



Methyl blue removal from synthetic wastewater employing activated carbon and bio adsorbent material derived from the leaves of Nettle

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Abstract

Adsorption is a process used for the purification of contaminated water. Among different types of adsorbents, activated carbon is the most widely utilized substance for the removal of venomous heavy metals and dyes. In this study, activated carbon was derived from Nettle under the chemical activation method, and non-activated bio-adsorbent carbon was prepared from it for adsorption. The activated carbon (AC) and bio adsorbent (BA) were described by Fourier transform infrared spectroscopy (FT-IR), and powder x-ray diffraction (XRD). The effect of methylene blue load, pH at zero-point charge, contact time, and adsorbent dose were determined where optimum adsorption of MB was achieved by AC at pH = 10, 90 min, 5 mg/L MB, and 0.2 g adsorbent dosage, and the optimum adsorption of MB by BA occurs at pH = 10, 60 min, 5 mg/L MB, and 0.2 g adsorbent dose. The Langmuir and Freundlich isotherm models were used to investigate the adsorption process of MB on activated carbon and bio adsorbent. The equilibrium data showed that the Langmuir model is more likely to fit bio- and activated adsorbents compared to the Freundlich model, which reveals that the adsorption process adopted a monolayer adsorption process. Meanwhile, the pseudo-second-order kinetics model was appropriated with pseudo-first-order kinetics, implying that the adsorption interaction benevolence electrostatic interaction between bio-adsorbents and activated carbon. In this study, the percentage removal of MB dye from wastewater using activated carbon (96%) was higher than that of the bio-adsorbents (82%).

Keywords: Adsorption, Nettle, UV/Vis spectrophotometry, FT-IR, Activated carbon

1. Introduction

Waste discharged from industries and urban areas hurts the water body and soil. Presently, huge amounts of toxic organic and inorganic compounds have been introduced into the environment. Industries such as pulp and paper, leather, cosmetics, food, dyeing, textiles, etc. discharge major pollutants containing dyes into the environment **including** water bodies and soil [1].

Dyes comprise compounds that have the molecular structure of aromatics because they are highly resistant to light, temperature, and oxidizing agents. This characteristic makes them non-degradable and easily accumulated in living organisms, causing severe diseases and disorders [2]. Some dyes contain carcinogenic compounds, which can cause serious hazards to aquatic life and humans [3]. Many studies have been conducted to investigate the use of easily available adsorbents as an alternative technique for the removal of dyes by the adsorption process [4].

Different kinds of technologies that are effective, low-cost, and economically feasible should be used to threaten water pollutants. Accordingly, many scholars have reported various methods to eradicate contaminants from wastewaters before they are discharged into the environment [5].

The most frequently used dye removal technologies are coagulation/flocculation, photo-catalytic discoloration, microbial decomposition, photocatalytic degradation, photocatalysis, and electrochemical methods. Among these, adsorption is one of the most useful and broadly used method in water purification technologies due to its low-cost, well performance, easy procedure and effective efficiencies [6]. Biosorption is a procedure that uses low-cost living matter and is predominantly suitable for deducting toxic chemical discharges from households and huge industries. Moreover, these materials are inexpensive, environmentally friendly, and renewable nature [7].

Agricultural waste is a promising material to be one of the top starting materials because of its low-cost and high adsorption efficiency.

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In this study, both adsorbents, namely activated carbons and bioadsorbents, were prepared from Nettle. These adsorbents were used to mitigate contaminated water systems through the adsorption process. The performance of the adsorbents was studied based on several main parameters, including initial dye concentration, adsorbent dosage, pH, and contact time.

2. Materials and Method

2.1. Sample collection and treatment

A sample of the leaf of Nettle was collected from the vicinity of Debre Berhan City. The collected sample was transported to Debre Berhan University, Chemistry laboratory using plastic bags. After removing the course debris from the nettle, the sample was washed three times with tap water.

In addition to this, the sample was washed with deionized water to make it cleaner. Finally, the sample was dried (at room temperature) and ground to use as an adsorbent for the removal of methyl blue from synthetic wastewater.

