

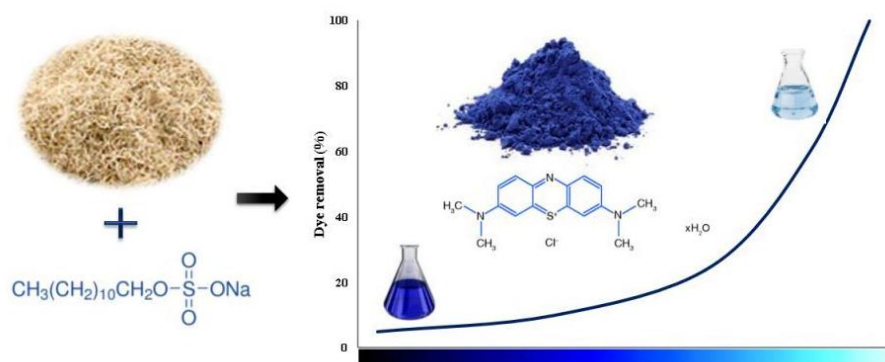
Removal of Methylene Blue from Aqueous Solutions Using Luffa Adsorbent Modified with Sodium Dodecyl Sulfate Anionic Surfactant

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GRAPHICAL ABSTRACT



Abstract

Methylene blue is one of the most widely used dyes in various industries such as textiles and dyeing which, due to toxicity, causes several environmental problems as well as difficulties in wastewater treatment process. Therefore, many studies have been carried out on the removal of the dye from industrial wastewater and aqueous solutions using various adsorbents. In the present study, a Luffa adsorbent surface was first modified by sodium dodecyl sulfate anionic surfactant and then methylene blue dye removal from aqueous solution was studied under various operating conditions in batch experiments. The parameters addressed included of the dye solution pH, adsorbent amount, initial methylene blue concentration in the dye medium, and the duration of adsorption. The use of anionic surfactant changed the adsorbent surface charge and

thus increasing adsorbent ion exchange capacity. The results showed that the highest removal efficiency occurs in mediums with an initial concentration of 50 mg L⁻¹ and pH 6-9, where 99% of the dye was removed from the medium using 1 gr modified adsorbent in 60 minutes. Since the obtained pH range covered the neutral and near neutral media, the adsorbent can be used in a variety of industries. Finally, the dye adsorption process was modeled and examining the adsorption isotherms, it was observed that the empirical data appropriately followed the Freundlich model.

Keywords: Anionic surfactant, Luffa L20, methylene blue, isotherm, removal efficiency.

1. Introduction

The presence of dye compounds in industrial wastewater and water resources, the negative environmental consequences, and the effects on the health of individuals, plants and aquatic animals has always been a challenge in wastewater treatment [1]. Methylene blue, which is known as a polar organic water soluble material [2], is a toxic compound that can cause respiratory disease and eye damage [3]. The difficulty of removing synthetic dyes from wastewater and aqueous solutions has led to the development of strict environmental laws [4]. Hence, extensive efforts have been made to remove this compound from aquatic solutions and industrial wastewaters. Several methods have been used to remove dye compounds, but the high efficiency dye compounds removal using adsorbents, has made adsorption into one of the most ideal methods [5]. One of the most commonly used methods for dye removal is biological removal and activated carbon adsorption; however, recently the use of biodegradable adsorbents and adsorbents from agricultural waste has also been considered frequently [6]. For example, Kannan et al reviewed the kinetics and methylene blue adsorption mechanism with carbon activators obtained from materials such as rice stems, bamboo skin and coconut shell. The results increased dye removal efficiency with adsorption particles size reduction, initial methylene blue concentration, and increase in the medium pH, the adsorbent amount, and contact time [7]. Singh et al. investigated dye adsorption from wastewater using sugar cane stem powder. The results showed that optimal conditions occur by adsorbent particle size decrease, the initial dye concentration, and adsorption pH and temperature at 7.5 and 25°C, respectively. Interestingly, as the dye concentration increased from 6 mg L⁻¹ to 12 mg L⁻¹, the removal percentage of methylene blue dye was reduced from 90.78 to 78.02% [8]. Also, the kinetics of removing

