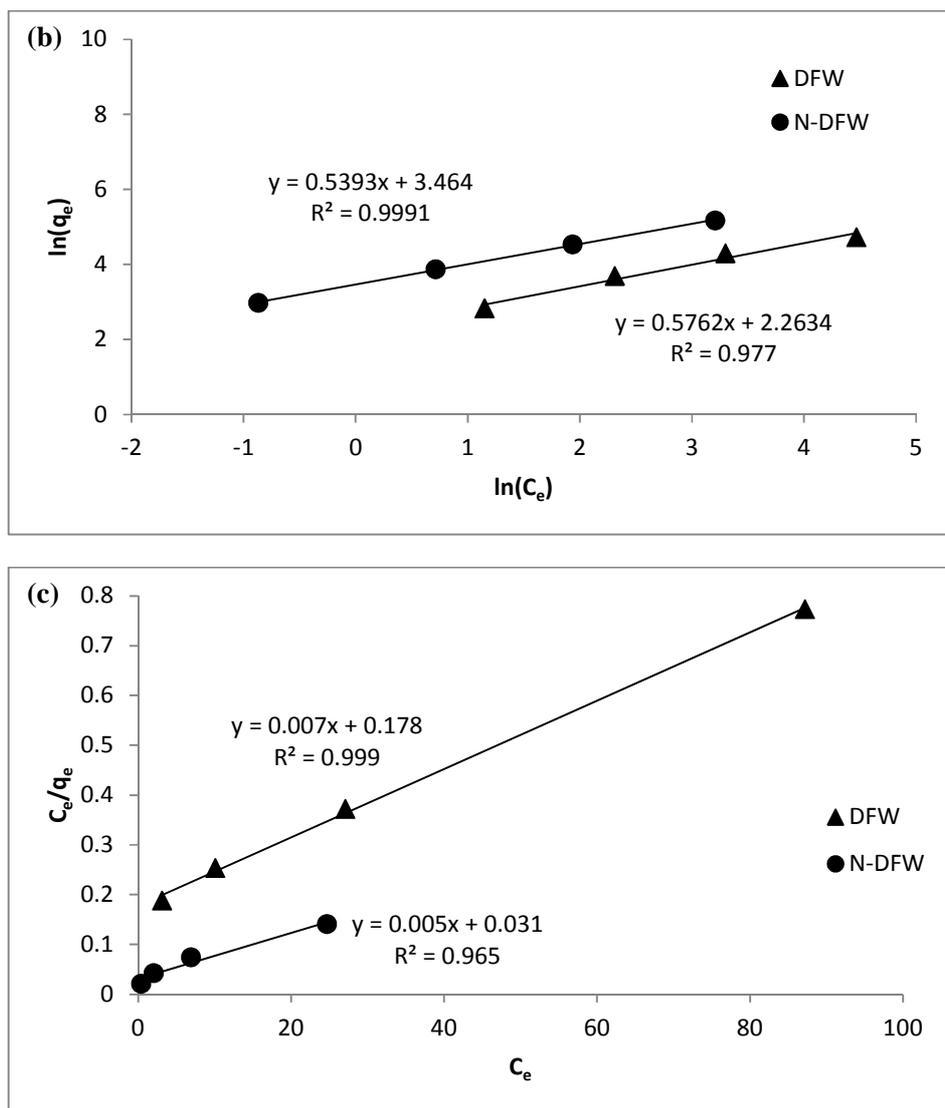


Fig. 4. Pseudo-second-order kinetic (a), Freundlich isotherm (b) and Langmuir isotherm (c) for adsorption of MB on DFW and N-DFW

3.5 Effect of initial concentration on MB adsorption

As shown in Fig. 5, initial dye concentration had clear influence on the amount of MB absorbed on DFW and N-DFW. As seen from the figure, the equilibrium adsorption capacity (q_e) of DFW and N-DFW increased from 15.9 to 112.8 mg/g and from 19.6 to 175.3 mg/g, respectively, by increasing initial MB concentration from 20 to 200 mg/L. In fact, initial dye concentration produces driving force such as van der Waal's force to overcome the mass transfer resistance of MB to the active sites of the adsorbent [25]. Therefore, with the increase in adsorbate concentration, the mass transfer driving force becomes larger, hence resulting in higher MB adsorption capacity. As the adsorbents offer a finite number of surface binding sites, at higher initial MB concentrations, the percentage removal of MB decreased and showed a saturation trend.

