

Removal of synthetic cationic dye from aqueous solution using date palm leaf fibers as an adsorbent

Shagufta², Rahul Dhar¹, Bong-Sik Kim¹, Amani Alblooshi², Irshad Ahmad²

¹ Department of Mathematics and Natural Sciences, School of Arts and Sciences

² Department of Chemical and Petroleum Engineering, School of Engineering American University of Ras Al Khaimah, P. O. Box 10021, Ras Al Khaimah, UAE

*Corresponding author E-mail: shagufta.waseem@aurak.ac.ae

Abstract

An ecofriendly and economical adsorbent was studied as an alternative substitution of activated carbon for removal of synthetic dye from wastewater. Date palm leaf fibers were utilized as a biodegradable adsorbent to remove methylene blue dye from aqueous solution by adsorption. Several experiments were conducted to study the effect of adsorbent dosage, pH and dye concentration with time and we revealed that the adsorption percentage of methylene blue dye varied with these changes. The equilibrium adsorption data were analyzed by using Freundlich and Temkin isotherms and adsorption was found to well-fit into these two models. The equilibrium adsorption capacity (q_e) increases with increasing the initial concentration of the dye and decreases with the adsorbent dosage and pH. The pseudo-second order kinetic model fits very well with the dynamic behavior of the adsorption of methylene blue dye on date palm leaf fibers under different adsorbent dosage, and dye concentrations. Based on the linearized correlation coefficient, the Freundlich equation is the best fit equilibrium isotherm for the sorption of methylene blue dye onto date palm leaf fibers. We can expect that in the future, date palm leaf fibers could be effectively used as an alternative to expensive adsorbents in the treatment of industrial wastewater containing synthetic dyes.

Keywords: Adsorption; Date Palm Leaf; Methylene Blue; Synthetic Dye; Water Purification; Biomass.

1. Introduction

Water pollution is a major concern to the environmentalists worldwide due to industrial growth. The effluents of several chemical industries such as textile, paper, plastic and dyestuff contain a decent concentration of dyes. Most of these dyes which are in use are of synthetic origin and serious threat to human beings and aquatic ecosystem due to its toxicity and persistence after being released in water [1]. The major problem associated with dye contamination includes visible pollution, limited penetration of light into the water body and toxicity due to potential carcinogenic and genotoxic effects [2]. The dye pollution is also responsible for various health related problems such as allergy, dermatitis and skin irritation [3]. The very low concentration of these dyes in water is recognizable and not acceptable. Therefore removal of dyes from industrial effluents has become a very challenging problem in wastewater treatment.

More than 100,000 dyes with different chemical structures are commercially available in the market. Based on their ionic nature, they are divided into three categories; cationic, anionic and non-ionic. The most toxic dye among these is cationic dye [4]. The synthetic origin and aromatic structure, which is biologically non-degradable and toxic makes the treatment of dye effluents more challenging. Researcher's worldwide, making continuous efforts in the development of efficient processes to remove dye from industrial effluents [5]. The conventional techniques such as coagulation, precipitation and flocculation have been used in wastewater treatment [6]. Photo-oxidation and biological degradation of the reactive dye have been reported for treatment of dye effluents however, due to their high

cost and nature to create secondary pollution makes them not feasible for large quantity of water treatment [7]. Among all the physical and chemical methods available for dye removal from wastewater, the adsorption process is the most effective technique [8]. The adsorbent such as activated carbon and polymers have shown promising results in dye removal from wastewater, but are quite expensive [9]. Several low cost natural adsorbent obtained from agricultural wastes have been reported for dye removal from wastewater and this includes rice husk, sawdust, tea waste, orange peel, wheat shell, peanut shell, pineapple stem and coconut based sorbent etc. [10]. Worldwide tons of green waste are generated each year and few percentage of the total waste generated is waste biomass, which is mostly dumped in the landfill [11]. Date palm leaf constitute a major section of the generated waste biomass and it is known to have very limited use. The only use of date palm leaf is in the creation of mats, baskets and even fans. Therefore, it is highly desirable to find a solution to the problem of date palm leaf disposal and discover development activities that can utilize this waste material. In recent years, researchers have utilized date palm, mostly date pits based adsorbent for water treatment, however, the date leaf are not much utilized in wastewater treatment [12]. Additionally, several reports suggest that the methylene blue, a cationic dye, is used in many textile manufacturers and it releases aromatic amines (e.g., benzidine, methylene) and is a potential carcinogen. Continuous efforts are being made by researchers around the world to remove methylene blue from wastewater using different adsorbents [13]. In 2012, U J Etim et al. removed the cationic dye from the aqueous solution successfully using coconut coir dust [14]. Coconut coir dust showed very promising adsorption of dye without any physical and chemical surface modifications or activations. Recent development and results motivated us and we decided to quest for more efficient and

economical adsorbent and therefore the present study is undertaken to investigate the efficacy of raw date palm leaf without physical/chemical modification or activation as an inexpensive adsorbent for the removal of methylene blue from aqueous solution. The effect of contact time, concentration of the dye, amount of adsorbent, pH on methylene blue adsorption was studied. Additionally, adsorption isotherm and kinetics parameters were also evaluated, presented and discussed.

2. Experimental methods

2.1. Materials

The bio-degradable adsorbent, date palm leaf was obtained from household date palm tree. Methylene blue was purchased from Sigma-Aldrich, USA. Methylene blue has molecular formula $C_{16}H_{18}N_3ClS$ and molecular weight 319.85 g/mol and was used without further purification. All the reagents used in the experiment were of analytical grade. Throughout the experiment only deionized water was used. Instruments used for the work includes UV-visible spectrophotometer (Shimadzu UV-1080), magnetic shaker (WiseShake SHR-1D), electric oven (Quincy Lab Model 20GC), balance (Citizen CY-204), pH meter (Hanna Instruments pH 211), centrifuge (WiseSpin CF-10) and grinder (Panasonic MX-GX1521).

2.2. Preparation of adsorbent

Date palm leaf were collected and cut into small pieces (~ 1 inch) using a pair of scissors. The pieces of leaf were washed several times with tap water and finally with deionized water. Initially the pieces were air dried for one day and then kept for drying in oven at 60 °C for 24 h. The leaf were then pulverized with the help of a blender and then transferred in a crucible. The pulverized particles of date palm leaf were again dried in the oven at the 60 °C for 3-4 hours. It was stored in a sealed plastic container prior to use for adsorption studies. Before adsorption experiments no chemical or physical treatment was performed on dried pulverized particles.

