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Removal of metyl blue from synthetic wastewater using activated carbon and bio adsorbent derived from leaves of Nettle

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Abstract

Adsorption is a process used for the purification of contaminated water. Activated carbon is one of the most commonly used adsorbents for the removal of dyes and toxic heavy metals. In this study, activated carbon was prepared 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 characterized 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 dose, 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 obeyed the Langmuir model compared to Freundlich for both adsorbents, which shows that the adsorption process proceeds through monolayer adsorption. The pseudo-second-order kinetics model was found to be better fitted than pseudo-first-order kinetics, which implies that the adsorption mechanism favours electrostatic interaction between both 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

Industrialization and urbanization are greatly attributed to the pollution of the environment. Currently, large numbers of organic and industrial effluents have been introduced into the environment. Water pollution due to dyeing industry is the matter of great concern since large quantity of effluent is discharged into the water bodies. Industries such as pulp and paper, leather, cosmetic, food, and dyeing, etc. discharge major pollutants containing dyes into the environment including water bodies [1].

Dyes have complex aromatic molecular structure and are generally resistant to light, temperature and oxidizing agents. This characteristic feature makes the dye non-degradable and therefore causes bioaccumulation in living organisms, leading to severe diseases and disorders [2]. Dyes contain carcinogenic compounds which can cause serious hazards to the aquatic life and humans which used it [3]. Many studies have been conducted to investigate the use of low-cost adsorbent as an alternative technique for the adsorption of dye [4]. The diversity of water pollutants calls for a wide range of treatment methods that are not only effective, but also technologically and economically feasible. Various treatment technologies have been reported to remove these contaminants from wastewaters [5].

Nowadays great attention has been given to elimination of the effluents bearing dyes due to their potential toxicity and visibility problems. Various methods of treatment for dye/colour removal are adopted in order to decrease their impact on the environment. These methods include adsorption, coagulation/flocculation, photo-catalytic discoloration, microbial decomposition, wet air oxidation, and electrochemical methods. Among these methods, adsorption has been reported as the most effective method to treat dye effluents discharged from various industries [6]. Biosorption is a process that uses low-cost biomass and is particularly suitable for removal of pollutants from industrial effluents. The search for a low-cost and locally available adsorbent has led to the selection of materials from agricultural and biological origin, along with industrial by-products as adsorbents to greatly reduce the levels of contaminants to

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environmentally acceptable limits in reasonable cost [7].

In the present study, activated carbons and bio adsorbent prepared from Nettle, have been used as an adsorbent for removal of MB dye. The effects of various parameters such as initial dye concentration, adsorbent dosage, pH, and contact time were studied.

1. 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. Then, the collected sample was washed with tap water continually after the debris removed from the leaf of nettle then again washed with deionized water. Finally, the sample was dried (at room temperature) and ground to use as adsorbent.

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 used for characterization were a UV-Vis spectrophotometer (AE-1408013) to determine the concentration of adsorbents after adsorption, an X-ray diffractometer (XRD) to determine the structure of the adsorbent, and a Fourier transform infrared (FT-IR) to determine the functional groups involved in 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 followed by distilled water; it was then 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 dried and milled 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 carbonized in a muffle furnace at 400°C for 30 minutes. The carbon was powdered and activated in a muffle furnace at 400°C for a period of 10 minutes. The activated carbon was washed sufficiently with 4N HCl to remove the remaining KOH (Figure 1). Moreover, the material was washed with distilled water and kept for 2h in an oven at 110 °C. Finally, the activated carbon was cooled, and stored until the adsorption process was carried out.

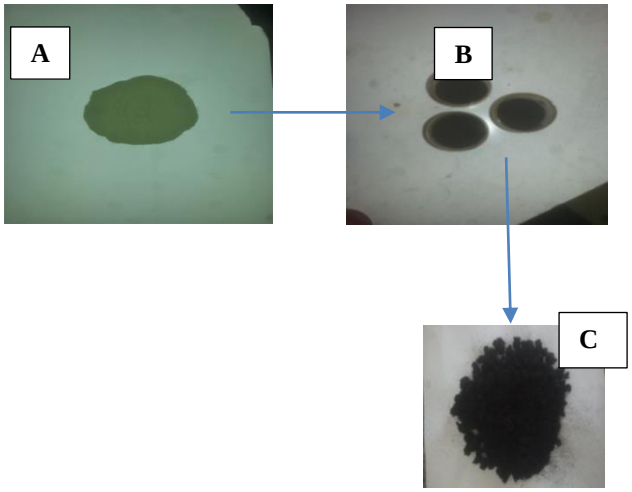


Figure 1. A. Powdered nettle leaf (Bio adsorbent); B. Bio adsorbent after carbonization; C. Bio adsorbent after carbonization and HCl washing.

