



Tea industry waste activated carbon as a low-cost adsorbent for methylene blue removal from wastewater

A.H.P. Hettiarachchi¹ and C.S.K. Rajapakse^{2*}

Department of Chemistry, University of Kelaniya, Kelaniya, Sri Lanka
shashikala@kln.ac.lk

Available online at: www.isca.in, www.isca.me

Received 14th February 2018, revised 24th April 2018, accepted 15th May 2018

Abstract

The possible utilization of tea industry waste activated carbon (TIWAC) as an inexpensive, eco-friendly bio adsorbent for methylene blue (MB) removal from wastewater was studied. Phosphoric acid was used as the activating agent for the preparation of TIWAC and Scanning Electron Microscopy and Fourier Transformed Infrared Spectroscopy were used to characterize TIWAC. In this work batch experiments were carried out at pH 7 and at temperature of 30 ± 2 °C to study the efficiency of MB adsorption on to TIWAC under different conditions such as TIWAC dosage, MB concentration, pH of the solution, and agitation time. The adsorption characteristics of the sorbent was tested with Freundlich and Langmuir adsorption models and the kinetic studies were conducted to determine the order of the adsorption process. The adsorption capacity of MB and the maximum % removal of MB by TIWAC were found to be 233.51 mg g⁻¹ and 77.8% respectively at the optimized adsorption conditions (TIWAC dosage= 0.001 g, MB concentration= 300 mg/L, agitation time=6 hrs) at pH 7. Isotherm data were satisfied Langmuir model than Freundlich model and kinetic data were best fitted with the pseudo first order model. Most importantly, the Langmuir constant, the maximum adsorption capacity value (q_0); obtained for adsorption of MB onto TIWAC was 303.3 mg g⁻¹, which is significantly greater than that of the adsorption of MB by various other bio-sorbents reported in the literature. Bench-scale fixed-bed column experiments were also carried out at various flow rates to study the practical usability of the adsorbent and it was found out that the breakthrough time was decreased with increasing flow rate. The results of this study indicate that TIWAC is an effective and environmental friendly adsorbent for removal of dye from wastewater.

Keywords: Tea waste activated carbon, Methylene Blue, Sorption, Isotherm studies.

Introduction

Color is an important aspect in human world. As synthetic dyes have many advantages due to its low manufacturing cost, intense colors, and better resistance to environmental factors over natural dyes, synthetic dyes have used in various industrial applications including textile, printing, rubber, leather, food, drug, cosmetics, etc¹.

The effluent released by those factories contains a significant percentage of dye molecules. It is estimated that total world dye production is about 800,000 tons/year of which 50% are textile dyes². There are more than 100,000 commercially available dyes and about 10-15% of the used dyes are discharged into the environment through wastes³. These dyes are harmful to the environment, as they are resistant to bio-degradation processes and carcinogenic⁴. Colored effluents discharge by various industries can cause severe effects on water resources, soil fertility, and aquatic biota. Most of the countries have environmental regulations on decolorizing the dye-containing effluents prior to discharge.

Currently, various chemical and physical practices are used to treat dye containing wastewaters⁵. However, many of these

methods are not cost effective and cannot be used effectively to remove different types of dyes. Due to the several advantages compared to the conventional dye removal methods, adsorption methods using activated carbons are widely used to eliminate or mitigate dye compounds from wastewaters. Even though commercial activated carbon is widely used to remove dye by adsorption, its high production cost has encouraged scientists to find more cost-effective alternatives. Among the alternatives for commercial activated carbon, activated carbon derived from agricultural waste has received the attention as a promising dye adsorbents due to its natural abundance, renewability and biodegradability⁶.

In this research, tea factory waste was used to prepare TIWAC and studied its dye adsorption potential. Tea is one of the major plantation crops in Sri Lanka and spreads in both low country and up country⁷. During the tea production procedure overgrown shoots, and petiole are finally formed in to tea factory waste. For instance, during the process of black tea production, 3-5% of waste tea is generated⁸. Currently there are no effective methods to manage waste tea in Sri Lanka.

Therefore, in this study, the possibility of using tea industry waste activated carbon (TIWAC) as a low-cost sorbent for

methylene blue (MB) removal (Figure-1) from wastewater was investigated and which can be considered as economically and environmentally important application. Further, the isotherm studies and kinetic studies were performed to understand the sorption process of MB by TIWAC.