2.3. Preparation of adsorbent

In the present study the water soluble dye methylene blue is used and its characteristic information is provided in the materials section. The dye stock solution of concentration 1 g/L was prepared by dissolving 1 g methylene blue in 1L of deionized water in 1 L volumetric flask. The working solutions of the desired concentration, i.e. 2 mg/L to 12 mg/L were obtained by successive dilution of the dye stock solution. The calibration curve (Fig 1a) is obtained by measuring the absorbance of methylene blue at concentration range from 2 to 12 mg/L at room temperature with $(25 \pm 0.5 \text{ }^\circ\text{C})$ λ_{max} 665nm (Figure 1b).

2.4. Adsorption experiments

2.4.1. Time optimization

To optimize the shaking time, 50 mL of the 4mg/L dye solution was taken in a 250 mL flask and 100 mg of the adsorbent (fixed amount) was added. Samples were collected after every 5 minutes for the next 30 minutes. The samples were tested in the spectrophotometer and the absorbance was noted at 665 nm. The results suggested that dye adsorption increased with the shaking time and reached a constant value at equilibrium that is approx. 20 minutes. Additionally, at the initial stage of contact time the uptake of the dye was fast and near to equilibrium becomes slower and subsequently reached a steady value at equilibrium.

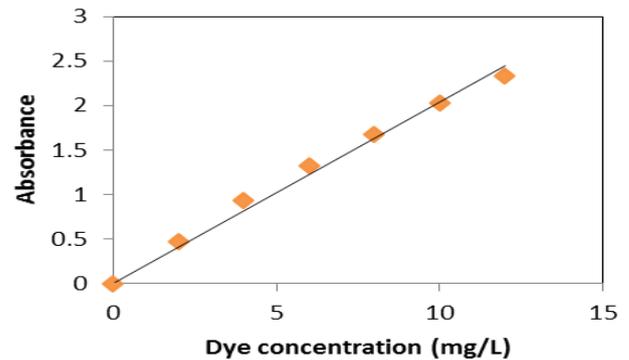


Fig. 1: A).

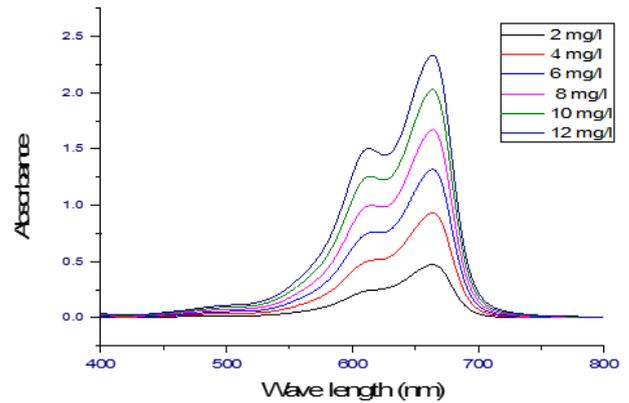


Fig. 1: B).

Figure 1 (a) Standard curve of methylene blue at concentration range from 2 to 12 mg/L at room temperature ($25 \pm 0.5 \text{ }^\circ\text{C}$). (b) UV-Vis absorption spectra of methylene blue solution at concentrations ranging from 2 to 12 mg/L.

2.4.2. Adsorption process

All the adsorption experiments were performed in 250 mL flask at room temperature with 50 ml volume of the reaction solution. All experiments were conducted in batches and were shaken at 200 rpm until equilibrium time (20 minutes) in a mechanical shaker. To study the effect of adsorbent dosage on the removal of methylene blue, experiments with different adsorbent dosage specifically 0.05 g to 0.30 g in a 50 ml dye solution of 4 mg/L concentration were performed. The equilibrium data were analyzed using the Freundlich [15] and Temkin [16] isotherms and the characteristic parameters for each isotherm were determined. The effect of the pH on the methylene blue removal was studied through experiments with pH ranging from 2.0 to 10 and with fixed adsorbent dosage of 200 mg, in a 4 mg/L dye solution concentration with in the time 20 minutes. The pH of the dye solution was adjusted using dilute sulfuric acid (H_2SO_4) and dilute sodium hydroxide (NaOH). To study the effect of contact time and initial concentration several experiments were conducted using 0.2 g of adsorbent at pH 6 and ambient temperature and with different time intervals and different initial concentrations. The adsorption kinetic experiments were performed by using 0.2 g of adsorbent with 50 ml of methylene blue aqueous solution (3 to 6 mg/L) in a series of 250 ml flasks at ambient temperature and optimal conditions. The flasks were taken out after some intervals and the solid adsorbent were separated from the supernatants by centrifugation. The samples were centrifuged 8-10 times at 1300 rpm and then analyzed in a UV-Visible spectrophotometer by recording the absorbance at λ_{max} 665 nm. The percentage removal of dye (R%) was calculated using Equation 1:

$$\%R = (C_0 - C_e) / C_0 * 100$$

The amount of dye absorbed per gm of adsorbent (q_e) is calculated using Equation 2:

$$q_e = [V/m](C_o - C_e)$$

where C_o is the initial and C_e is the equilibrium concentrations of methylene blue respectively (mg/L), V is the volume (L) of methylene blue solution and the m is the mass of the adsorbent (g).

3. Results and discussion

3.1. Effect of operational variables on dye removal

3.1.1. Adsorbent dosage

The adsorption dose determines the capacity of adsorbent for a given initial concentration of the dye solution and therefore it is used as an important parameter in adsorption studies. Literature reports suggested that the adsorption of the dye increases with the increase in adsorption dosage due to increase in adsorption surface and availability of more adsorption sites. To study the effect of date palm leaf powder dosage on the amount of dye adsorbed was examined through mixing 50 ml of dye solution of concentration 4 mg/L with the adsorbent. The adsorbent dosage was varied (0.05, 0.10, 0.15, 0.20, 0.25, 0.30) and all the experiments were performed at room temperature (25 ± 0.5 °C), optimum pH of 6.0 and with contact time 20 minutes and shaking speed of 200 rpm. After equilibrium the sample was centrifuged and the supernatant solution was collected and analyzed using UV-vis spectrophotometer. As evident from the graph (Figure 2a) the increase in adsorbent dosage increases the percentage of dye removal. For example the adsorption increases from 80.7% to 91.0% when the adsorbent dosage increased from 0.05 g to 0.2 g. The effect of adsorption dosage was not with the increase of adsorbent dosage from 0.20 to 0.30 g suggesting that adsorption was almost complete with 0.20 g of adsorbent. On the other hand, when the graph (Figure 2b) was plotted between adsorption dosage and amount of dye adsorbed per gram of adsorbent (q_e ; mg/g), it was observed that the adsorption capacity decrease with an increase in the amount of adsorbent. Similar results were observed by other research groups and it was proposed with the increase in adsorbent dosage overlapping or aggregation of adsorption site increases and therefore the total adsorption surface area available to the dye reduces and diffusion path length increases [14-17].