2.2. Chemicals and reagents

In this work, methylene blue, potassium hydroxide 10% (KOH), hydrochloric acid (4N HCl), sodium chloride (NaCl), distilled water, and sodium hydroxide 0.1 M (NaOH) were used.

2.3. Instrumentation

A digital magnetic stirrer, an electric grinder, different mesh size sieves, and furnace (DFW-7000) were used for the adsorption process. The instruments employed for characterization were a UV-Vis spectrophotometer (AE-1408013) to determine the concentration of adsorbents after adsorption, an X-ray diffractometer (XRD) to quantify the structure of the adsorbent, and a Fourier transform infrared (FT-IR) to recognize the functional groups involved in the adsorbent before and after the adsorption process.

2.4. Preparation of adsorbents

2.4.1. Preparation of bio adsorbent (BA)

The target bio adsorbent was prepared from the leaf of the nettle by washing the nettle leaf sample with tap water and distilled water, respectively. Then, it was dried at room temperature, milled with a pestle and mortar, sieved, and packed with polyethylene bags until analysis.

2.4.2. Preparation of activated carbon (AC)

The pounded leaves of nettle were soaked with a 10% KOH solution and kept for 24 h. After discarding excess KOH solution, the material was dried, and then converted into carbon in a muffle furnace at 400°C for 30 minutes. The carbonized material was washed appropriately with 4N HCl to remove the remaining KOH (Figure 1). Moreover, the material was washed with distilled water and kept for 2 h in an oven at 110 °C to remove the moisture. Finally, the activated carbon was cooled and stowed until the adsorption process was carried out.

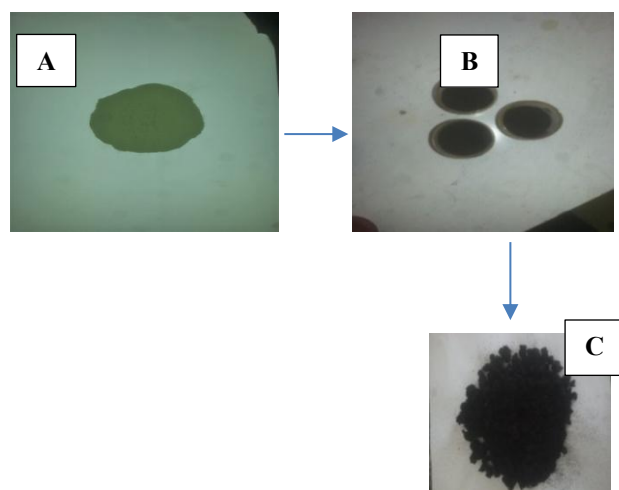


Figure 1. A. Powdered nettle leaf (Bio adsorbent); B. Bio adsorbent after carbonization; C. Bio adsorbent after carbonization and HCl washing.

2.4.3. Preparation and analysis of methyl blue dye

1000 mg/L of a stock standard solution of methyl blue was prepared by weighing an appropriate quantity of methylene blue in distilled water, while the working standard solution was set by diluting the stock standard solution with distilled water in the range of 5–25 mg/L with a 5 mg/L interval. Finally, the concentration of methyl blue was quantified using the UV-visible spectrophotometer at 665 nm.

3. Results and discussion

3.1. Characterizations of the Adsorbents

3.1.1. Determination of point of zero charge (pH pzc)

The point of zero charge (PZC) is determined by plotting the change in pH versus the initial pH. From the graph, the point at which the net electrical charge of the adsorbent's surface is zero, expressing the point of zero charge [8]. The p_{ZC} for the activated carbon and bio- adsorbent were 6.65 and 6.68, respectively. Thus, depending on the type of synthetic wastewater, the pH

of the solution, and the concentration of the electrolyte, the surfaces of the adsorbents can behave as cation exchangers, anion exchangers, or have no charge.

Electrostatically, MB (cationic pollutant) can be adsorbed by anionic adsorbents. In our study, the pH of the solution was greater than the PZC for AC and BA where the surface attracts a cationic MB dye.