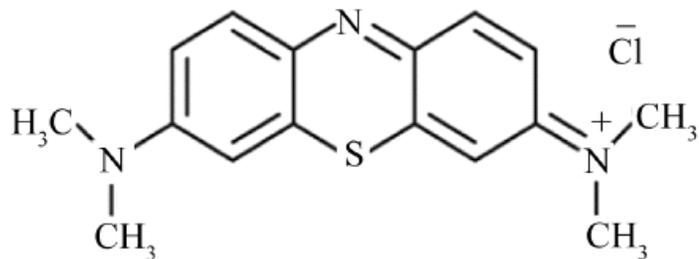


Figure-1: Chemical structure of methylene blue²⁹.

Materials and methods

Preparation of TIWAC: The tea industry waste collected from a tea plant in Nuwaraeliya, Sri Lanka, was washed with distilled water and heated in an oven until it was free from moisture. The dried tea waste was impregnated in H₃PO₄ acid solution (85%) and the resulting slurry was oven dried at 110^oC. Carbonization of impregnated tea waste was done using two methods. In the first method dried sample was subjected to microwave treatment (700 W, 2.45 GHz) for 15 min. using a household type microwave furnace (LG, MS-194AS, 800 W). In the second method, the dried sample was carbonized in muffle furnace (Griffin electric furnace 67005) at 400^oC for 1 hour. Then the cooled carbonized samples were washed with distilled water until pH of water becomes neutral. Then the activated carbon was dried for 12 h at 110^oC.

Characterization of TIWAC: Yield of activated carbon: The equation (1) was used to calculate the activated carbon yield,

$$X (\%) = m/m_0 \times 100 \quad (1)$$

Where, X = activated carbon yield (%), m = mass (g) of activated carbon and m₀ = mass of the raw sample (g).

Bulk density: A (25 mL) glass cylinder was filled with powdered activated carbon up to 10 mL mark and dried in an oven at 80^oC for 12 hrs and tapped for 2 minutes to compressed the carbon. The equation (2) was used to calculate the bulk density of activated carbon and presented as g mL⁻¹.

$$\text{Bulk density} = \frac{\text{Weight of dry material (g)}}{\text{Volume of packed dry material (mL)}} \quad (2)$$

Attrition: One gram of TIWAC was placed in an Erlenmeyer flask containing 100 mL of acetate buffer [0.2 M sodium acetate and 0.2 M acetic acid (pH 4.8)]. The solution was stirred for 24 hours at 29±0.5 ^oC on magnetic stirrer and filtered. After filtration, the remaining carbon was washed with 250 mL of de-ionized water and then transferred to a pre-weighed silica

crucible, dried at 90 ^oC in an oven for 5 hrs and cooled in a desiccator and weighed. The equation (3) was used to calculate the percentage of attrition⁹.

$$\text{Attrition} = \frac{\text{Weight of carbon retained (g)}}{\text{Initial sample weight (g)}} \times 100 \quad (3)$$

Fourier Transformation Infrared (FTIR) Spectroscopy: FTIR spectra of, TIWAC and MB adsorbed TIWAC were obtained from a Bruker Alpha-T spectrometer using Attenuated Total Reflection (ATR) method. The FTIR spectrum obtained for TIWAC was compared with the FTIR spectrum of MB bound TIWAC in order to compare the specific structural changes occurred during MB adsorption.

Morphology studies: The surface morphology of raw tea waste and TIWAC were examined by Scanning Electron Microscopy (SEM). A scanning electron microscope (VEGA3 SEM, TESCAN) with a tungsten heated filament was used to scan each gold-palladium-coated specimen in turn. SEM observation was taken by changing the magnification to identify the surface porosity of activated carbon and raw tea waste.

Preparation of synthetic wastewater: The simulated wastewater samples were prepared by using MB blue (Merck specialties, λ_{max} = 665 nm). First a stock solution of MB (1000 ppm) was prepared in deionized water. Successive dilutions were made to obtain the experimental solutions with the desired concentrations.

Commercial granular activated carbon (GAC): GAC (particle size=300 mesh; surface area= 800 m²/g; moisture=3% (maximum); ash content=2.5% (maximum); acid soluble=2.5% (maximum); water-soluble=1.5% (maximum), pH value=6.5-7.5) derived from coconut shell supplied by E. Merck, India was used without further grinding and sieving for the study.