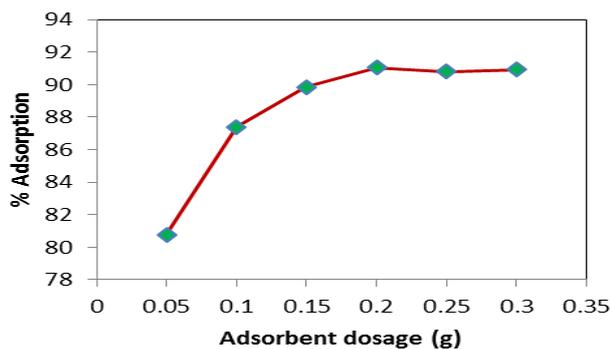


Fig. 2: A).

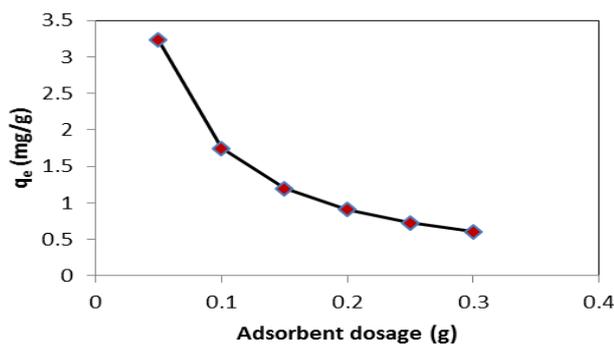


Fig. 2: B).

Figure 2 (a) Effect of adsorbent dosage on the % adsorption of methylene blue onto date palm leaf powder at room temperature (25 ± 0.5 °C), pH = 6.0, 4mg/L, stirring speed = 1300 rpm and time = 20 min. (b) Effect of adsorbent dosage on the amount of methylene blue adsorbed per gram of adsorbent (q_e) at room temperature (25 ± 0.5 °C), pH = 6.0, 4 mg/L, stirring speed = 1300 rpm and time = 20 min.

3.1.2. Initial dye concentration/ time effect

Literature reports suggest that dye removal percentage depends on the initial amount of dye concentration [18]. It was observed that with the increase in initial dye concentration the dye removal percentage decreases as a result of the saturation of adsorption sites on adsorption surface. Also increase in adsorption capacity was observed with the increase in initial dye concentration. It was suggested that at the low concentration possibility of existence of unoccupied active sites on the adsorbent surface is high, whereas with the increase in initial dye concentration the availability of the active site for dye adsorption will be reduced. To study the effect of the initial concentration of dye vs time of adsorption on the dye removal percentage a few experiments were conducted with different initial concentrations of dye solution (3, 4, 5, 6, 8 and 10 mg/L) and the results are illustrated in Figure 3. As evident from the graph, most of the dye that is above 80% was removed in the first two minutes of adsorption and slowly reached maximum at equilibrium (around 20 minutes). It was also observed that the increase in dye concentration was showing insignificant effect on percentage adsorption. The dye solution of 4, 5, 6 and 8 mg/L showed only minor difference in adsorption percentage and 3 mg/L and 10 mg/L dye solution exhibited same adsorption percentage. The results are similar to literature reports, the increase in adsorption percentage was observed with the contact time for all the tested dye solutions.

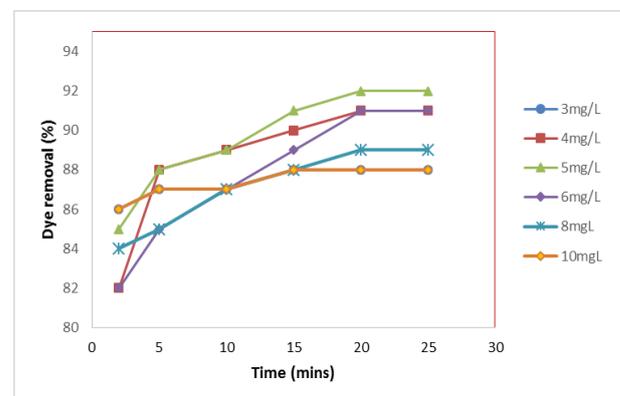


Fig. 3: Time/Concentration Effect of Methylene Blue Adsorption onto Date Palm Leaf Powder at Room Temperature (25 ± 0.5 °C), Dosage 0.20 G, Ph = 6.0 and Stirring Speed = 1300 Rpm.

3.1.3. Effect of pH

For the dye adsorption studies, the pH factor is considered significant and the rate of adsorption varies with the pH of aqueous solution. It was as a consequence of pH of a medium that controls the magnitude of electrostatic charges which included both the ionized dye molecules as well as the charge on the surface of the adsorbent. Literature reports suggest that methylene blue adsorption decreases at lower pH due to increase in H^+ ions that compete with dye cations and functional groups in date palm leaf fibers for the adsorption sites [19].

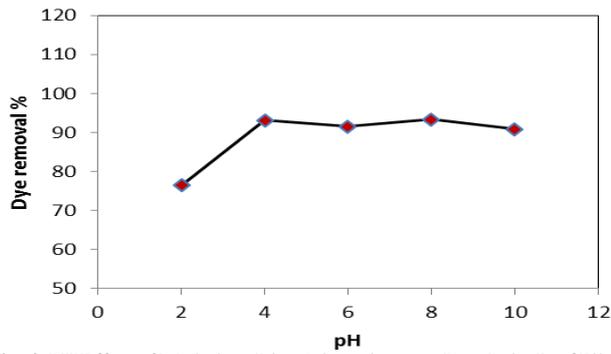


Fig. 4: PH Effect of Methylene Blue Adsorption onto Date Palm Leaf Fibers at Room Temperature (25 ± 0.5 °C), Adsorption Dosage = 200 Mg, Time = 20 Min, Initial Dye Concentration = 4 Mg/L And Stirring Speed = 1300 Rpm.

With the increase in pH the number of negatively charged surface sites on the adsorbent increases, this resulted in the adsorption of cationic dye to electrostatic attraction. Nevertheless, it was also observed that only slight change was observed when pH was within the range of 4 to 10 suggesting that not only electrostatic mechanism but also chemical reaction between the adsorbent and dye molecules was responsible for dye adsorption in solution. In order to find the effect of pH, a series of experiments were conducted at different pH ranging from 2 to 10 in acidic and alkaline conditions respectively. As is evident from the figure 4 the dye removal percentage by date palm leaf fibers increases from 76 to 91 % with the increase in pH from 2 to 4 respectively. However, further increase in pH from 4 to 10 showed slight differences in dye removal percentage.