2.4.3. Preparation and analysis of methyl blue dye

A stock solution of 1000 mg/L methyl blue was prepared by dissolving an appropriate amount of methylene blue in distilled water. The working solution was prepared by diluting the stock solution with distilled water in the range of 5–25 mg/L with a 5 mg/L interval. Finally, the concentration of MB was determined at 665 nm by the UV-visible spectrophotometer.

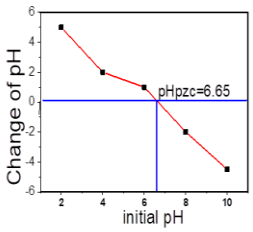
3. Results and discussion

3.1. Characterizations of the Adsorbents

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

The point of zero charge (PZC) is defined as the pH value at which the change in pH (pH final – pH initial) curve versus pH initial intersects the straight line corresponding to pH initial = pH final. This physical parameter is extremely crucial in the adsorption process of pollutants from water samples to determine the surface charge of the adsorbents [8]. The $_{PZC}$ for the activated carbon and bio- adsorbent were 6.65 and 6.68, respectively. Thus, depending on the pH of the

solution and the concentration of the electrolyte, these surfaces can behave as cation exchangers having a net negative charge, anion exchangers bearing a positive charge, or neutral species having 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.



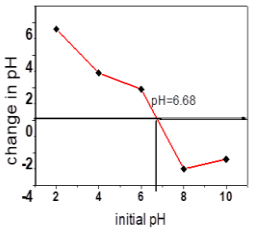
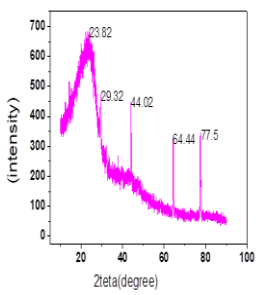


Figure 2. Zero-point charge of AC Figure **3**. Zero-point charge of BA

3.1.2. Powdered x-ray diffraction (XRD) Analysis

XRD analysis was performed on activated carbon and bio-adsorbent in order to determine the degree of crystallinity or amorphous nature. The appearance of a broad diffraction background and the absence of a sharp peak reveal a predominantly 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 2θ = 23.83°, 29.32°, 44.02°, 64.44°, and 77.5° for BA and 21.48°, 29.36°, 43.28°, 64.380°, and 77.48° for AC in the spectrum. In this case, diffraction within the range 2θ = 21-39° shows developed separated peaks with maxima at 2θ = 23.82^0 for BA and 2θ =21.48° for AC. This observation may be proposed to indicate fragmented, developed crystallites. The strong and weak diffraction peaks emerged at such 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 revealed 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



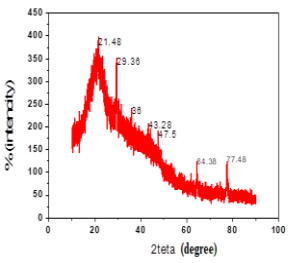
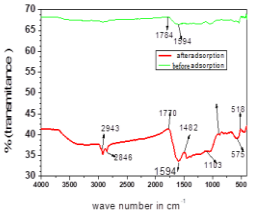


Figure 4. XRD pattern of BA **Figure 5**. XRD pattern of AC

3.1.3. Fourier Transform Infrared Spectroscopy (FT-IR)

The FTIR spectra of the adsorbents were measured within the range of 4000–400 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 1594cm^{-1} is assigned to olefin C=C [9], 1770cm^{-1} indicate C=O bands, at 1482 cm^{-1} CH_2 is detected [10], the bands at 1103cm^{-1} shows C-O functional group and weak signal at 518-575 cm^{-1} represents halogen function group. For bio- adsorbent, the FTIR detected at 3323cm^{-1} indicates OH or NH functional groups, at 1633cm^{-1} C=C stretching, at 2918cm^{-1} C-H group, and 1042cm^{-1} C-O functional groups.