methylene blue from salty media was studied using pine fruit. It was observed that with the increase in salt concentration in the dye medium, the amount of adsorption decreased. Further, dye removal was also in perfect agreement with the Langmuir model [9]. In another study, activated carbon adsorbent was prepared by sawdust and adsorption was recommended at pH 3 or lower [10]. Namasivayam et al investigated red Congo dye removal by coconut outer shell and suggested environment acidity contributes to absorb the dye [11]. In a study on malachite green dye removal by Garg et al. using modified sawdust, it was observed that the sulfuric-acid-modified adsorbent had better adsorption capacity than formaldehyde-modified adsorbent and both adsorbents had the best performance at pH 6-9 media [12]. The same corrective action was performed on acacia wood where pH 7 was proposed as optimal [13]. In the recent years, other studies have also been carried out on the dye removal using other adsorbents and available techniques. For example, the crystal violet removal from wastewater using SDS-modified alumina yielded 99% dye removal [14]. In 2017, George Z. Kyzas et al studied dye removal using Graphene composites as adsorbents. It was observed that adsorption capacity of graphene composites can reach up to 1300 mg/g depending on the dye molecule [15]. Also, dye removal from aqueous solutions using other adsorbents such as ash and bentonite, volcanic glass, magnesium chloride [16-18], and graphene oxide [19-21] has been studied. In addition to adsorption, other methods such as ultrafiltration, nanofiltration, electrocoagulation [22, 25], and positive plasma use [26] have been used for dye removal.

Luffa is a cellulosic compound known as a suitable adsorbent for porous structure, low density, and high adsorption capacity. As a natural adsorbent, Luffa does not have the environmental problems associated with synthetic adsorbents [27, 28].

1.2. Novelty

Previous studies are mostly based on the modification of synthetic adsorbents. In the present study, a natural adsorbent is used to remove dye from aqueous solutions to reduce the cost of synthesizing synthetic adsorbents. Natural adsorbents often have low absorption capacity. The combination of Luffa with an anionic surfactant can increase the removal of Methylene Blue. It has also been shown that the use of a larger amount of adsorbent does not necessarily increase absorption capacity.

2. Materials and Methods

The equipment and materials used in this research include:

Methylene blue dye made by Panreac Spain, Luffa fibers (Luffa L20) by French Lessonia, Sodium Dodecyl Sulfate with 90% purity made by Merck Germany, NaOH (0.1 mol L^{-1}) and HCl (0.1 mol L^{-1}) by Merck, Spectrophotometer Model 6850 made by JENWAY UK, incubator with shaker (Labcon), centrifuge model EBA20 by Hettich Germany, electric oven model UN11z by Memmert Germany, the pH meter model 827 manufactured by Metrohm, Switzerland.

Methylene blue specifications:

The specifications and characteristics of the methylene blue used in this study are presented in Table 1 [32,33]:

< The approximate placement of Table 1 >

Anionic surfactant specifications:

The anionic surfactant specifications and chemical structure used to modify the Luffa particles are given in Table 2:

< The approximate placement of Table 2 >

Initially, methylene blue stocks solution was prepared at a concentration of 2000 mg L^{-1} . Then, to calibrate the spectrophotometer, solutions with different concentrations ($2\text{-}250 \text{ mg L}^{-1}$) of methylene blue were prepared using the stocks solution. Calibration curve was plotted using Microsoft Excel program based on the absorbance for each solution at the maximum adsorption time [31].

The Luffa L20 particles were in the form of 40-80 mesh fibers, which were first washed with distilled water several times and then placed in an oven at 105°C for two hours to remove moisture. To prevent moisture adsorption, Luffa particles were transferred to the desiccator and stored. To improve dye adsorption, Luffa particles were modified by an anionic surfactant. Accordingly, the sodium lauryl sulfate 10% solution was first prepared. This solution is an anionic surfactant, which can be used to absorb cationic compounds such as methylene blue. Luffa particles were placed in contact with sodium lauryl sulfate solution 10% for 2 hours at 300 rpm, so that the surface structure of the material was modified and would have anionic surface charge. The Luffa particles were then rinsed with distilled water several times and dried at 105°C for 4 hours in the oven before being moving to the desiccator.