3.2. Adsorption isotherm

To understand the adsorption behavior the adsorption isotherm derived models are very important. It provides information regarding the adsorbate interaction with adsorbent and are necessary to design and analyze the adsorption process that plays a major role in understanding the adsorption process. At the equilibrium state of the adsorption reaction, the adsorption isotherm helps to understand the distribution of adsorbate molecules between the solid phase and liquid phase. As evident in literature, different models obtained from adsorption isotherms help to study the adsorption mechanism and the surface properties and affinities of the adsorbent [20]. It is important to establish the appropriate correlation of suitable curves to optimize the conditions for designing adsorption systems. In our study, we build Freundlich and Temkin isotherms to understand the adsorption behaviour. We believe that both the models can be used to explain adsorption behavior.

The Freundlich isotherm model is mainly used to describe the adsorption characteristics of the heterogeneous surfaces and interaction between adsorbed molecules. According to this model exponential decrease in adsorption energy is possible on the completion of the sorptional centers in the adsorbent. The empirical equation proposed by Freundlich is as follows:

$$q_e = K_F C_e^{1/n}$$

Where, K_F = Freundlich isotherm constant related to the adsorption capacity of the adsorbent ($\text{mg}^{1-1/n} \text{L}^{1/n} \text{g}^{-1}$), q_e is the amount of dye adsorbed per unit mass of adsorbent at equilibrium (mg/g), C_e is the equilibrium concentration (mg/L) and n is a dimensionless constant used to measure adsorption intensity. Linearized Freundlich equation is represented as:

$$\text{Log } q_e = \text{Log } K_F + 1/n \text{ Log } C_e$$

Figure 5a shows the Freundlich plots of $\log q_e$ versus $\log C_e$ and the value of K_F and n are calculated from the intercepts and slopes of the plot. The isotherm parameters derived from Freundlich plots are depicted in Table 1. As evident from the Table 1 the value of n is

greater than one for the adsorption of the dye at all adsorption dosages except 50 mg, indicating that the sorption of methylene blue onto date palm leaf powder is favorable. With the increase in adsorption dosage the decrease in K_F value was observed, suggesting that the adsorption capacity of the adsorbent decreases with increase in adsorbent dosage.

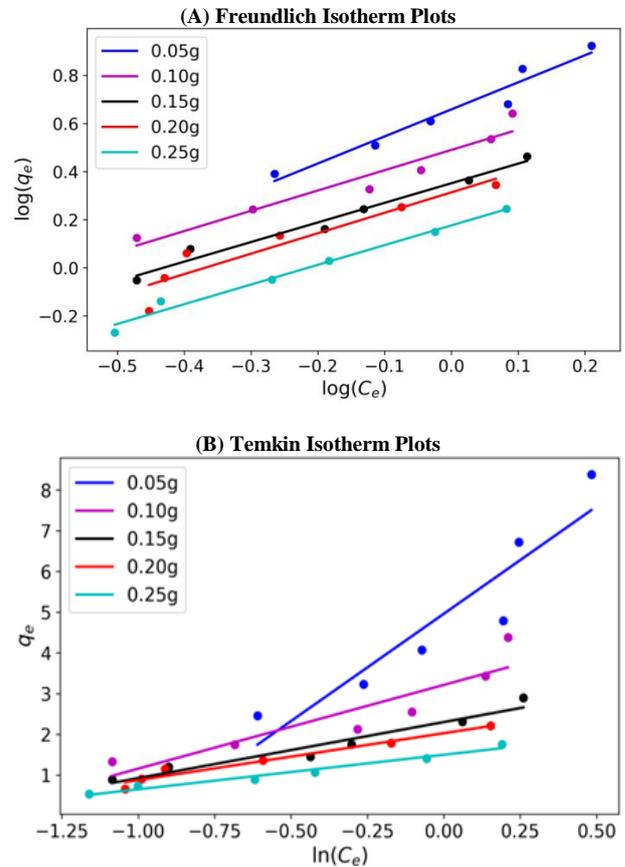


Fig. 5: Freundlich and Temkin Isotherm Plots for the Adsorption of Methylene Blue onto Date Palm Leaf Fibers at Different Adsorbent Dosage.

The Temkin isotherm model comprises a factor that explicitly takes into account adsorbent-adsorbate interactions. This model assumes that heat of adsorption of all molecules in the layer would decrease linearly rather than logarithmic with coverage due to adsorbent-adsorbent interaction [21]. Temkin equation derivation is characterized by a uniform distribution of binding energies, up to some maximum binding energy. The linear form of Temkin isotherm is represented as:

$$q_e = B_1 \ln K_T + B_1 \ln C_e$$

where B_1 is the Temkin constant related to the heat of adsorption and is given as: $B_1 = RT/b$ (R = universal gas constant (8.314 J/mol/K); T = Temperature at 298 K ; b = Temkin isotherm constant). K_T is equilibrium binding constant (L mg^{-1}). Figure 5b showed the Temkin isotherm plot of q_e versus C_e and the values of K_T and B_1 was obtained from the intercepts and slopes and are presented in Table 1. As evident in the table the value of K_T increases and the value of B_1 decrease with increase in adsorbent dosage. This indicates that an increase in the adsorbent dosage cause decrease in the heat of adsorption and increase in the equilibrium binding constant. Both the Freundlich ($R^2 > 0.886$) and Temkin ($R^2 > 0.823$) isotherm model used in our study exhibited significant coefficient with the experimental data, thus indicating that the obtained adsorption data fit the two studied isotherm models. Several literature reports also suggest the fit of experimental adsorption data to more than one isotherm models [22].

Nevertheless, the Freundlich isotherm model showed more promising results with the highest correlation coefficient range (R^2 :

0.886 – 0.984) and therefore considered as the best models for our study.

Table 1: Isotherm Parameters for the Adsorption of Methylene Blue on Date Palm Leaf Fibers

| Isotherm Model | Parameters | Adsorbent dosage (mg) | | | | |
|----------------|-------------------------------------|-----------------------|-------|-------|-------|-------|
| | | 50 | 100 | 150 | 200 | 250 |
| Freundlich | K_F (mg^{-1}) | 4.554 | 3.090 | 2.246 | 2.059 | 1.500 |
| | $1/nL^{1/n}$ (g^{-1}) | 0.889 | 1.186 | 1.227 | 1.177 | 1.221 |
| | R^2 | 0.948 | 0.932 | 0.977 | 0.886 | 0.984 |
| Temkin | K_T (L mg^{-1}) | 2.563 | 4.775 | 5.326 | 5.827 | 5.856 |
| | B_1 | 5.269 | 2.055 | 1.376 | 1.150 | 0.848 |
| | R^2 | 0.867 | 0.823 | 0.940 | 0.964 | 0.971 |
| | | | | | | |

Both the Freundlich ($R^2 > 0.886$) and Temkin ($R^2 > 0.823$) isotherm model used in our study exhibited significant coefficient with the experimental data, thus indicating that the obtained adsorption data fit the two studied isotherm models. Several literature reports also suggest the fit of experimental adsorption data to more than one isotherm models [22]. Nevertheless, the Freundlich isotherm model showed more promising results with the highest correlation coefficient range (R^2 : 0.886 – 0.984) and therefore considered as the best models for our study.