Batch adsorption studies: A series of batch experiments were performed to investigate the factors affecting the sorption of MB onto TIWAC. The effect of initial TIWAC dose on MB adsorption was examined by agitating the TIWAC (0.001 g, 0.005 g, 0.010 g, 0.015 g, 0.020 g and 0.025 g) with 10 mL of dye solution (300 mg/L) at neutral pH and room temperature (30 ± 2 ^oC) in a shaker for six hours. After the agitation period, dye solutions were separated from the adsorbents by gravity filtration and the absorbance of filtrates were measured at 665.0 nm using a UV-Vis spectrophotometer (Orion AquaMate 8000). Initial pH of dye solutions was adjusted to pH values of 3, 5, 7, 10 and 13 using 0.1 M HCl and NaOH solutions as required to investigate the effect of pH of the MB solution on dye adsorption onto TIWAC. The effect of initial MB concentration was studied by varying the MB concentrations (100 mg/L, 200 mg/L, 300 mg/L, 400 mg/L, and 500 mg/L) and the effect of agitation time was also determined by shaking the solutions for 1 hr, 2 hrs, 6 hrs, 12 hrs and 24 hrs. The adsorption mechanism of MB adsorption onto TIWAC was tested by using Langmuir and Freundlich isotherms.

Further, fixed-bed column studies were performed to study the practical applicability of use of the adsorbent for dye removal from wastewater. A column (height: 6.0 cm, inner diameter: 1.0 cm) packed with a fixed-bed of TIWAC particles (4.9 g) was used. TIWAC particles were first wetted for 24 hrs in distilled water. Then the column was packed with the slurry of the adsorbent and allowed to settle for 24 hrs. and which was eluted with a MB solution (500 mg/L, 500 mL) at a constant flow rate (2 mL/min and 10 mL/min) using a reservoir. The concentration of the effluent stream was monitored by periodic sampling and the data were used to obtain the breakthrough curve.

Also, an experiment was carried out to compare the performance of fixed bed column packed with TIWAC and commercially available GAC separately for the removal of MB. Equation (4) was used to calculate the MB adsorption capacity (q).

$$q \text{ (mg/g)} = \frac{\text{adsorbed weight of MB onto TIWAC (mg)}}{\text{weight of TIWAC used (g)}} \quad (4)$$

Results and discussion

Characterization of TIWAC: TIWAC was prepared by two methods; by microwave method and muffle furnace method.

The yield %, bulk density and attrition of the TIWAC: The yield %, bulk density and attrition of the prepared TIWAC by two methods are tabulated in Table-1.

Table-1: Yield %, bulk density and attrition of TIWAC.

Raw material	Parameter		
	Yield %	Bulk density (g/mL)	Attrition %
TIWAC by microwave method	46.34±1.02	0.36±0.04	71±1.21
TIWAC by muffle furnace method	40.50±1.34	0.34±0.02	69±1.37

As can be seen from Table-1, a higher yield% of TIWAC was obtained with the microwave method. This should be attributed to the lower temperature used in the chemical activation at microwave method, which reduced the amount of compounds liberated by volatilization. In addition, at low temperatures, the development of a cross-linked structure and the pyrolytic decomposition of the precursor was facilitated by phosphoric acid¹⁰. Compared to microwave method muffle furnace method uses high temperatures (~ 400°C).

Hardness or attrition is a measure of the mechanical strength of an adsorbent. Attrition provides an indication regarding adsorbent's (activated carbon's) relative loss during the transportation, handling and regeneration¹¹. Compared to muffle furnace method, TIWAC prepared using microwave method had a higher attrition. This means that the loss of TIWAC in preparation is less when use microwave method.

Bulk density of TIWAC was also higher when used microwave method. Higher the bulk density lowers the porosity of the TIWAC¹². Therefore, TIWAC from microwave method may have lower porosity compared to TIWAC obtained from muffle furnace method. Due to the higher yield% and higher attrition, all the batch experiments and fixed bed column experiments were conducted using TIWAC prepared from microwave method.