In this study, the effects of solution pH, adsorbent content, initial methylene blue concentration, and adsorbent-dye solution contact duration were studied under batch conditions.

< The approximate placement of Table 3 >

In each experiment, 100 cc of dye solutions at required concentration was prepared from stocks solution. All experiments were carried out in a shaker incubator at 25°C and 115 rpm to provide the required conditions for methylene blue dye adsorption such as temperature and adsorbent rate and dye solution mix. To separate

suspended particles, after each test the dye solutions were transferred to the test tube and centrifuged for 3 minutes at 3000 rpm. Then, to determine the methylene blue concentration at dye medium, the absorbance of each dye solution at its maximum absorption wavelength (664 nm) was measured by spectrophotometer. Then, according to the calibration curve, the final concentration of methylene blue was obtained after adsorption. To ensure the repeatability of the results, each test was repeated twice.

Equations (1) and (2) were used to calculate the removal percentage of dye and adsorption capacity [29, 30].

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

$$\% = \frac{(C_0 - C_f)}{C_0} \quad (2)$$

Where, q_e is adsorption capacity (mg g^{-1}); C_0 is the initial concentration of methylene blue (mg L^{-1}); C_e is the equilibrium dye concentration (mg L^{-1}); C_f is the final concentration (mg L^{-1}); V is the volume of the dye solution (L) and m is the adsorbent mass (gr).

3. Analysis Results

In this section, the effect of adsorbent surface modification by sodium dodecyl sulfate anionic surfactant on the removal of methylene blue from aqueous solutions is presented and then the effects of parameters such as pH, initial dye concentration, adsorbent amount, adsorbent-dye solution contact duration on methylene blue removal and adsorption capacity of the adsorbent were investigated.

The removal percentage of methylene blue using modified Luffa L20 and unmodified Luffa is shown in Fig. 1. The results indicate that modifying Luffa by anionic

surfactant, the percentage of dye removal was increased by 9% after 0.25g of adsorbent was applied and by 1.5% after applying 2.5g adsorbent. The difference was decreased by increasing the amount of adsorbent and saturation of the medium by adsorbent. In fact, when negatively charged by an anionic surfactant, the strength and ability of Luffa to absorb methylene blue (a cationic material) increases.

3.1. The effect of pH on dye removal and adsorption capacity

In order to study the effect of pH on the amount of methylene blue removal, adsorption capacity, and to simulate the dye medium with industrial wastewater, dye solutions were prepared with different pHs. Thus, the dye solutions of methylene blue were prepared with an initial concentration of 20 ppm and pH values of 3, 6, 7, 9 and 12 and 0.5 grams of modified Luffa adsorbent was added to each solution. Then, the adsorption and dye concentration were measured after 60 minutes. Sodium Hydroxide (NaOH) and HCl (0.1 M) were used to adjust the pH of each solution. The results are shown in Fig. 1.

< The approximate placement of Figure 1 >

As shown in Fig. 1, as pH increases from 3 to 6, the dye removal percentage and adsorption capacity increases. At low pH levels, the H^+ ions present in the medium attach to the adsorbent surface anions, neutralizing the adsorbent charge which reduces methylene blue absorption. But with increasing pH and reducing H^+ concentrations in the medium, more anions are available to absorb dye on the surface adsorbents, and therefore, the adsorption capacity and the percentage of dye removal are increased. At 6 – 9 pH levels, there is little change in the adsorption capacity and the percentage of dye removal. This is because the strength of the H^+ and

OH⁻ groups in this range is not high enough to have a significant effect on methylene blue adsorption. In fact, at pH levels 6 to 7, the positive surface charge of the dye is stronger than the protons in the solution and also the adsorbent surface charge is greater than the hydroxyl groups in the dye solution at pH 7 to 9 which results in greater tendency to absorb the dye. At pH values higher than 9 while increasing OH⁻ concentration in the dye solution, the adsorption capacity is reduced and the percentage of dye removal decreases, because the OH⁻ is attached to cationic dye particles reducing ion exchange capacity by neutralizing the surface charge. Therefore, the maximum capacity and the percentage of dye removal occur in the media with pH values of 6 to 9. Given the fact that the range covers the neutral and near-neutral media, these modified adsorbents can be used in a variety of industries that contain wastewater within this pH range.