3.3. Adsorption equilibrium kinetics

Further adsorption kinetics in terms of the order of the rate constant was used to study the dynamics of the adsorption [23]. We examined the adsorption rate using pseudo-second order kinetics model and made an effort to design an effective model. In literature, it is reported that pseudo- first order model is able to provide very good correlation coefficient for dye concentrations more than 10 mg/L with experimental data [24]. As in our experiment, we used the dye concentrations of less than 10 mg/L therefore we focused our study on pseudo-second order model that is based on the adsorption capacity similar to pseudo-first order and able to predict the behavior of adsorption process for all the dye concentrations. Additionally, it is also applicable to predict the chemisorption processes. The expression for pseudo-second order kinetic model is as follows:

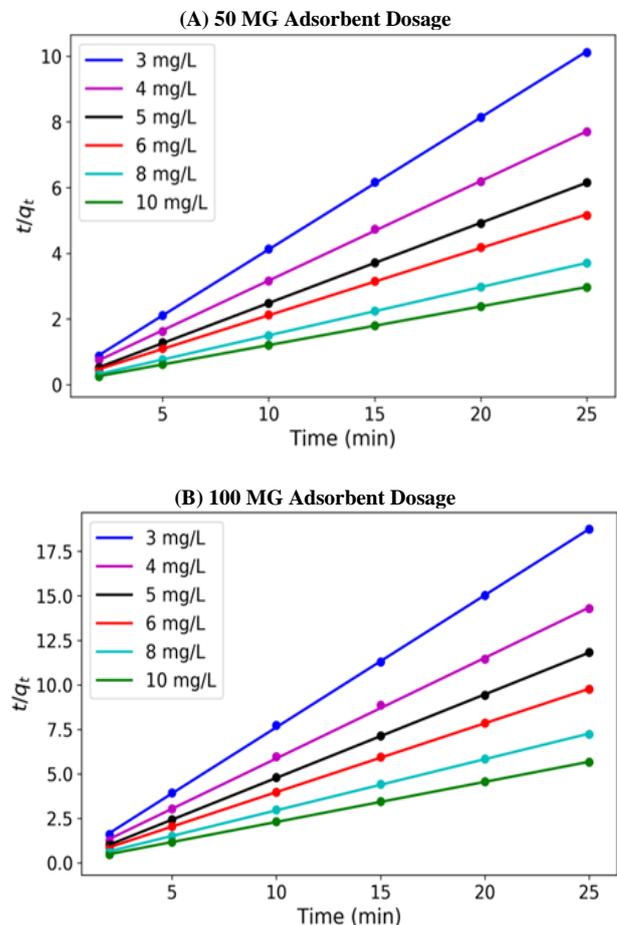
$$t/q_t = 1/(k_2 q_e^2) + (1/q_e)t$$

Where k_2 represents the rate constant of pseudo-second order adsorption ($\text{g mg}^{-1} \text{min}^{-1}$). The pseudo- second order plots for the adsorption process of six different concentrations (3, 4, 5, 6, 8 and 10 mg L^{-1}) at a different adsorbent dosage (50, 100, 150, 200, 250 mg) are shown in Figure 6 a-e. The pseudo-second order kinetics plot for the adsorption of Methylene blue onto date palm leaf fibers at adsorbent dosage 50, 100, 150, 200 and 250 mg is shown in Table 2. As evident from the Table 2 the values of obtained experiment data (q_e, exp) are almost same with that of the theory (q_e, cal) with all the adsorbent dosage. The equilibrium adsorption capacity (q_e) increases with increasing the initial concentration of the dye. Additionally, the correlation coefficient (R^2) value for the dye concentration range was [1] in all the plots indicating that the process perfectly fit to the second order kinetic model and it's helpful in explaining adsorption data.

Table 2: Kinetic Parameters for the Adsorption of Methylene Blue onto Date Palm Leaf Fibers at Different Adsorbent Dosage

| Conc. of dye (mg L^{-1}) | q_e, exp (mg g^{-1}) | Pseudo-second order | | | |
|--|---|-----------------------------|---|-------|-------------------------|
| | | k_2 (g/mg min) | q_e, cal (mg g^{-1}) | R^2 | H (mg/g min) |
| 3 | 2.46 | 1.63 | 2.49 | 1 | 10.11 |
| 4 | 3.23 | 0.65 | 3.30 | 1 | 7.07 |
| 5 | 4.07 | 1.35 | 4.09 | 1 | 22.58 |
| 6 | 4.79 | 0.63 | 4.88 | 1 | 15.0 |
| 8 | 6.72 | 0.67 | 6.80 | 1 | 30.98 |
| 10 | 8.38 | 0.50 | 8.48 | 1 | 35.9 |

| Adsorbent dosage 100 mg | | | | | | |
|--|---|--------------------------------|---|-------|----------------------------|--|
| Conc. of dye (mg L^{-1}) | q_e, exp (mg g^{-1}) | k_2 (g/mg min) | q_e, cal (mg g^{-1}) | R^2 | h (mg/g min) | |
| 3 | 1.33 | 2.96 | 1.35 | 1 | 5.39 | |
| 4 | 1.75 | 1.54 | 1.77 | 1 | 4.82 | |
| 5 | 2.12 | 2.88 | 2.13 | 1 | 13.06 | |
| 6 | 2.55 | 1.53 | 2.58 | 1 | 10.18 | |
| 8 | 3.43 | 1.18 | 3.48 | 1 | 14.29 | |
| 10 | 4.38 | 1.36 | 4.43 | 1 | 26.68 | |
| Adsorbent dosage 150 mg | | | | | | |
| Conc. of dye (mg L^{-1}) | q_e, exp (mg g^{-1}) | k_2 (g/mg min) | q_e, cal (mg g^{-1}) | R^2 | h (mg/g min) | |
| 3 | 0.89 | 3.77 | 0.90 | 1 | 3.05 | |
| 4 | 1.20 | 1.34 | 1.22 | 1 | 1.99 | |
| 5 | 1.45 | 3.77 | 1.46 | 1 | 8.03 | |
| 6 | 1.75 | 2.53 | 1.77 | 1 | 7.93 | |
| 8 | 2.31 | 2.69 | 2.34 | 1 | 14.7 | |
| 10 | 2.90 | 2.67 | 2.92 | 1 | 22.7 | |
| Adsorbent dosage 200 mg | | | | | | |
| Conc. of dye (mg L^{-1}) | q_e, exp (mg g^{-1}) | k_2 (g/mg min) | q_e, cal (mg g^{-1}) | R^2 | h (mg/g min) | |
| 3 | 0.66 | 4.34 | 0.67 | 1 | 1.94 | |
| 4 | 0.91 | 4.81 | 0.92 | 1 | 4.07 | |
| 5 | 1.15 | 2.92 | 1.16 | 1 | 3.93 | |
| 6 | 1.36 | 1.81 | 1.38 | 1 | 2.58 | |
| 8 | 1.79 | 1.88 | 1.81 | 1 | 6.15 | |
| 10 | 2.21 | 4.90 | 2.22 | 1 | 24.1 | |
| Adsorbent dosage 250 mg | | | | | | |
| Conc. of dye (mg L^{-1}) | q_e, exp (mg g^{-1}) | k_2 (g/mg min) | q_e, cal (mg g^{-1}) | R^2 | h (mg/g min) | |
| 3 | 0.53 | 8.46 | 0.54 | 1 | 2.46 | |
| 4 | 0.73 | 3.22 | 0.74 | 1 | 1.76 | |
| 5 | 0.89 | 3.07 | 0.90 | 1 | 2.48 | |
| 6 | 1.07 | 2.04 | 1.09 | 1 | 2.42 | |
| 8 | 1.41 | 2.68 | 1.43 | 1 | 5.48 | |
| 10 | 1.76 | 3.82 | 1.76 | 1 | 11.8 | |