FTIR analysis of TIWAC: FTIR of TIWAC and MB adsorbed TIWAC are depicted in Figure-2. In spectrum of TIWAC (Figure-2a), the broad band at 3116 cm⁻¹ was observed and which may correspond to the O-H stretching vibration of alcohols, phenols and carboxylic acids. It may also indicate the presence of moisture. The peak at 2162 cm⁻¹ is due to the alkenyl C=C stretch. The very weak peak at 1557 cm⁻¹ corresponds to C=C stretching of the aromatic rings. This band may also be attributed to C=O groups conjugated with aromatic rings, secondary amide and N-H bending with C-N vibrations. The peak at 985 cm⁻¹ is associated with stretching vibration of C-C or C-H groups or C=O group¹³. The peaks at 1061 cm⁻¹, 587 cm⁻¹ and 556 cm⁻¹ may be due to C-Br aromatic stretch, C-Cl aliphatic stretch or C-Br aromatic stretch respectively¹⁴. As the mechanism of the adsorption process may include hydrogen bonding formation, and/or π - π interaction between the π electrons of graphene layers and those of MB present in the TIWAC surface¹² the presence of such functional groups (indicated above) in the TIWAC can be considered to be connected with the adsorption mechanism.

In spectrum of MB adsorbed TIWAC (Figure-2b) all the above-described IR peaks are present in slightly lower frequency values except the disappearance of the peak at 985 cm⁻¹. After adsorption, significant shifts were observed for the bands correspond to OH, C=O and C=C stretching indicating that MB molecules may mostly bind at -OH, C=O and C=C groups. In addition, the IR spectrum of MB adsorbed TIWAC showed some additional peaks, which were not present in the IR spectrum of TIWAC. The very weak peak at about 1150 cm⁻¹ may correspond to the stretching vibration of C-O group in alcohol, phenol, ether, or ester. It could also be attributed to carboxylic groups, including -CO₃ group and the phenolic -OH group¹⁵. The peak at 385 cm⁻¹ may be attributed to the N-H stretching vibrations. These additional peaks may be attributed to the adsorbed MB molecule¹⁵. This confirms the presence of interactions between TIWAC and MB as MB binds to the binding sites in TIWAC, normal vibration scheme is affected due to the formation of new MB-TIWAC bonds.

SEM: The surface morphology of the raw tea waste and TIWAC samples was analyzed using SEM. The SEM images of TIWAC and the raw tea waste under different magnifications were depicted in Figure-3. As depicted in Figure-3(b), (c) and (d), it is clear that, activation process has produced extensive external surface with more micro pores (diameter of 10 μ m to 20 μ m) on the surface of the TIWAC where as raw tea waste

has an even surface with low porosity (Figure-3a). These pores were generated due to the evaporation of the volatile organic compounds during carbonization, leaving empty spaces.

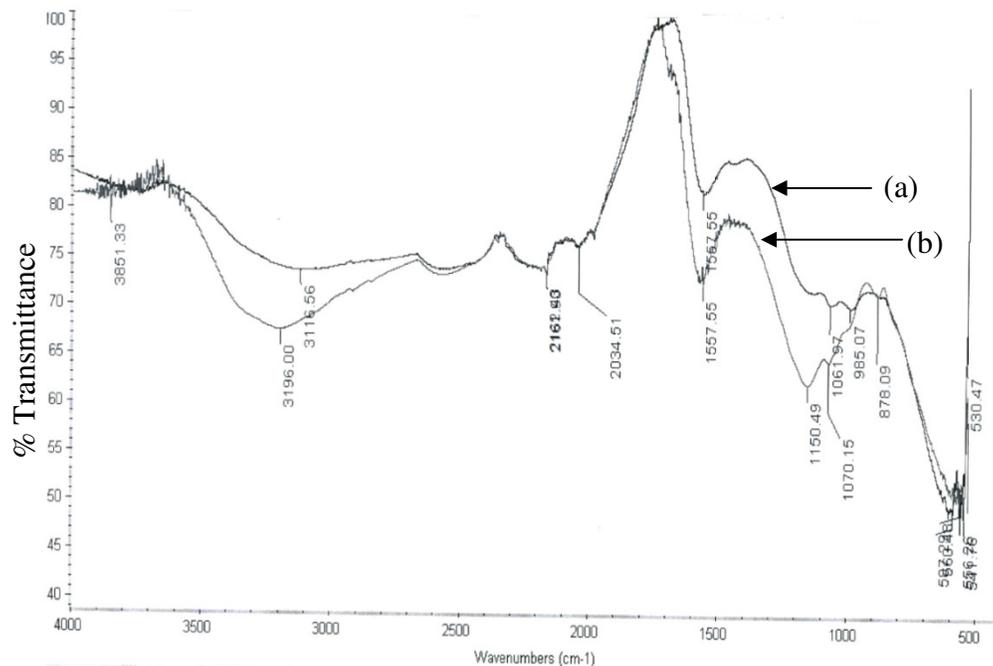


Figure-2: FTIR spectra of (a) TIWAC (b) MB adsorbed TIWAC.