3.2. The effect of initial dye concentration on dye removal and adsorption capacity

To investigate the effect of initial dye concentration on the methylene blue removal efficiency and the adsorption capacity, solutions of methylene blue dye were prepared with concentrations of 2, 10, 20, 50, 100, 150 and 200 mg L⁻¹. The amount of 0.5 g of adsorbent was added to each solution and the adsorption was performed for one hour at 25°C. In all experiments, the pH of the solution was adjusted to 6. As shown in Fig. 2, with an increase the initial dye concentration, the adsorption capacity increases thanks to the availability of larger amounts of dye per unit of adsorbent. By increasing dye solution concentration to 50 mg L⁻¹, the dye removal efficiency increases from 98% to 99% and then with further increase in concentration, the efficiency decreases and reaches 97.5% at 200 mg L⁻¹. Therefore, the highest percentage of dye removal occurs at an initial concentration of 50 mg L⁻¹.

< The approximate placement of Figure 2 >

3.3. Effect of adsorbent content on dye removal

In order to study the effect of adsorbent content on dye removal, methylene blue solution (20 mg L⁻¹) was prepared and the pH was adjusted to 6. In each experiment, 100 cc of the solution was used and a certain amount of adsorbent was added to each solution. After 60 minutes, adsorption amount and dye concentration were measured. The results are shown in Fig. 3. By increasing the amount of adsorbent, the adsorption capacity had a descending rate and decreased from 7.6 mg g⁻¹ (in 0.25 mg g⁻¹ adsorbent) to 0.8 mg g⁻¹ (in 2.5 mg L⁻¹ adsorbent). Also, the highest removal efficiency occurred at the adsorbent content of 1 gr and then, due to the saturation of the dye medium with adsorbent, and the reduced circulation of the adsorbent in this medium which consequently lead to decreased adsorbent-dye contact, the percentage of dye removal dropped.

< The approximate placement of Figure 3 >

3.4. The effect of contact time on dye removal

The solutions used contained 20 mg L⁻¹ methylene blue and with pH 6. For each experiment, an amount of 0.5 mg of modified Luffa adsorbent was used and the amount of dye adsorption was measured at 25°C at various times. The effect of adsorbent-dye solution contact time on the adsorption capacity and removal percentage of methylene blue is shown in Fig. 4.

< The approximate placement of Figure 4 >

As it can be observed, as time elapses from 20 to 90 minutes, dye removal percentage and adsorption capacity are increased. By increasing the contact time from 60 to 90 minutes, the change in the adsorption capacity and the percentage of dye removal can be ignored for the 30 minute difference between the two time points. So, it can be claimed that after 60 minutes,

equilibrium occurs in the removal of methylene blue by modified Luffa adsorbent, which quite conforms to the 99% dye removal and adsorption capacity of 3.96 mg g⁻¹.

4. Determining the adsorption isotherm

By determining the dye adsorption isotherm, a pattern and an equation can be derived to generalize the results and study the removal of methylene blue under other concentrations and operating conditions, thus formulating the dye removal by the modified Luffa adsorbent.

Langmuir and Freundlich models were used to obtain the isotherm of methylene blue adsorption by the modified Luffa adsorbent. Langmuir and Freundlich models are shown in equations (3) and (4) respectively [34].

Langmuir equation:

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m K_l C_e} \quad (3)$$

Where, q_e is the amount of absorbed dye per amount of adsorbent (mg g⁻¹); q_m is the maximum dye needed for single layer formation (mg g⁻¹); C_e is the equilibrium concentration (mg L⁻¹) and K_l is Langmuir constant.

Freundlich equation:

$$q_e = K_f C_e^{\frac{1}{n}} \quad (4)$$

Where K_f and n are Langmuir constants [35].