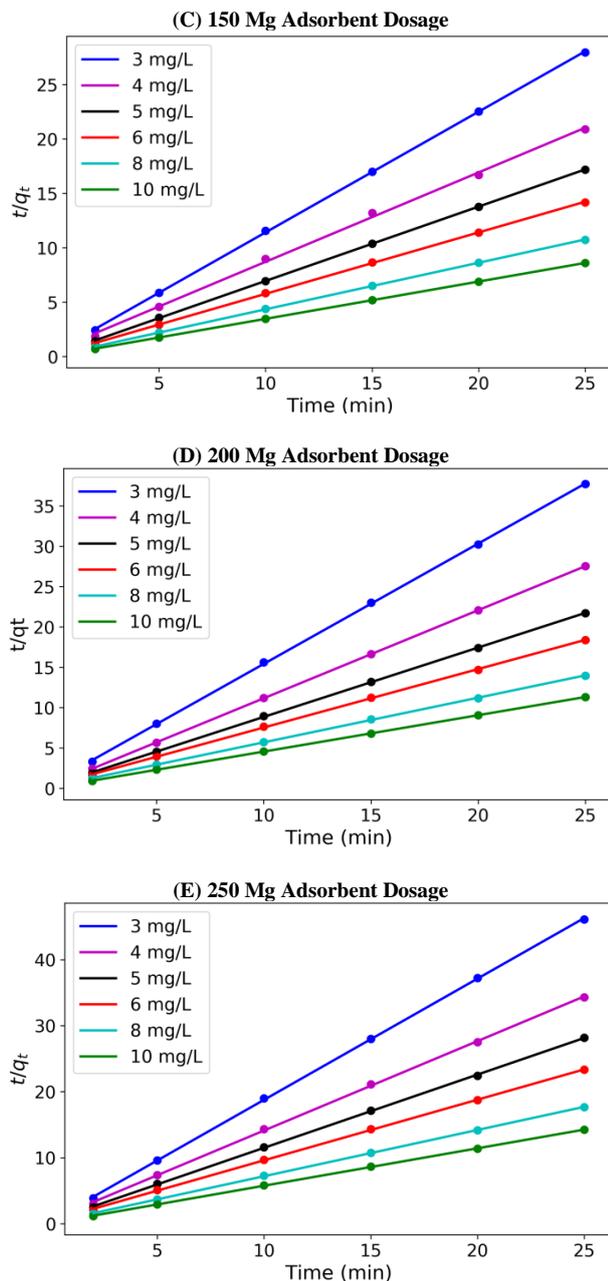


Fig. 6: Pseudo-Second Order Kinetics Plot for the Adsorption of Methylene Blue onto Date Palm Leaf Fibers at Different Adsorbent Dosage.

The initial adsorption rate is represented as:

$$h = k_2 q_e^2$$

For initial dye concentration 3 to 5 mg/L the values of initial adsorption rate (h) is not regular however, for initial dye concentrations 6, 8 and 10 mg/L the initial adsorption rate increases with an increase in initial concentration.

4. Conclusion

On the basis of our encouraging results we can conclude that date palm leaf fibers can be used as an effective, low-cost adsorbent for the removal of methylene blue from aqueous solutions. At different dye concentrations the adsorbent showed a very good adsorption capacity and efficiently adsorb more than 80% in the first two minutes of adsorption. The Freundlich and Temkin isotherms were used to calculate adsorption parameters and to provide mechanism of the adsorption process as indicated by the virtuous linear correlation coefficient values. The adsorption kinetic data were significantly explained by the pseudo-second order kinetic models and the

q_e values calculated from this kinetic model were same to the experimental q_e values obtained from several experiments. The date palm leaf is natural, abundant and economical source for the effective removal of dye particularly methylene blue from aqueous solution. It is an adequate alternative material to activated carbon and could be effectively applied in industry for the treatment of industrial wastewater containing dyes.

Acknowledgement

The author appreciate the financial support provided by the School of Graduate Studies and Research, American University of Ras Al Khaimah, Ras Al Khaimah, UAE through seed grant funded project No. AAS/005/18.