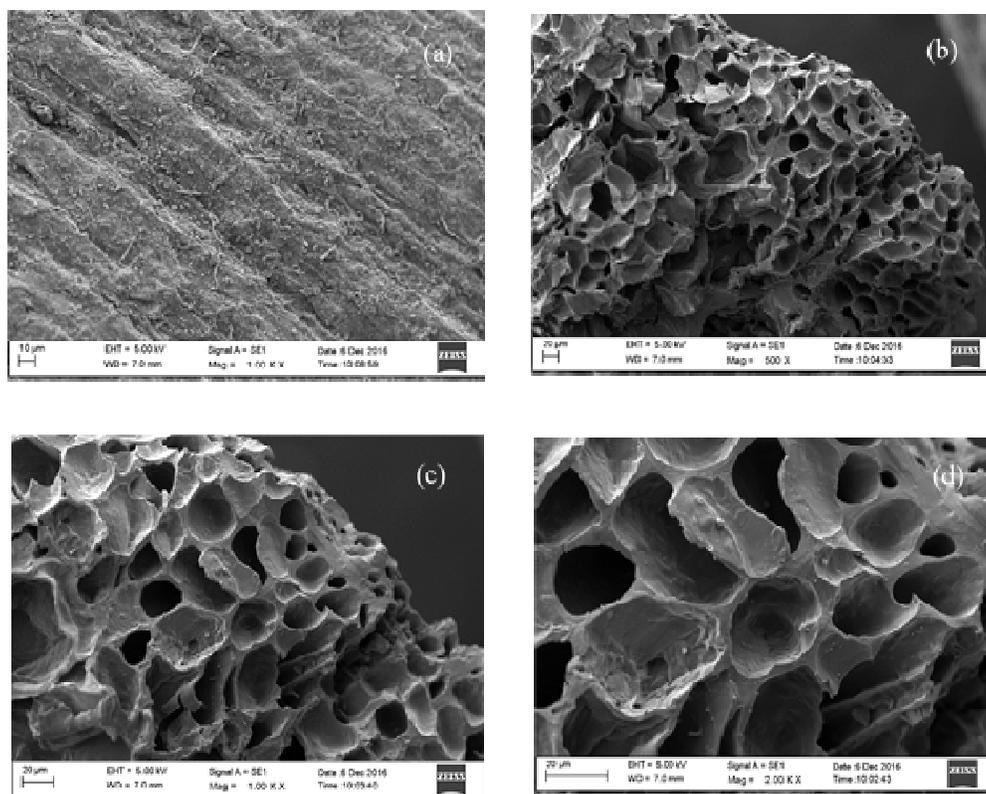


Figure-3: SEM images of raw tea waste and TIWAC 1000× (a) raw tea waste 1000× (b) TIWAC 500× (c) TIWAC 1000× (d) TIWAC 2000×

Batch adsorption tests: Effect of initial TIWAC dosage: A batch experiment was conducted by varying the TIWAC dose from 0.001 g to 0.025 g and keeping the initial concentration of MB constant (300 mg/L) in order to investigate the effect of adsorbent dosage on adsorption of MB onto TIWAC and the results are depicted in Figure-4. When the dosage of the adsorbent was increased, MB adsorption capacity of TIWAC was decreased and this may be attributed to two reasons. At a constant MB concentration, an increase in dosage of TIWAC may lead to increased number of unsaturated adsorption sites. Secondly, at high adsorbent dosage, the aggregation of adsorbents would lead to a decrease in surface area of the adsorbent¹⁶. TIWAC dosage (0.001 g) which gave the optimum adsorption capacity was used for other batch adsorption studies, kinetic studies and isotherm studies.

Effect of initial MB concentration: As shown in Figure-5, when increasing the initial MB concentration, adsorption capacity has increased to a maximum value (203.32±43 mg/g)

and then upon further increasing, adsorption capacity becomes constant. At low concentration, all MB molecules may in contact with adsorbent sites but at high concentration of MB, all adsorbate molecules will not contact with the active adsorbent sites due to the saturation of the active sites. MB concentration (300 mg/L) which gave optimum adsorption capacity was used for further adsorption studies, kinetic studies and isotherm studies.