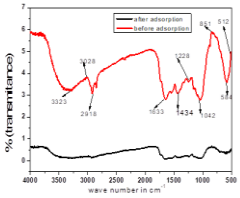


Figure 6. FTIR spectra before and after adsorption by BA **Figure 7.** FTIR spectra before and after adsorption by AC

3.2 Batch adsorption experiments

The batch adsorption experiments of MB on AC and BA were conducted in a set of 100 mL Erlenmeyer flasks containing 30 mL of MB solution. The flasks were shaken at a speed of 115 rpm/min until equilibrium was achieved. Batch adsorption experiments were carried out by manipulating several experimental variables, such as adsorbent dosage (0.05 to 0.8 g), initial pH (2 to 10), initial dye concentrations (5 to 25 mg/L), and contact time (30 to 150 min). The adsorption capacity at equilibrium, qe (mg/g), and the percentage of color removal (R%) were calculated as stated below, respectively.

$$q_e = \frac{(Co-Ce)V}{W} \quad (1)$$

$$\%R = \frac{(Co-Ce)100}{Co} \quad (2)$$

Where Co is the initial dye concentration (mg/L);
Ce is the dye concentration at equilibrium (mg/L);
V is the volume of dye solution used (mL);
W is the dry mass of the adsorbent used (g)

Adsorption experiments were conducted in triplicate under identical conditions and the results are reported as average values.

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.

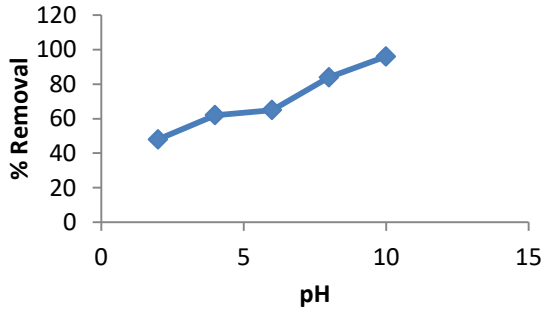


Figure 8. Effects of pH on adsorption of MB by AC

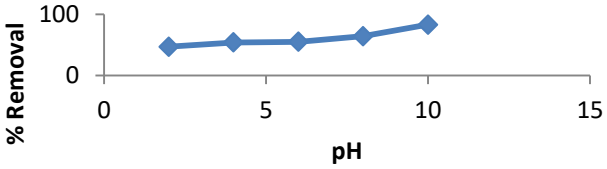
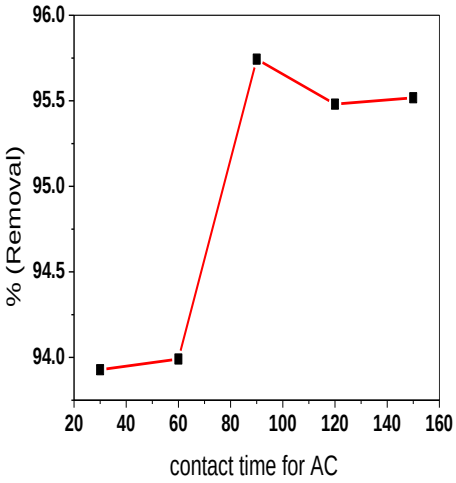


Figure 9. Effects of pH on adsorption of MB by BA

3.2.1.2. Effect of Contact Time

The contact time between adsorbate and adsorbent is one of the most significant design parameters that affect the performance of adsorption processes at the optimum pH. 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 Initially, a large number of vacant sites are available for adsorption, and after some time, the remaining sites may be difficult to occupy due to repulsive forces between adsorbate ions on the solid and in the solution. 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.