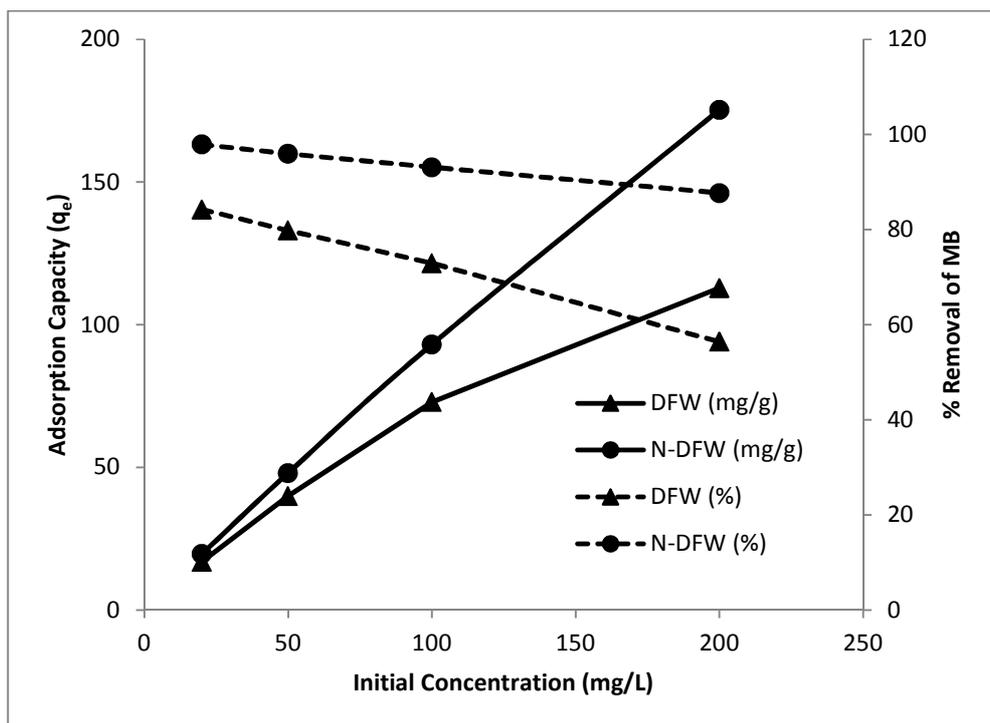


Fig. 5. Effect of Initial dye concentration on the adsorption of MB on DFW and N-DFW (Adsorbent dose=1 g/L, contact time=120 min, solution volume=100 mL, temperature=25 °C, pH=8)

3.6 Adsorption isotherms

Adsorption isotherm is basically important to describe the sorption mechanisms. Isotherm analysis of adsorption data is critical in optimizing the use of adsorbents and designing the sorption system [26]. In the present study three isotherm equations, namely, Langmuir, Freundlich and Dubinin-Radushkevich (D-R) were fitted to the experimental data for MB adsorption onto DFW and N-DFW. The isotherm parameters are shown in Table 2.

The Langmuir isotherm model presumes monolayer and uniform adsorption onto a surface with a finite number of adsorption sites [27]. The linear form of the Langmuir isotherm model is given by eq. (5):

$$\frac{C_e}{q_e} = \frac{C_e}{Q_m} + \frac{1}{bQ_m} \quad (5)$$

where C_e (mg/L) is the equilibrium concentration of the adsorbate (MB), q_e (mg/g) is the equilibrium adsorption capacity of the adsorbent, Q_m (maximum sorption capacity of monolayer adsorbent, mg/g) and b (Langmuir constants related to rate of adsorption, L/mg) can be obtained from the slope and intercept of the plot between C_e/Q_e and C_e .