Effect of pH of the solution: The extent of ionization of the adsorbate and the adsorbent's surface properties are greatly influenced by the pH of the medium¹⁷. A study on the effect of pH on adsorption of MB onto TIWAC was conducted at pH range of 3-13 for 6 h agitation period using a MB concentration of 300 mg/L. The plot of MB adsorption capacity of TIWAC vs solution pH is depicted in Figure-6. According to the experimental results the MB adsorption capacity of TIWAC was increased from pH 3-13.

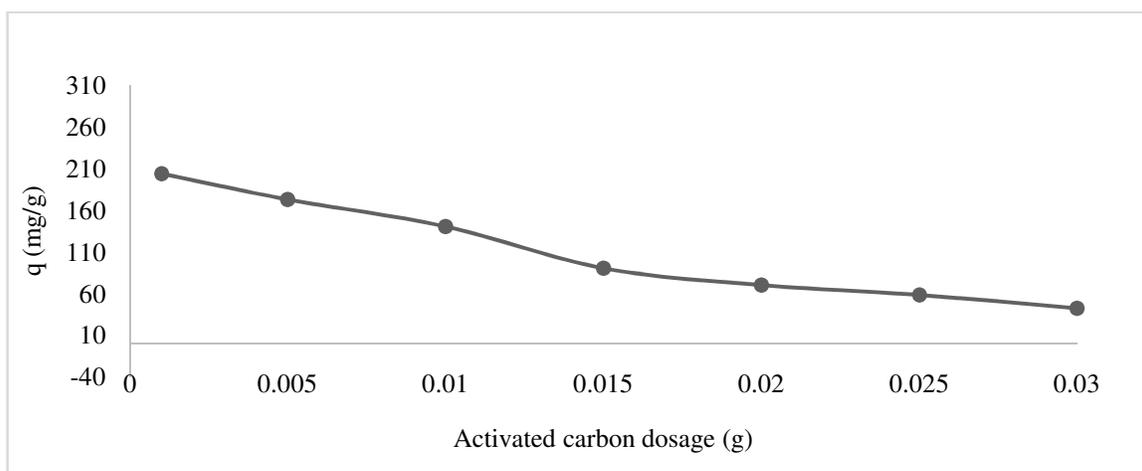


Figure-4: The graph of MB adsorption capacity of TIWAC vs TIWAC dosage. (MB 300 mg/L, pH=7, agitation period =6 hours, temperature 30 ±2 °C).

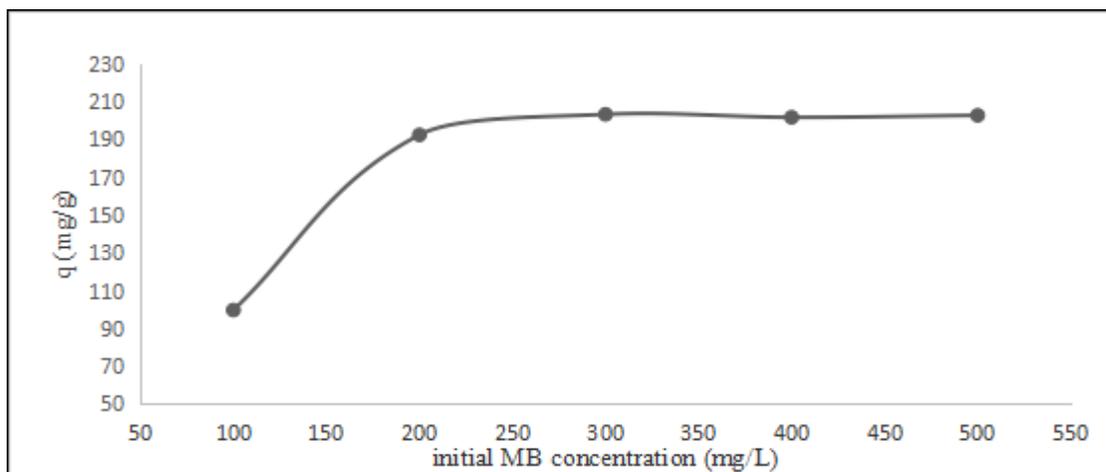


Figure-5: The graph of MB adsorption capacity of TIWAC vs. MB concentration. (TIWAC= 0.001 g, pH=7, agitation period = 6 hours, 30 ±2 °C).

The MB adsorption capacity is governed by the surface charge of the adsorbent. In water, as MB is a basic dye, it produces anions (CH^-) and cations (C^+). In alkaline medium, as the negative charge density on the TIWAC surface increases the adsorption of MB onto TIWAC is facilitated. Furthermore, in the acidic medium, the basic dye becomes protonated and therefore at low pH values sorption of MB by TIWAC is decreased¹⁸. Even though maximum adsorption of MB on to TIWAC occurs at pH 13, other sorption studies, isotherm and kinetic studies were conducted at neural pH as pH of the water bodies ranges between 6-8.