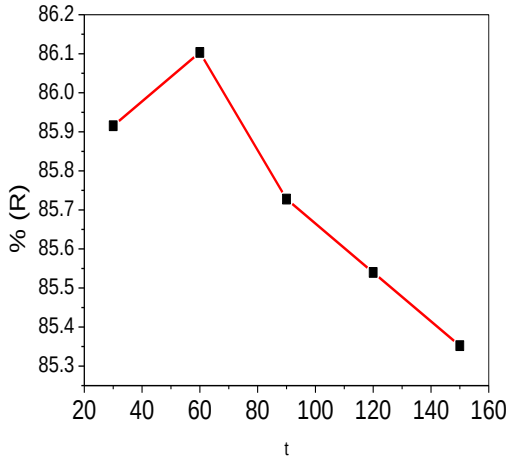


Figure 10. Effects of Contact Time on Adsorption
Figure 11. Effects of contact time on of MB by AC adsorption of MB by BA

3.2.1.3. Effect of adsorbent dosage

The removal efficiency of MB (30 ml of 15 mg/l sample) was investigated at different adsorbent doses, i.e., 0.05–0.8 g, keeping the other experimental parameters constant (i.e., pH = 10, contact time = 90 min for AC and 60 min for BA). The results given in Figures 12 and 13 show that the percentage removal of MB increased rapidly with an increase in the dosage of AC. However, the maximum removal efficiency was

exhibited for the adsorbent dose of 0.2 g, which was found to be 96%, and thus this dose was taken as optimum. This may mainly be due to the fact that the availability of exchangeable sites for the ions increases with an increase in the adsorbent doses [5] and beyond 0.2 g, the adsorption sites get saturated with the available MB ions. As a result, further addition of the adsorbent has not brought about a significant increase in the removal efficiency.

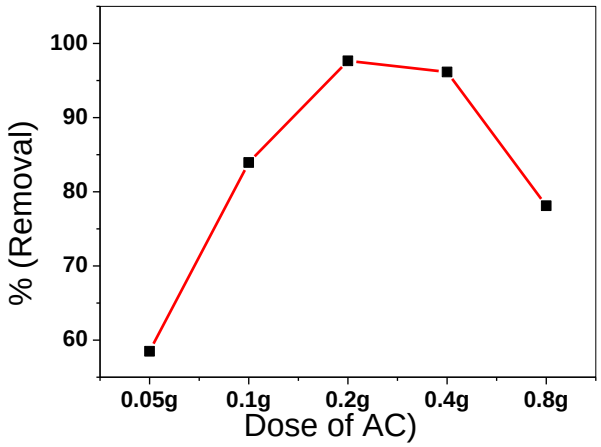


Figure12. Effect of Adsorbent Dosage by AC

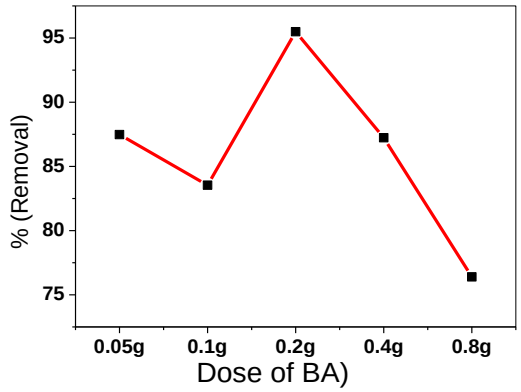


Figure 13. Effect of adsorbent Dosage by BA

3.2.1.4 Effect of initial concentration of mb on adsorption

The initial adsorbate concentration provides an important driving force to overcome all mass transfer resistances between the aqueous MB and solid phases of the adsorbent. Generally, the removal rates increase with the initial concentration until the maximum adsorption capacity. The higher adsorption at the initial concentration may be due to an increased number of vacant sites on the adsorbent available at the initial stage. In the case of low concentrations, the ratio of the initial number of moles to the available surface area of the adsorbent is large, and consequently, fractional adsorption becomes independent of the initial concentration [11]. To evaluate the effect of the initial concentration of MB on its percentage removal by the AC and BA, different initial concentrations in the range of 5–25 mg/L were investigated, keeping all other experimental parameters constant.

The adsorption efficiency of AC and BA decreased from 94% to 80% and 85% to 35%, respectively, as the initial concentration increased from 5 to 25 mg/L. Maximum efficiency of 94% for AC and 85% for BA was observed at 5 mg/L initial concentration. As the concentration of MB increased, there was a decrease in the percentage removal of MB. This can be attributed to the accumulation of particles on the surface of the adsorbent.