The essential characteristics of the Langmuir isotherm can be expressed by a dimensionless constant, i.e. equilibrium parameter (R_L) [28], which is defined as

$$R_L = \frac{1}{1+bC_0} \quad (6)$$

where C_0 is the highest dye concentration (mg/L). The magnitude of R_L indicates the type of the isotherm to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$) [29]. The values of R_L were found to be 0.11 and 0.03 for the adsorption of MB onto DFW and N-DFW, respectively. Therefore, the adsorption of MB on both adsorbents was favorable under the conditions used in this study.

The Freundlich isotherm model assumes multilayer adsorption on heterogeneous surface at sites with non-uniform distribution of adsorption over the surface [30]. This isotherm can be written in the following linear form:

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

where n and K_f (mg/g(1/mg) n) are Freundlich isotherm constants related to the sorption capacity and sorption intensity, respectively, and could be determined through plotting $\ln q_e$ against $\ln C_e$, respectively (Fig. 4 (b)). The magnitude of n gives a measure of adsorption favorability. The adsorption is favorable at n values higher than one [31]. As illustrated in Table 2, the values of n for the adsorption of MB onto DFW and N-DFW were 1.543 and 1.866, respectively, representing a beneficial sorption which indicates favorable adsorption.

The Dubinin–Radushkevich (D-R) isotherm model assumes a gaussian energy distribution onto a heterogeneous surface and describes the nature of sorption (physical or chemical) [32]. The linear form of D-R isotherm is expressed as follow:

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \quad (8)$$

where q_m (mg/g) is the theoretical sorption capacity at saturation state, β (kJ/mol) is a constant related to energy and ε , Polanyi potential, is acquired by the following equation [31]:

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \quad (9)$$

where R (kJ/mol.°K) is the universal gas constant (8.314 j/mol.°K) and T (°K) is the solution absolute temperature. q_m and β could be obtained from the intercept and slope of the plot of $\ln(q_e)$ versus ε^2 . Mean sorption energy, E (kJ/mol), which is defined as the free energy transfer of one mol of solute from infinity of the surface of the sorbent could be derived from constant β as follow:

$$E = \frac{1}{\sqrt{-2\beta}} \quad (10)$$

The magnitude of E can give information about the type of adsorption mechanism. For the values of $E < 8$ kJ/mol, the adsorption process is of physical nature, while for values of E between 8 to 16 kJ/mol, the adsorption process supposed to proceed through chemisorptions [33]. As shown in Table 2, the magnitudes of E (0.30 and 1.63 kJ/mol for DFW and N-DFW, respectively) are below 8 kJ/mol under studied conditions, indicating that the adsorption nature of MB onto DFW and N-DFW is physisorption.

According to Fig. 4 (b and c), the equilibrium data of MB adsorption onto DFW and N-DFW best fitted to the Langmuir and Freundlich isotherms, respectively. The fitness of the adsorption data to the Freundlich isotherm implies the multilayer adsorption of MB onto heterogenous surface of NaOH-modified DFW. Chakraborty et al (2011) and Chowdhury et al (2011) also reported that the adsorption of Crystal violet and Malachite Green onto NaOH-modified rice husk best fitted to the Freundlich isotherm model [17, 33].

Table 2. Langmuir, Freundlich and D-R isotherm parameters for the adsorption of MB onto DFW and N-DFW

Sorbent	Langmuir isotherm			Freundlich isotherm			D-R isotherm		
	Q_m (mg/g)	b (L/mg)	R^2	K_f	n	R^2	Q_m (mg/g)	E (kJ/mol)	R^2
DFW	165.3	0.024	0.997	6.84	1.543	0.985	73.3	2.99	0.802
N-DFW	215.4	0.156	0.967	32.36	1.866	0.998	101.8	16.10	0.772

3.7 Effect of adsorbent dose on MB sorption

To study the effect of adsorbents dose on MB uptake, the experiments were performed at initial MB of 50 mg/L, while the amount of adsorbent added was varied from 0.5 to 8 g/L. Fig. 6 shows the percentage removal of MB as a function of adsorbent dose. At equilibrium time, the percentage removal increased from 74.64 to 95.90% for an increase in DFW dose from 0.5 to 1.0 g/L. The increase in removal rate of the dye was due to the increase in the available sorption surface sites. Since the removal rate were near to 100% for DFW doses of 2 to 8 g/L and for all the applied doses of N-DFW, the influence of adsorbent dose on the percentage removal of MB was not significant.