Figure (5) shows the graph obtained by mapping $1/q_e$ versus $1/C_e$. It is seen that the intersection of the line is negative. Therefore, the empirical data do not match the Langmuir equation which can be due to the lack of adsorption of dye as a single layer.

< The approximate placement of Figure 5 >

Therefore, it is better to use the Freundlich equation to obtain the isotherm. By plotting $\log q_e$ against $\log C_e$, it is possible to calculate kinetic parameters. As shown in Fig. 6, the obtained data are in good agreement with the Freundlich model ($R^2=0.98$). In Table 4, the kinetic parameters of the Freundlich equation are calculated and presented.

< The approximate placement of Figure 6 >

< The approximate placement of Table 4 >

Several isotherm models such as Redlich–Peterson, Dubinin–Radushkevich, Temkin, Toth, Koble–Corrigan, Sips, Khan, Hill, Flory–Huggins and Radke–Prausnitz have been studied by George Z Kyzas and his colleagues in 2017 and the models can be used for further research[36].

5. Conclusion

Methylene blue dye removal was performed by Luffa L20 adsorbent modified with anionic surfactant under different operating conditions. The results are as follows:

1. Luffa L20 adsorbent modification with anionic surfactant (SDS 10%) increases the adsorption capacity and the removal efficiency of methylene blue from aqueous solution by 6%.
2. The best removal efficiency and highest dye adsorption capacity are related to adsorption at pH levels from 6 to 9. At pH levels below 6 and above 9, the removal percentage and adsorption capacity are reduced due to the effect of concentration of H⁺ and OH⁻ ions. Since the obtained pH range covered the neutral and near neutral media, the adsorbent can be used in a variety of industries.
3. The results showed that the highest dye removal percentage occurs when 1 g adsorbent is used where the adsorption capacity equals 5 mg g⁻¹.

4. The highest dye removal efficiency was observed in a medium where the initial concentration of methylene blue was 50 mg L^{-1} where 99% of the dye was removed.
5. After a period of 60 minutes, it is possible to obtain the methylene blue removal equilibrium concentration, which given 99% dye removal, is relatively a good time in methylene blue removal.
6. The experimental data are consistent with Freundlich adsorption isotherm. However, the lack of agreement between the experimental data and Langmuir model shows that methylene blue dye adsorption by modified Luffa adsorbent does not occur as single-layer.

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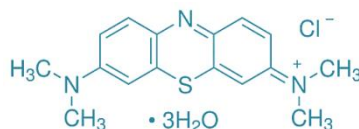
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Tables:

Table 1: Chemical properties of methylene blue



Chemical name	Methylene blue
Chemical formula	$C_{16}H_{18}ClN_3S$
Melting point	$180^{\circ}C$
Solubility (@ $20^{\circ}C$)	50 g L^{-1} (H_2O)
λ_{max}	660-665 nm
Mw	319.86 g mol^{-1}

Table 2. Anionic surfactant specification used to modify the Luffa adsorbent structure



Chemical name	SODIUM LAURYL SULFATE
Chemical formula	$C_{12}H_{25}NaO_4S$
Melting point	$205-207^{\circ}C$
pH (@ $20^{\circ}C$)	6-9 (10 g L^{-1} , H_2O)
Density (@ $20^{\circ}C$)	1.1 g cm^{-3}
Mw	288.38 g mol^{-1}

Table 3- Effective parameters in adsorption of methylene blue by Luffa L20 modified adsorbent

Parameter	Contact time (min)	Initial concentration of methylene blue (mg L^{-1})	Adsorbent dosage (mg)	pH
Levels	20, 60, 90, 100, 120, 240	2, 10, 50, 100, 200	0.25, 0.5, 1, 1.5, 2, 2.5	3, 6, 7, 9, 12

Table 4 - The kinetic parameters of Freundlich model in methylene blue adsorption with modified Luffa

Slope	Intercept	n	K_f
0.9485	1.069	1.054	11.72

Figures:

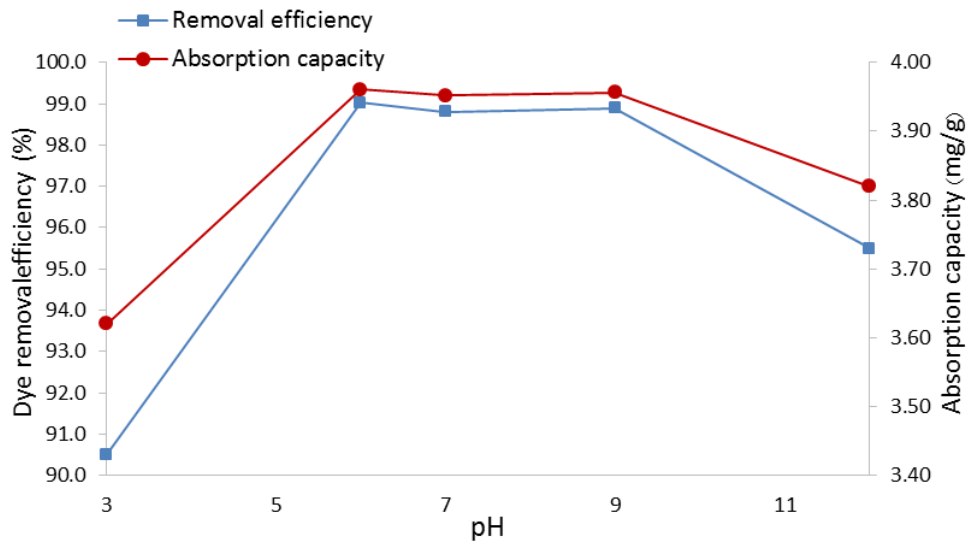


Figure 1. Effect of dye medium pH on the methylene blue dye removal percentage and adsorption capacity

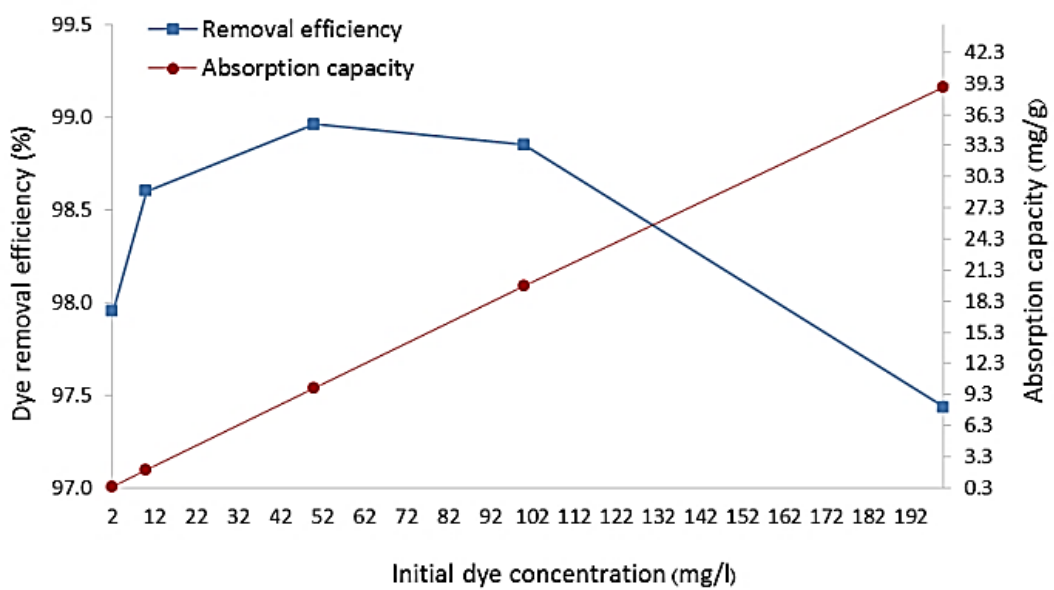


Figure 2- The effect of initial concentration of methylene blue on dye removal percentage and adsorption capacity