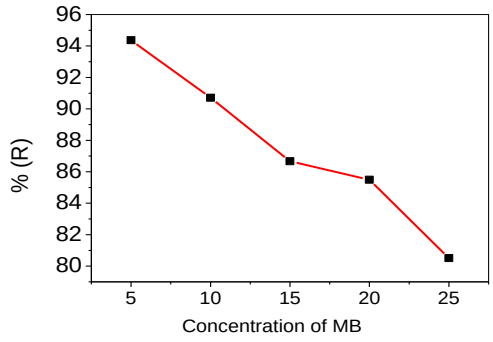


Figure 14. Effect of initial concentration of MB on adsorption by AC

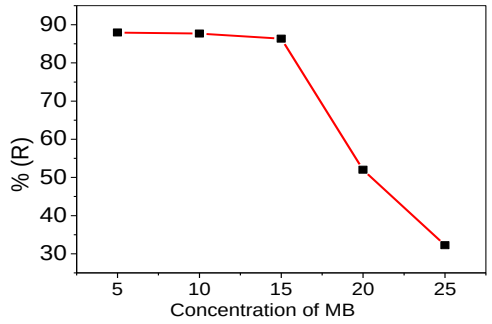


Figure 15. Effect of initial concentration of MB by BA

3.3. Adsorption isotherms and models

3.3.1. Langmuir adsorption isotherm

Langmuir isotherm is valid for monolayer adsorption onto a surface containing a finite number of identical sites. The model assumes uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface. The value of Qo and KL is determined by plotting ln Ce/q_e vs. Ce from intercept and slop. In the current study, the values of

R_L were 0.954 L/mg and 0.855 L/mg, whereas Qo was 669 mg/g and 128.2 mg/g for AC and BA, respectively. These results indicated the favourable 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 qe vs. ln Ce from intercept and slop, respectively. The higher correlation coefficient obtained from the Langmuir model (R^2 = 0.99) for AC and (R^2 = 0.98) for BA is compared to the Freundlich model (R^2 = 0.67) for AC and (R^2 = 0.905) for BA adsorption. 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_O 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	0.90 52	0.6372	1.8911

3.4 Kinetics Models

Adsorption kinetics is one of the main factors that must be understood before determining the applicability of any adsorbent. In every adsorption process, linear or nonlinear analysis of the kinetics is applied.

Pseudo–first order kinetics

The pseudo–first order rate equation is generally expressed as follows [12]:

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

where "q_t" (mg g^{-1}) is the concentration of methyl blue adsorbed at time "t" (min) and "k_1" (min^{-1}) is the rate constant of the pseudo–first order equation. Integrating and rearranging of 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:

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

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 slop 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.

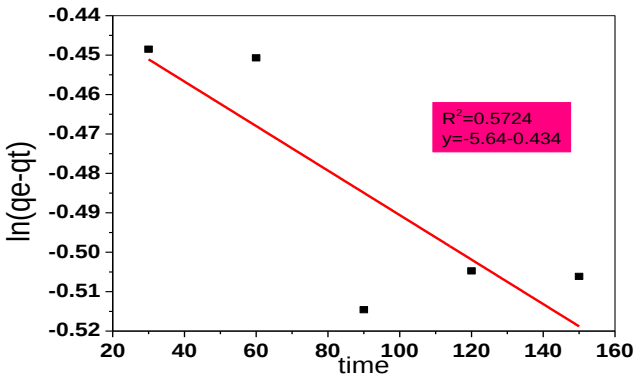


Figure 16. Pseudo first orders for AC

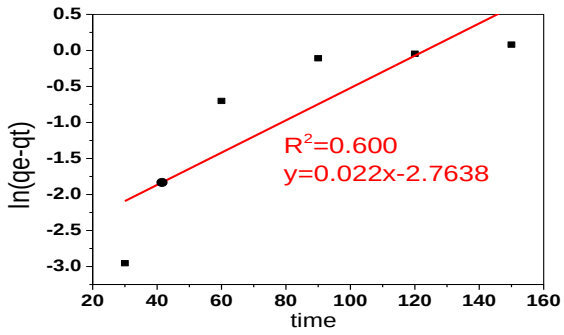


Figure 17. Pseudo first order for BA

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 in good agreement with those obtained by other scholars. The applicability of this model suggested that the adsorption of MB was based on a chemical reaction between methyl blue and activated carbon. Therefore, the adsorption of the PSO model shows a better fit compared to the PFO model. The analysis of kinetic data by the PSO showed that the rate-controlling step is chemisorption for AC, which involves valence forces through the exchange or sharing of electrons between the adsorbate molecules and the surface functional groups of adsorbents [13].