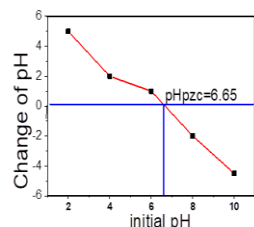


Figure 2. Zero-point of charge AC

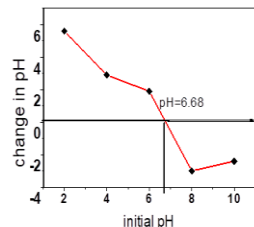


Figure 3. Zero-point of charge of BA

3.1.2. Powdered x-ray diffraction (XRD) Analysis

The degree of crystallinity or amorphous nature of activated carbon and bio-adsorbents was determined by XRD. The presence of broad diffraction on XRD analysis revealed an amorphous structure. Figures 4 and 5 illustrates XRD pattern of the BA and AC, respectively. The diffraction peaks are observed at the diffraction angles of $2\theta = 23.83^\circ, 29.32^\circ, 44.02^\circ, 64.44^\circ$, and 77.5° for BA and $21.48^\circ, 29.36^\circ, 43.28^\circ, 64.38^\circ$, and 77.48° for AC in the spectrum. In this case, diffraction within the range $2\theta = 21-39^\circ$ shows developed separated peaks with maxima at $2\theta = 23.82^\circ$ for BA and $2\theta = 21.48^\circ$ for AC. Figure 4 shows the fragmented and developed crystallites of the material. The strong and weak diffraction peaks occurred at diffraction angles indicates the existence of graphite crystallite in activated carbon (JCPDS00-055-5159,59). In conclusion, it is quite clear that pure SiC were composed of silica (SiO_2) of nettle and carbon (C) in which the oxygen is illuminated during the calcination process. From XRD results, it is observed that pure SiC and graphite were detected with no other impurities and it confirms the amorphous nature of the carbon that was extracted from carbonated

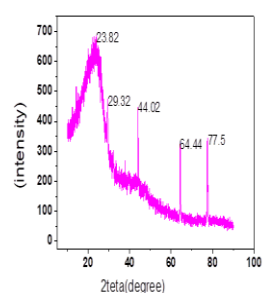


Figure 4. XRD pattern of BA

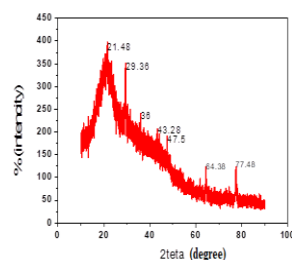


Figure 5. XRD pattern of AC

3.1.3. Fourier Transform Infrared Spectroscopy (FT-IR)

The FTIR spectra of the adsorbents were measured within the range of $4000-400 \text{ cm}^{-1}$. Figures 6 and 7 show, the FTIR spectra of the removal of methyl blue, before and after, using bio and activated carbon adsorbent, respectively. In activated carbon, the band at 2943 cm^{-1} indicates aliphatic C-H group; the band at 1594 cm^{-1} is allocated to olefin C=C [9], 1770 cm^{-1} indicate C=O bands, at 1482 cm^{-1} CH_2 is detected [10], the bands at 1103 cm^{-1} shows C-O functional group and weak signal at $518-575 \text{ cm}^{-1}$ represents halogen function group. For bio- adsorbent, the FTIR detected at 3323 cm^{-1} indicates OH or NH functional groups, at 1633 cm^{-1} C=C stretching, at 2918 cm^{-1} C-H group, and 1042 cm^{-1} C-O functional groups.

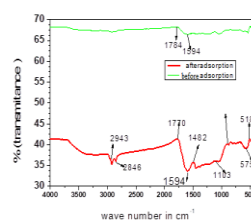


Figure 6. FTIR spectra before and after adsorption by BA

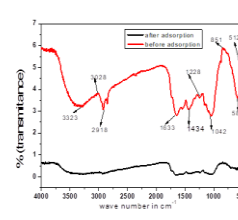


Figure 7. FTIR spectra before and after adsorption by AC

3.2. Batch adsorption experiments

To conduct the batch adsorption tests, two 100-mL Erlenmeyer flasks containing 30 mL of methyl blue solution each were filled with the required amount of activated carbon and bio adsorbent. After then, the flasks were shaken at a rate of 115 revolutions per minute until they reached equilibrium. Then, important experimental factors were examined in batch adsorption tests, including initial pH (2 to 10), adsorbent dosage (0.05 to 0.8 g), contact period (30 to 150 min), and initial concentrations of methyl blue (5 to 25 mg/L). The following formulas were used to determine the methyl blue removal percentage (R%) and the adsorbent's equilibrium adsorption capacity, q_e (mg/g).