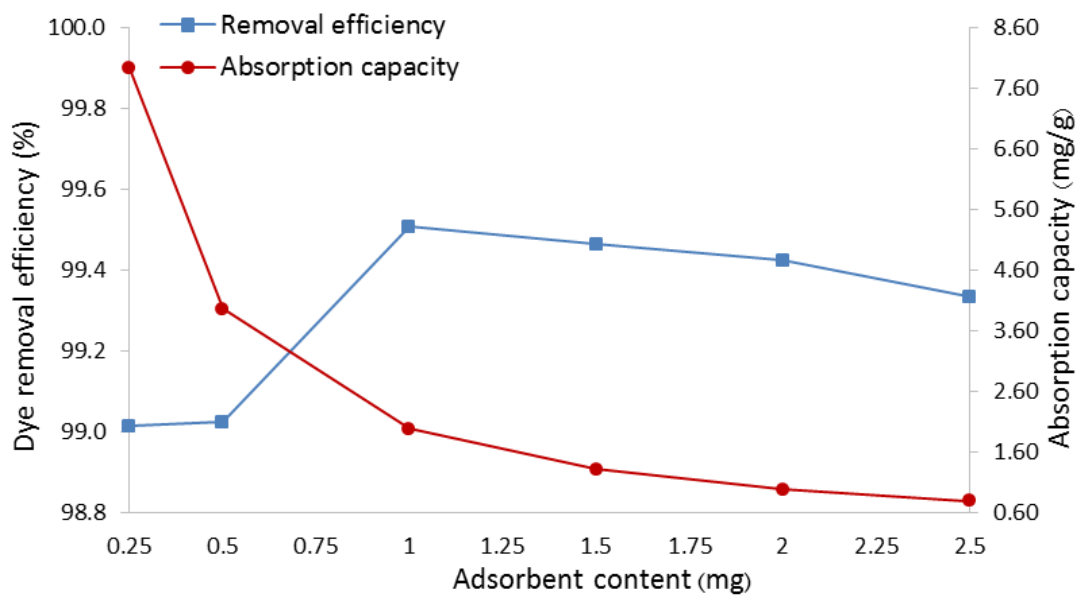


Figure 3. The effect of adsorbent dosage on adsorption capacity and removal efficiency of methylene blue

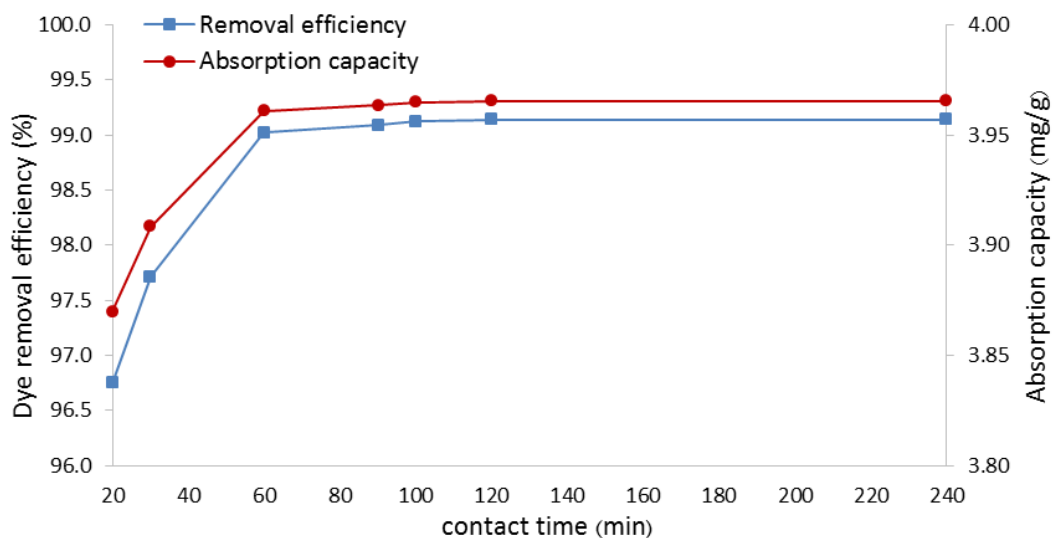


Figure 4. The effect of contact time between adsorbent and dye solution on the adsorption capacity and removal percentage of methylene blue