References

- [1] Ratna, Padhi, B. S., (2012), Pollution due to synthetic dyes toxicity & carcinogenicity studies and remediation. *International Journal of Environmental Sciences*, 3(3), 940-955.
- [2] Kant, R., (2012), Textile dyeing industry an environmental hazard. *Natural Science*, 4 (1), 22-26. (b) Joshi, M., Bansal, R., Purwar, R., (2004), Colour removal from textile effluents. *Indian Journal of Fibre & Textile Research*, 29, 239-259.
- [3] Leucea, D. I., (2010), the effects of azo dyes on human health. *Industria textilă*, 61(6), 304-309. (b) Pereira, L., Alves, M., (2012), Dyes-Environmental Impact and Remediation, in: Malik, A., Grohmann, E., (Eds.) *Environmental Protection Strategies for Sustainable Development*, Springer, New York, pp. 111-162.
- [4] Hao, O. J., Kim, H., Chiang, P. C., (2000), Decolorization of wastewater. *Critical review. Environmental Science and Technology*, 30, 449-505. (b) Robinson, T., McMullan, G., Marchant, R., Nigam, P., (2001), Remediation of dyes in textiles effluent: a critical review on current treatment technologies with a proposed alternative. *Bioresource Technology*, 77, 247-255.
- [5] Gupta, V. K., Suhas, (2009), Application of low-cost adsorbents for dye removal-A review. *J. Environ. Manage.* 90, 2313-2342. (b) Forgacs, E., Cserhádi, T., Oros, G., (2004), Removal of synthetic dyes from wastewaters: a review. *Environment International*, 30, 953-971.
- [6] Ismail, I. M., Fawzy, A. S., Abdel-Monem, N. M., Mahmoud, M. H., El-Halwany, M. A., (2012), Combined coagulation flocculation pretreatment unit for municipal wastewater. *Journal of Advanced Research*, 3(4), 331-336. (b) Wang, L. K., Vaccari, D. A., Li, Y., Shammam, N. K., (2005), Chemical Precipitation. In: Wang, L. K., Hung, Y. T., Shammam, N. K., (eds) *Physicochemical Treatment Processes. Handbook of Environmental Engineering*, vol. 3. Humana Press, pp. 141-197.
- [7] Sharma, S., Buddhdev, J., Patel, M., Ruparelia, J. P., (2013), Studies on Degradation of Reactive Red 135 Dye in Wastewater using Ozone. *Procedia Engineering*, 51, 451-455. (b) Lade, H., Kadam, A., Paul, D., Govindwar, S., (2015), Biodegradation and detoxification of textile azo dyes by bacterial consortium under sequential microaerophilic/aerobic processes. *EXCLI J*, 14, 158-174. (c) Keharia, H., Madamwar, D., (2003), Bioremediation concepts for treatment of dye containing wastewater: A review. *Indian Journal of Experimental Biology*, 41, 1068- 1075.
- [8] Vital, R. K., Saibaba, K. V. N., Shaik, K. B., Gopinath, R., (2016), Dye Removal by Adsorption: A Review. *Journal of Bioremediation & Biodegradation*, 7, 371. doi: 10.4172/2155-6199.10003. (b) Seow, T. W., Lim, C. K., (2016), Removal of Dye by Adsorption: A Review. *International Journal of Applied Engineering Research*, 11(4), 2675-2679.
- [9] Chowdhury, A. N., Jesmeen, S. R, Hossain, M. M., (2004), Removal of dyes from water by conducting polymeric adsorbent. *Polymer advanced technologies*, 15(11): 633-638. (b) Dhodapkar, R., Rao, N. N., Pande, S. P., Kaul, S. N., (2006), Removal of basic dyes from aqueous medium using a novel polymer. *Jalshakti. Bioresource Technology*, 97(7): 877-885. (c) El-Zahhar, A. A., Awwad, N. S., El-Katori, E. E., (2014), Removal of bromophenol blue dye from industrial wastewater by synthesizing polymer-clay composite. *Journal of Molecular Liquids*, 199, 454-461. (d) Malik, P. K., (2004), Dye removal from wastewater using activated carbon developed from sawdust: adsorption equilibrium and kinetics. *Journal of Hazardous Materials*, 113, 81-88. (e) Foo, K. Y., Hameed, B. H., (2010), an overview of dye removal via activated carbon adsorption process. *Journal Desalination and Water Treatment*, 19, 255-274. (f) Singh, K. P.,