$$\%R = \frac{(C_o - C_e) \times 100}{C_o} \quad (1)$$

$$q_e = \frac{(C_o - C_e)V}{W} \quad (2)$$

Where:

C_e is the methyl blue concentration at equilibrium (mg/L);

C_o is the initial methyl blue concentration (mg/L);

W is the dry mass of the adsorbent (g);

V is the volume of methyl blue solution (L)

In this experiment, the analysis was conducted in triplicate under identical conditions, and their average values were reported.

3.2.1. Factors affecting the adsorption process

3.2.1.1. Effects of pH

The experiments were carried out with two adsorbents (0.2g), activated carbon (AC) and bio- adsorbent (BA) in the pH range of 2, 4, 6, 8, and 10 with 30 ml of 15 ppm methyl blue. As shown in Figures. 8 and 9, the maximum percent removal of methyl blue in activated carbon (96%) and bio- adsorbent (83%) is at pH 10, which is the optimum pH. As increasing of pH value, the percent removal of MB increases from 48% to 96% and from 47% to 83%, respectively. The greater efficiency of adsorption shown in the basic region for both AC and BA is due to the strong electrostatic attraction of cationic methyl blue and the negative surface of the adsorbents AC and BA. In the current study, we can see the adsorption efficiency of AC and BA. The percent removal of MB from synthesized waste water on AC is greater than that of BA due to the presence of an active site on AC.

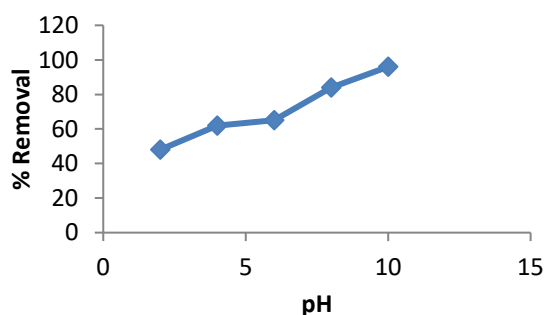


Figure 8. Effects of pH on adsorption of MB by AC

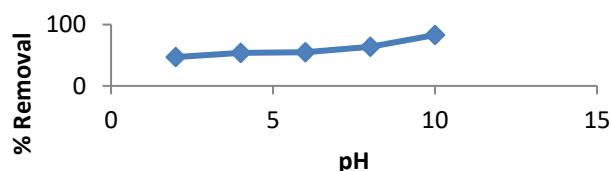


Figure 9. Effects of pH on adsorption of MB by BA

3.2.1.2. Effect of Contact Time

In the adsorption process, the investigation of the contact time taken to adsorb adsorbate on the adsorbent from the solution at the optimum pH determines the performance of the process. Figures 10

and 11 show the contact time of adsorption of MB on the two adsorbents. The figures show an increasing trend of removal up to a reaction time of 90 min for AC and 60 min for BA. The percent removal decreases as contact time increases. This is due to the lack of vacant sites on the AC and BA. The percent of adsorption of AC (95.7%) showed a slight decrease from 90 min to 150 min, and the percent removal of BA was 86% at 60 min and it was decreased to 85%. This is due to the fact that the active site of BA was smaller in number than that of AC.