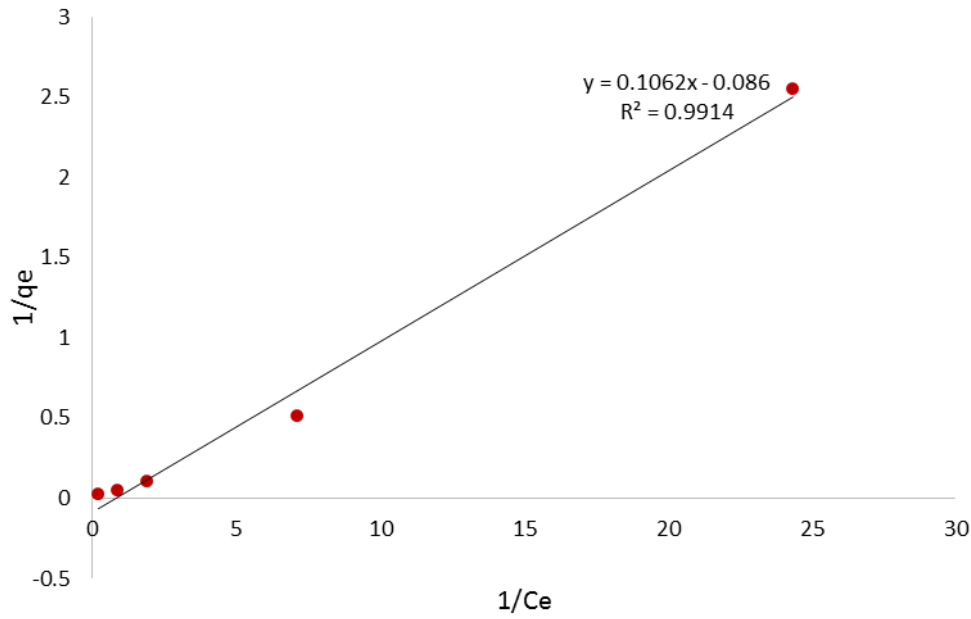


Figure 5- Mapping $1/q_e$ versus $1/C_e$ (Langmuir model)

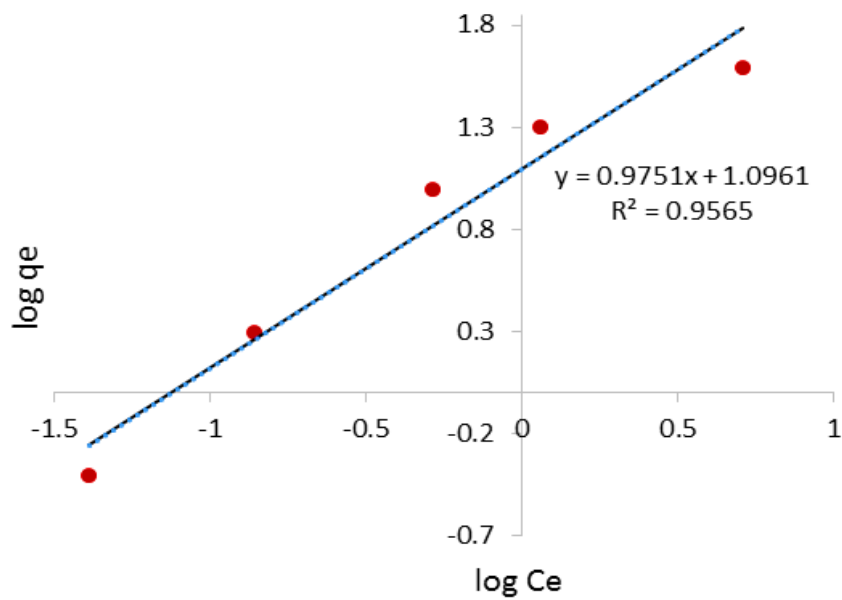


Figure 6- $\log q_e$ against $\log C_e$ and determination of kinetic parameters of Freundlich model