Table 2. Pseudo first and second order kinetic model

Adsorbent	Pseudo first order			Pseudo second order			
	R^2	Q_O mg/	Kmin n^{-1}	R^2	Q_{calc}	Q_{exp}	K_2

		g					
AC	0.511	1.54	3.10	0.997	2.16	2.71	0.55
BA	0.851	0.94	0.005	0.98	0.77	1.96	0.05

Conclusion

A low-cost, locally available, and environmentally friendly activated carbon and bio-adsorbent was utilized for the adsorption of MB dye. The prepared activated carbon and bio-adsorbent were characterized by powder XRD and FTIR instrumentations. The adsorption efficiency 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. The results obtained revealed that activated carbon has exhibited a rapid adsorption rate and good adsorption capacity for MB dye. Various parameters have affected the adsorption process, including pH, contact time, adsorbent dose and initial adsorbate concentration, 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, suggesting monolayer coverage of the adsorbent surface. The kinetic study also revealed that the adsorption process in the present study obeyed a pseudo-second-order model.

Acknowledgments

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References

1. David SN, Rajan MR: Impact of dyeing industry effluent on groundwater quality by water quality index and correlation analysis. *Journal of Pollution Effects and Control* 2014, **2**: 126.
2. Nageeb M: Adsorption technique for the removal of organic pollutants from water and wastewater 2013.
3. Balakrishnan M, Antony S, Natarajan R: Impact of dyeing industrial effluents on the groundwater quality in Kanchipuram. Indian *Journal* of Science and Technology 2008, **1** (7):1-8.
4. Norzita N, Chin CE, Nor AY: Removal of methylene blue dye by using eggshell powder 2013.
5. Mousavi ZH, Seyedi SR: Nettle ash as a low-cost adsorbent for the removal of nickel and cadmium from wastewater. *International Journal of Environmental Science and Technology* 2011, **8**(1): 195-202.
6. Priya, M, Saravanan A, Lemongrass powder used an adsorbent for treatment of chromium from tannery waste water. *International Journal of Environmental Science and Technology* 2019, **12**(02): 141-151.
7. Umesh DB, Basavaraj GK, E-Harbawic M.M: Fly ash as an adsorbent for the removal of reactive blue dye from aqueous solutions: optimization, kinetic and isotherm, (Investigations Proceedings of the Estonian Academy of Sciences) 2017, **66**(3):300-308.
8. Bansal RC, Goyal M: Activated carbon adsorption. CRC press, New York 2005.
9. Abdel RM, Abdulraheim MA: Removal of Heavy Metals from Industrial Waste Water by Biomass-Based Materials. *A Review Journal of Pollution Effects and Control* 2017, **5**(1): 1-13.
10. Ramlah AR,Ali HJ,mohd ABM, Nur NK: $FeCl_3$ - Activated carbon developed from coconut leaves: characterization and application for methylene blue removal Sains Malaysiana 2018,**47**(3):603–610.
11. Nethaji S,Sivasamy A, Mandal AB: Adsorption isotherms, kinetics and mechanism for the adsorption of cationic and anionic dyes onto carbonaceous particles prepared from Juglans Regia Shell Biomass. *International Journal of Environmental Science and Technology* 2011,**10**: 231–242.
12. Malik PK: Dye Removal from wastewater using activated carbon developed from sawdust: adsorption equilibrium and kinetics. *Journal of Hazardous Materials* 2004, **113**: 81–88.
13. Ho YS, McKay G: A comparison of chemisorption kinetic models applied to pollutant removal on various sorbents. Process Safety and *Environmental Protection* 1998, **76**: 332–340.