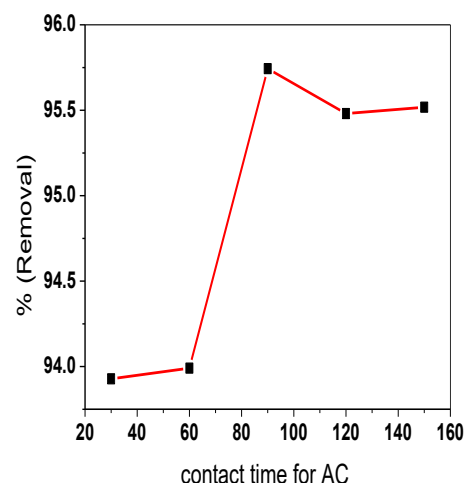


Figure 10. Effects of contact time by AC

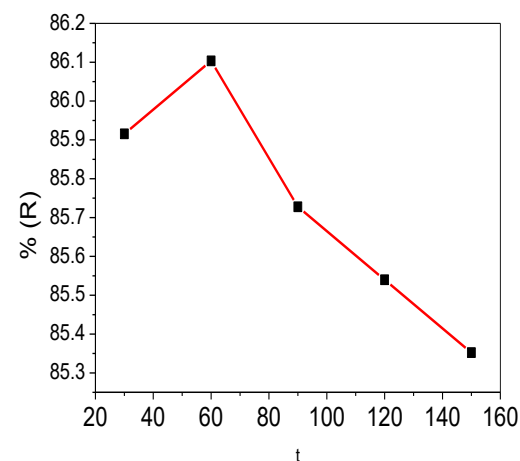


Figure 11. Effects of contact time by BA

3.2.1.3. Effect of adsorbent dosage

Maintaining the other experimental settings constant (pH = 10, contact period = 90 min for AC and 60 min for BA), the removal effectiveness of MB (30 ml of 15 mg/l sample) was examined at various adsorbent dosages in the range of 0.05–0.8 g. The findings displayed in Figures 12 and 13 demonstrate that when

the dosage of AC was raised, the % elimination of MB rose quickly. Nevertheless, the adsorbent dose of 0.2 g had the highest removal effectiveness, which was determined to be 96%; as a result, this dose was considered optimal. This could primarily be because as adsorbent doses rise, so does the availability of exchangeable sites for the ions [5].

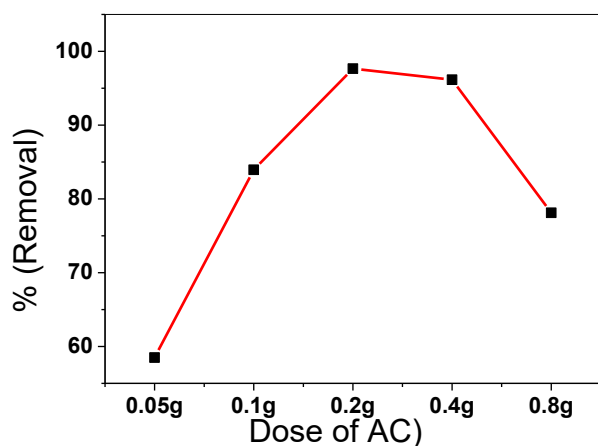


Figure 12. Effect of Adsorbent Dosage by AC

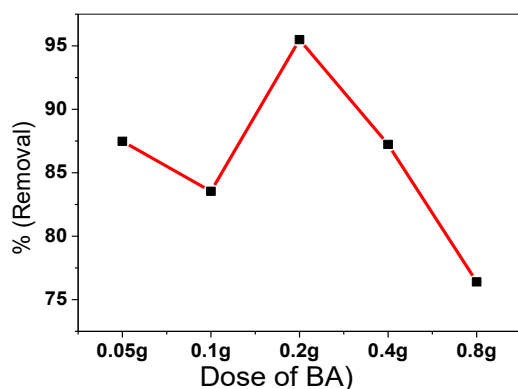


Figure 13. Effect of adsorbent Dosage by BA

3.2.1.4. Effect of initial concentration of methyl blue on adsorption

The total mass transfer resistances between the produced adsorbent and the aqueous MB are explained by the initial concentration of the adsorbate. The highest number of empty sites on the adsorbent that are available at the beginning stage may be the cause of the increased adsorption at the initial concentration. The initial number of moles to the adsorbent's accessible surface area has a considerable ratio at low concentrations. As a result, the starting concentration

no longer affects fractional adsorption [11]. Various beginning concentrations of MB in the range of 5–25 mg/L were studied, holding all other experimental parameters constant, in order to assess the impact of the initial concentration of MB on its percentage removal by the AC and BA. AC and BA's adsorption efficiency dropped from 94% to 80% and 85% to 35%, respectively, as the initial concentration increased from 5 to 25 mg/L. The percentage of MB that was removed decreased as MB concentration rose. This is due to the build-up of particles on the adsorbent's surface.