Effect of agitation time: The variation in MB adsorption capacity of TIWAC with the shaking time is depicted in Figure-7. The MB adsorption capacity of TIWAC was increased from 156.12 ± 0.12 mg/g to 247.56 ± 0.08 mg/g and from 113.12 ± 0.03 mg/g to 157.34 ± 0.15 mg/g at initial MB concentration of 300 mg/L and 200 mg/L respectively, when shaking time was increased from 1h to 6 hrs. When increasing the agitation time, the adsorption capacity of MB was increased and reached to a constant value as the system reached equilibrium due to the saturation of the adsorbent. For isotherm and kinetic studies agitation time of 8 hours and initial MB concentration 300 mg/L were selected based on the results of this experiment.

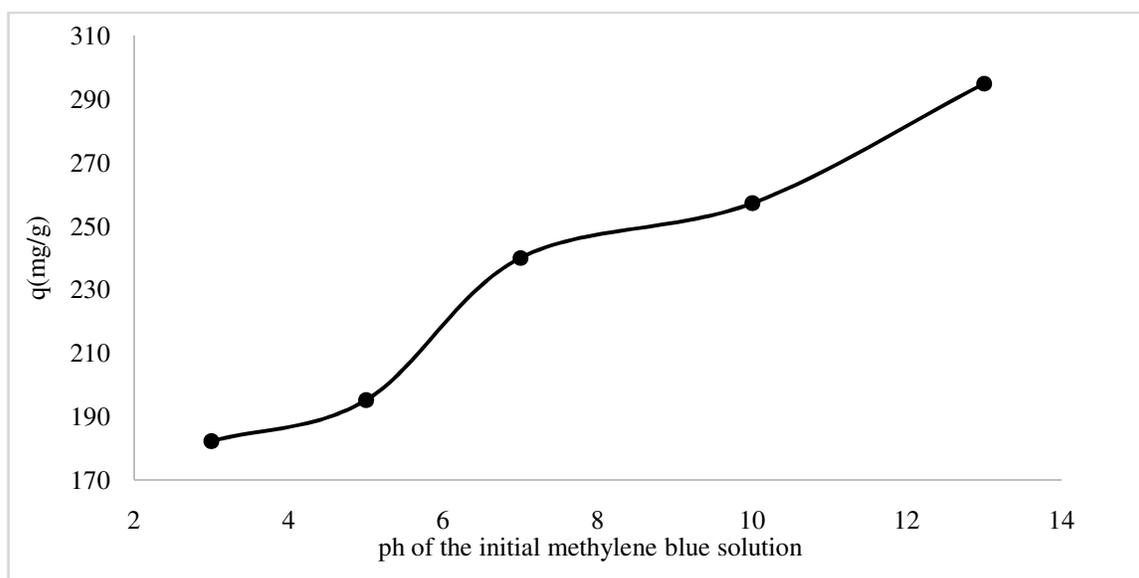


Figure-6: The graph of MB adsorption capacity of TIWAC vs pH. (TIWAC= 0.001 g, MB 300 mg/L, agitation period – 6 hours, 30 ± 2 °C).