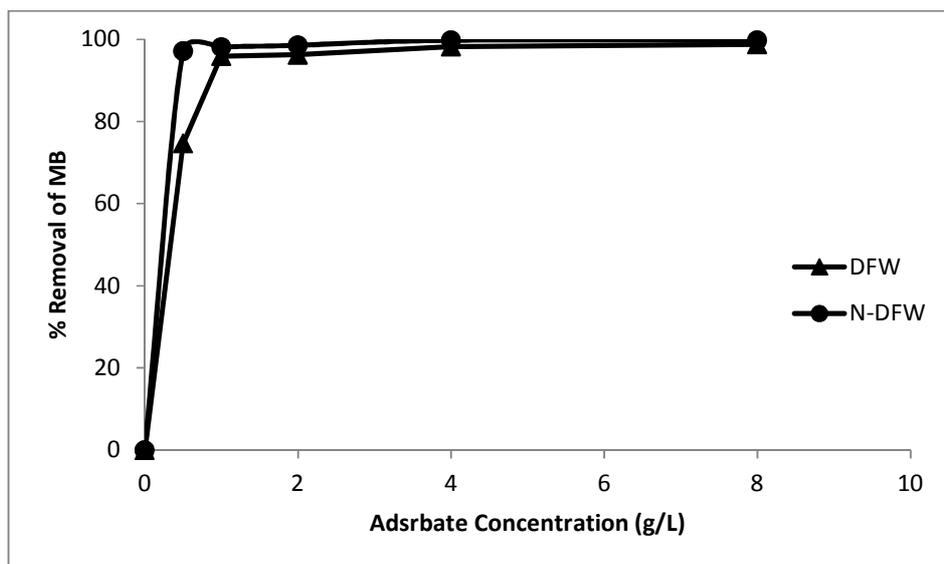


Fig. 6. Effect of adsorbent dose on the adsorption of MB on DFW and N-DFW (Contact time=120 min, initial MB concentration=50 mg/L, solution volume=100 mL, temperature=25 °C, pH=8)

3.8 Effect of NaOH on sorption capacity

According to the Langmuir isotherm, the maximum monolayer adsorption of N-DFW (215.4 mg/g) was higher than that of DFW (165.3 mg/g). Moreover, lower equilibrium parameter (R_L) value in Langmuir isotherm and higher n value in Freundlich isotherm in the case of MB adsorption onto N-DFW revealed the better adsorption properties of this sorbent than those of DFW. The higher adsorption capacity of N-DFW can be explained on the basis of NaOH treatment which improved the DFW surface with negatively charge. As the adsorbent surface is negatively charged, the increasing electrostatic attraction between the cationic dye species and negatively charged adsorbent would lead to the enhanced adsorption capacity.

The adsorption capacities of DFW and N-DFW along with some other agricultural by-products for MB adsorption are presented in Table 3. As can be seen, the adsorption capacity of raw and modified date fruit waste is comparable to other modified agricultural by-products. Overall, this study showed that date fruit waste, which may cause numerous environmental problems in dumping sites, could be considered as an excellent adsorbent for MB. In addition, NaOH modification of this material would improve its adsorption properties.

Table 3. MB adsorption capacity of various modified agricultural by-products

Adsorbent	Maximum adsorption capacity (mg/g)	References
Date fruit waste (DFW)	165.3	This work
NaOH-modified DFW	215.4	This work
NaOH-modified rejected tea	242.1	[29]
Modified wheat straw	432.8	[34]
Swede rape straw	246.4	[35]
Modified Ephedra strobilacea saw dust	37.0	[36]

CONCLUSION

Present study evaluated the potential of raw and NaOH-modified date fruit waste, an agricultural by-product, in the adsorption of MB from aqueous solution. The adsorption of MB onto both sorbents was highly pH dependent and was favored at high pH values. The adsorption of MB onto both sorbents followed pseudo-second-order kinetic model. The nature of MB adsorption onto both sorbents was physical adsorption according to the Dubinin-Radushkevich (D-R) isotherm model. The results of this study showed that date fruit waste is a high potential in the adsorption of MB. Moreover, alkali modification improved the capacity of this agricultural by-product.

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