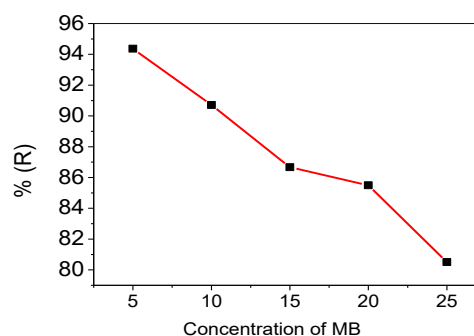


Figure 14. Effect of initial concentration of MB on adsorption by AC

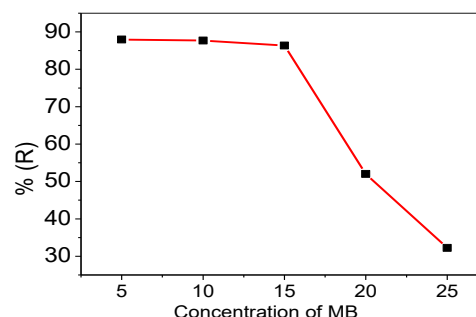


Figure 15. Effect of initial concentration of MB by BA

3.3. Adsorption isotherms and models

3.3.1. Langmuir adsorption isotherm

Monolayer adsorption gets its name because the Langmuir isotherm works best when the adsorbate is adsorbed onto a surface with a limited number of identical sites. The model postulates that there is no adsorbate movement in the surface plane and that there are uniform adsorption energies on the surface.

The value of Q_0 and K_L is determined by plotting $\ln C_e/q_e$ vs. C_e from intercept and slope. In the current study, the values of R_L were 0.954 L/mg and 0.855

L/mg, whereas Q_0 was 669 mg/g and 128.2 mg/g for AC and BA, respectively. These results indicated the favorable uptake of both AC and BA.

3.3.2. Freundlich adsorption isotherm model

The values of k_f and $1/n$ are determined by plotting $\ln q_e$ vs. $\ln C_e$ from intercept and slope, respectively. The correlation coefficients of the Langmuir model for both adsorbents were higher than the Freundlich model. The result reveals that the adsorption of the two species was better fitted to the Langmuir model than the Freundlich model, meaning that the adsorption of activated carbon and bio-adsorbent was a monolayer coverage process.

Table 1. Langmuir and Freundlich isotherm models

Adsorbent	Langmuir				Freundlich		
	R^2	Q_0 mg/g	R_L	K_L L/mg	R^2	K_F	$1/n$ (bf)
AC	0.99	669	0.9545	0.0031	0.67116	1.0379	0.9434
BA	0.98	128.2	0.855	0.00113	0.9052	0.6372	1.8911

3.4 Kinetics Models

Among the different factors that affect the performance of adsorbent adsorption kinetics. It should be identified the type of adsorption kinetics, whether it is pseudo-first-order or pseudo-second-order kinetics. In every adsorption process, linear or nonlinear analysis of the kinetics is applied.

Pseudo-first order kinetics

The pseudo-first order rate equation is expressed as [12]:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (3)$$

Where:

“ k_1 ” (min^{-1}) is the rate constant of the pseudo-first-order equation and “ q_t ” (mg g^{-1}) is the concentration of methyl blue adsorbed at the time “ t ” (min). Integrating and rearranging Eq. 3 for the boundary conditions; $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$ gives the linear form expressed as:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (4)$$

The values of “ q_e ” and “ k_1 ” in Eq. 4 were obtained from the slope and intercept of the plot of $\log(q_e - q_t)$ versus t .