- Mohan, D., Sinha, S., Tondon, G. S., Gosh, D., (2003), Color Removal from Wastewater Using Low-Cost Activated Carbon Derived from Agricultural Waste Material. *Industrial & Engineering Chemistry Research*, 42 (9), 1965-1976. (g) Banerjee, S., Chattopadhyaya, M. C., (2017), Adsorption characteristics for the removal of a toxic dye, tartrazine from aqueous solutions by a low cost agricultural by-product. *Arabian Journal of Chemistry*, 10, S1629-S1638.
- [10] Lakshmi, U. R., Srivastava, V. C., Deo Mall, I., Lataye, D. H., (2009), Rice husk ash as an effective adsorbent: evaluation of adsorptive characteristics for Indigo armine dye. *Journal of Environmental Management*, 90, 710-720. (b) Batzias, F. A., Sidiras, D. K., (2007), Dye adsorption by prehydrolysed beech sawdust in batch and fixed-bed systems. *Bioresource Technology*, 98, 1208-1217. (c) Temkin, M. J., Pyzhev, V., (1940), recent modification to Langmuir isotherms. *Acta Physicochemical USSR*, 12, 217-222. (d) Khaled, A., El Nemr, A., El-Sikaily, A., Abdelwahab, O., (2009), Removal of Direct N Blue-106 from artificial textile dye effluent using activated carbon from orange peel: adsorption isotherm and kinetic studies. *Journal of Hazardous Materials*, 165, 100-110. (e) Bulut, Y., Aydin, H., (2006), a kinetics and thermodynamics study of methylene blue adsorption on wheat shells. *Desalination*, 194, 259-267. (f) Tanyildizi, M. S., (2011), Modeling of adsorption isotherms and kinetics of reactive dye from aqueous solution by peanut hull. *Chemical Engineering Journal*, 168, 1234-1240. (g) Hameed, B. H., Krishni, R. R., Sata, S. A., (2009), A novel agricultural waste adsorbent for the removal of cationic dye from aqueous solutions. *Journal of Hazardous Materials*, 162, 305-311. (h) Hameed, B. H., Mahmoud, D. K., Ahmad, A. L., (2008), Equilibrium modeling and kinetic studies on the adsorption of basic dye by a low-cost adsorbent: coconut (*Cocos nucifera*) bunch waste. *Journal of Hazardous Materials* 158, 65-72. (i) de Sousa, D. A., de Oliveira, E., Nogueira, M. C., Esposito, B. P., (2010), Development of a heavy metal sorption system through the P=S functionalization of coconut (*Cocos nucifera*) fibers. *Bioresource Technology*, 101, 138-143. (j) Gupta, V. K., Jain, R., Shrivastava, M., (2010), Adsorptive removal of Cyanosine from wastewater using coconut husks. *Journal of Colloid and Interface Science*, 347, 309-314.
- [11] <https://www.thenational.ae/uae/environment/cementing-future-uses-for-date-palm-waste-1.134729>. (b) "UAE Waste to Increase by over 27% by 2017." *Khaleej Times*. N.p., 25 Oct. 2015. Web. 04 Mar. (2017).
- [12] Ahmad, T., Danish, M., Rafatullah, M., Ghazali, A., Sulaiman, O., Hashim, R., Nasir, M., Ibrahim, M., (2012), the use of date palm as a potential adsorbent for wastewater treatment: a review. *Environmental Science and Pollution Research*, 19, 1464-1484. <https://doi.org/10.1007/s11356-011-0709-8>.
- [13] Pathania, D., Sharma, S., Singh, P., (2017), Removal of methylene blue by adsorption onto activated carbon developed from *Ficus carica* bast. *Arabian Journal of Chemistry*, 10, S1445-S1451. (b) Mohammed, M. A., Shitu, A., Ibrahim, A., (2014), Removal of Methylene Blue Using Low Cost Adsorbent: A Review. *Research Journal of Chemical Sciences*, 4(1), 91-102. (c) Öden, M. K., Özdemir, C., (2014), Removal of Methylene Blue Dye From Aqueous Solution Using Natural Boron Ore And Leach Waste Material: Adsorption Optimization Criteria. *International Journal of Current Research Academic Review*, special issue 1, 66-71. (d) Reddy, B. S., Veni, V. K., Ravindhranath, K., (2012), Removal of methylene blue dye from waste waters using new bio-sorbents derived from *Annona squamosa* and *Azadiracta indica* plants. *Journal of Chemical and Pharmaceutical Research*, 4(11), 4682-4694. (e) Shashikala, M., Nagapadma, M., Pinto, L., Nambiar, S. N., (2013), Studies on the removal of methylene blue dye from water using chitosan. *International Journal of Development Research*, 3(8), 040-044.
- [14] Etim, U. J., Umoren, S. A., Eduok, U. M., (2016), Coconut coir dust as a low cost adsorbent for the removal of cationic dye from aqueous solution. *Journal of Saudi Chemical Society* 20, S67-S76. <https://doi.org/10.1016/j.jscs.2012.09.014>.
- [15] Jaroniec, M., (1975), Adsorption on heterogeneous surfaces: The exponential equation for the overall adsorption isotherm. *Surface Science*, 50(2), 553-564. (b) LeVan, D. M., Vermeulen T., (1981), Binary Langmuir and Freundlich isotherms for ideal adsorbed solutions. *The Journal of Physical Chemistry*, 85(22), 3247-3250. <https://doi.org/10.1021/j150622a009>.
- [16] Temkin, M. J., Pyzhev, V., (1940), recent modification to Langmuir isotherms. *Acta Physicochemical USSR*, 12, 217-222. (b) Dada, A. O., Olalekan, A. P., Olatunya, A. M., Dada, O., (2012), Langmuir, Freundlich, Temkin and Dubinin-Radushkevich Isotherms Studies of Equilibrium Sorption of Zn²⁺ Unto Phosphoric Acid Modified Rice Husk. *IOSR Journal of Applied Chemistry (IOSR-JAC)*, 3(1), 38-45.
- [17] El-Sayed, G. O., (2011), Removal of methylene blue and crystal violet from aqueous solutions by palm kernel fiber. *Desalination*, 272, 225-232. (b) Senthil, K. P., Ramalingam, S., Senthamarai, C., Niranjana, M., Vijayalakshmi, P., Sivanesan, S., (2010), Adsorption of dye from aqueous solution by cashew nut shell: studies on equilibrium isotherm, kinetics and thermodynamics of interactions. *Desalination*, 261, 52-60.
- [18] Salleh, M. A. M., Mahmoud, D. K., Karim, W. A., Idris, A., (2011), Cationic anionic dye adsorption by agricultural solid waste: a comprehensive review. *Desalination*, 280, 1-13. (b) Kannan, N., Sundaram, M. M., (2001), Kinetics and mechanism of removal of methylene blue by adsorption on various carbons -a comparative study. *Dyes and Pigments*, 51, 25-40. (c) Bulut, Y., Aydin, H., (2006), a kinetics and thermodynamics study of methylene blue adsorption on wheat shells. *Desalination*, 194, 259-267.
- [19] Onal, Y., Akmil-Basar, C., Eren, D., SarIci-O zdemir, C., Depci, T., (2006), Adsorption kinetics of malachite green onto activated carbon prepared from Tuncbilek lignite. *Journal of Hazardous Materials*, 128, 150-157. (b) Ponnusami, V., Gunasekar, V., Srivastava, S. N., (2009), Kinetics of methylene blue removal from aqueous solution using gulmohar (*Delonix regia*) plant leaf powder: multivariate regression analysis. *Journal of Hazardous Materials*, 169, 119-127. (c) Al-Degs, Y. S., El-Barghouthi, M. I., El-Sheikh, A. H., Walker, G. M., (2008), Effect of solution pH, ionic strength, and temperature on adsorption behavior of reactive dyes on activated carbon. *Dyes and Pigments*, 77, 16-23.
- [20] Ismadji, S., Bhatia, S. K., (2000), Adsorption of flavour esters on granular activated carbon. *Canadian Journal of Chemical Engineering*, 78, 892-901. (b) Tan, I. A. W., Ahmad, A. L., Hameed, B. H., (2008), Adsorption of basic dye on high surface area activated carbon prepared from coconut husk: equilibrium, kinetic and thermodynamic studies. *Journal of Hazardous Materials*, 154, 337-346. (c) Santhi, T., Manonmani, S., Smitha, T., (2010), Removal of methyl red from aqueous solution by activated carbon prepared from the *Annona squamosa* seed by adsorption. *Chemical Engineering Research Bulletin*, 14, 11-18.
- [21] Tempkin, M. I., Pyzhev, V., (1940), Kinetics of ammonia synthesis on promoted iron catalyst. *Acta Physicochimica URSS*, 12, 327-356. (b) Aharoni, C., Ungarish, M., (1977), Kinetics of activated chemisorption. Part 2. Theoretical models. *Journal of the Chemical Society, Faraday Transactions*, 73, 456-464.
- [22] Wang, L. G., Yan, G. B., (2011), Adsorptive removal of direct yellow 161 dye from aqueous solution using bamboo charcoals activated with different chemicals. *Desalination*, 274, 81-90. (b) Malana, M. A., Ijaz, S., Ashiq, N., (2010), Removal of various dyes from aqueous media onto polymeric gels by adsorption process; their kinetics and thermodynamics. *Desalination*, 263, 249-257.
- [23] Ho, Y. S., McKay, G., (1998), Kinetic models for the adsorption of dye from aqueous solution by wood. *Chemical Engineering Journal* 76, 183-191. (b) Ho, Y. S., McKay, G., (1998), Kinetic model for lead (II) sorption on to peat. *Adsorption Science & Technology* 16, 243-255. (c) Go´mez, V., Larrechi, M. S., Callao, M. P., (2007), Kinetic and adsorption study of acid dye removal-using activated carbon. *Chemosphere*, 69, 1151-1158.
- [24] Crini, G., Badot, P. M., (2008), Application of chitosan, a natural amino polysaccharide for dye removal from aqueous solutions by adsorption process using batch studies: a review of recent literature. *Progress in Polymer Science*, 33, 399-447. <https://doi.org/10.1016/j.progpolymsci.2007.11.001>.