The value of k_1 and q_e is determined, by plotting $\ln(q_e - q_t)$ vs. t , from slope and intercept respectively. In the current study, the correlation coefficients (R^2) of AC

and BA were 0.51 and 0.65, q_e of AC and BA were 1.507 and 0.98, and k_1 of AC and BA were 3.100 and 0.005, respectively.

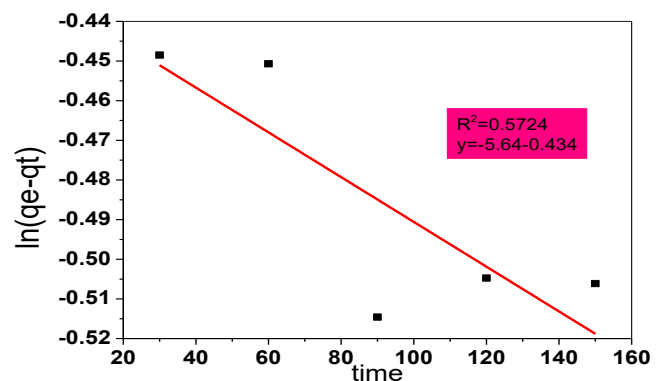


Figure 16. Pseudo first orders for AC

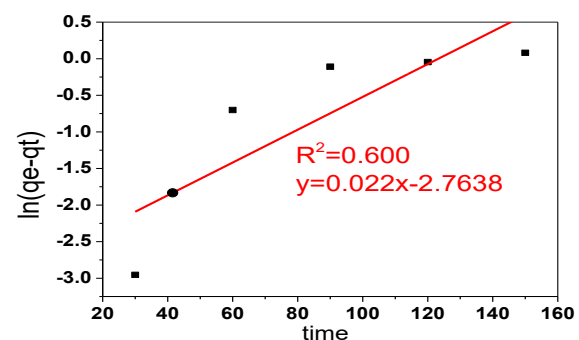


Figure 17. Pseudo first order for BA

Pseudo second order (PSO) model

In this study, the values of the correlation coefficients (R^2) of AC and BA were 0.999 and 0.984; q_{cal} was 2.16 and 0.77; q_{exp} was 2.71 and 1.96; and K_2 was 0.55 and 0.05, respectively. The results of the experimental q_e , calculated q_e , and pseudo-second-order rate constants are coincided with those obtained by other scholars. The adsorption of MB was shown to be a chemical adsorption between methyl blue and activated carbon. The analysis of kinetic data by the PSO exhibited that the rate-determining step is chemisorption for AC, which involves sharing of electrons between the surface functional groups of adsorbents and the adsorbate molecules [13]. Therefore, the adsorption of the PSO model shows a better fit compared to the PFO model.

Table 2. Pseudo first and second order kinetic model

Adsorbent	Pseudo first order	Pseudo second order
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	R^2	Q_0 mg/ g	K_{mi} n^{-1}	R^2	Q_{cal} c	Q_{ex} p	K_2
AC	0.51 1	1.54	3.10	0.99 7	2.1 6	2.7 1	0.5 5
BA	0.85 1	0.94	0.00 5	0.98	0.7 7	1.9 6	0.0 5

4. Conclusion

A low-cost, easily available, and eco-friendly activated carbon and bio-adsorbent were utilized for the adsorption of target dye. The prepared activated carbon and bio-adsorbent were characterized by powder XRD and FTIR instrumentations. The adsorption effectiveness of the two adsorbents is different due to their available vacant sites to adsorb MB. Comparatively, AC is more effective than BA to remove MB dye from waste water. Based on the output of the study, activated carbon has revealed a drastic adsorption rate and valid adsorption performance for MB dye. Various parameters, including contact time, pH, initial adsorbate concentration, and adsorbent dose, were optimized. The adsorption process was also validated by the Langmuir and Freundlich iso-thermic models and kinetic models. The adsorption of MB was fitted to the Langmuir isotherm, signifying monolayer coverage of the surface of adsorbent. The kinetic study also defined that the adsorption process in the present study followed a pseudo-second-order model.

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