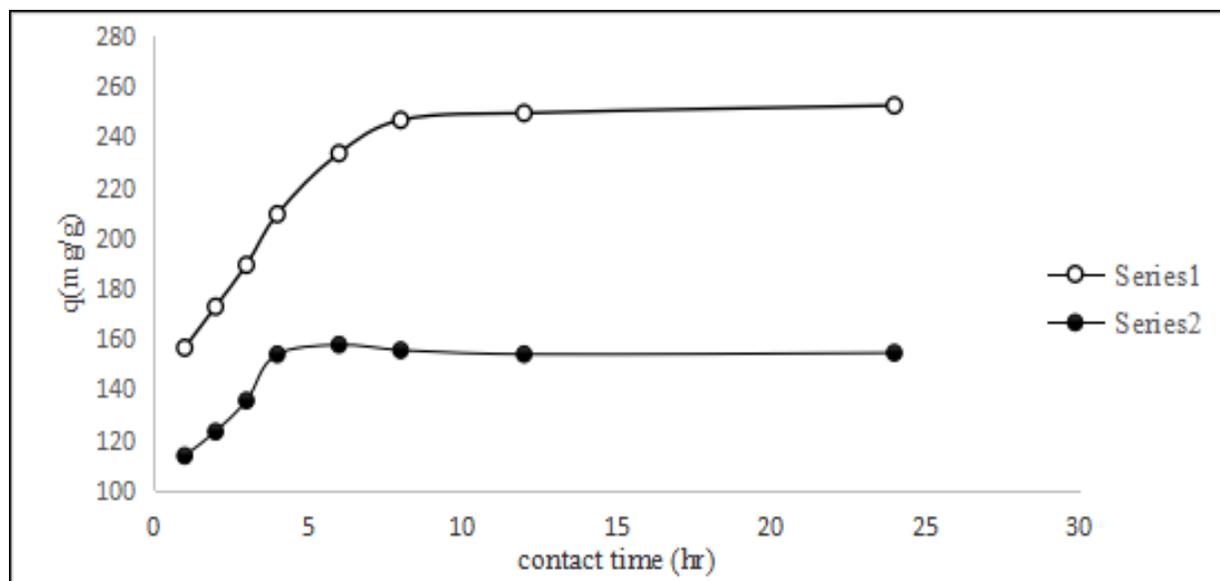


Figure-7: The graph of MB adsorption capacity of TIWAC vs agitation time. (TIWAC= 0.001 g, pH 7, 30 ± 2 °C at MB concentrations of 200 mg/L [series 2] and 300 mg/L [series 1]).

Adsorption isotherm studies: Langmuir and Freundlich isotherms were used to mathematically modeled the equilibrium data. Langmuir model is assumed that the maximum adsorption is corresponded to a saturated monolayer of adsorbate molecules on adsorbent surface¹⁹ and the linear form of the Langmuir isotherm equation is given as the equation (5),

$$\frac{1}{q_e} = \frac{1}{bq_0C} + \frac{1}{q_0} \quad (5)$$

Where, q_e is the amount of adsorbate adsorbed per gram of adsorbent at equilibrium, C is the equilibrium concentration of adsorbate, b is adsorption coefficient and q_0 is the amount of adsorbate adsorbed per unit weight of adsorbent corresponding to complete coverage of available sites¹⁹.

The Langmuir parameters, q_0 and b have been estimated from the intercept and the slope of the straight line of plot of $1/q_e$ versus $1/C$ respectively (Figure-8) and are presented in Table-3. The experimental data for MB adsorption on to TIWAC have been well fitted to Langmuir isotherm with R^2 value of 0.9824, indicating that the formation of monolayers of MB on homogeneous adsorbent surface²⁰. Comparable observations were stated for the different dye adsorption by activated carbon²¹⁻²³.

The maximum adsorption capacity (q_0), of MB on to different agricultural based adsorbents stated in the literature are tabulated in Table-2. According to the results, the q_0 obtained for adsorption of MB onto TIWAC was 303.3 mg/g and which is significantly a higher value compared to q_0 values for sorption of MB onto numerous bio-sorbents stated in previous studies. Therefore, the results of the study indicate that TIWAC could be used as an efficient MB dye removal agent in aqueous solutions including wastewater.

Table-2: Comparison of q_0 of TIWAC with some adsorbents reported in literature for MB adsorption.

Adsorbent	q_0 (mg g ⁻¹)
TIWAC (this work)	303.3
Coconut shell activated carbon ²⁷	277.8
Rice husk activated carbon ²²	343.5
Bamboo dust activated carbon ²³	143.20
Jute fiber activated carbon ²⁸	255.64
Almond shell-activated carbon ²³	1.33
Walnut shell-activated carbon ²³	3.53
NaOH-treated raw kaolin ²³	16.34

Freundlich isotherm is applicable to adsorption processes that occur on heterogenous adsorbents surfaces and associated with physisorption and it is normally used with low concentrations of the adsorbate²⁴. Equation (6) represents the linear form of the Freundlich isotherm;

$$\log q_e = n \log C + \log k \quad (6)$$

Freundlich's constants, n (0.371) and k (97.84) have been estimated from the slopes and intercepts of the straight lines of plot of (Figure-9) respectively and are tabulated in Table-3. Experimental data fits with Freundlich isotherm with R^2 value of 0.9158 which is lower than Langmuir model R^2 value (0.9824). Thus, R^2 values suggested that the Langmuir model is more applicable to represent the MB adsorption data than the Freundlich model (Table-3).

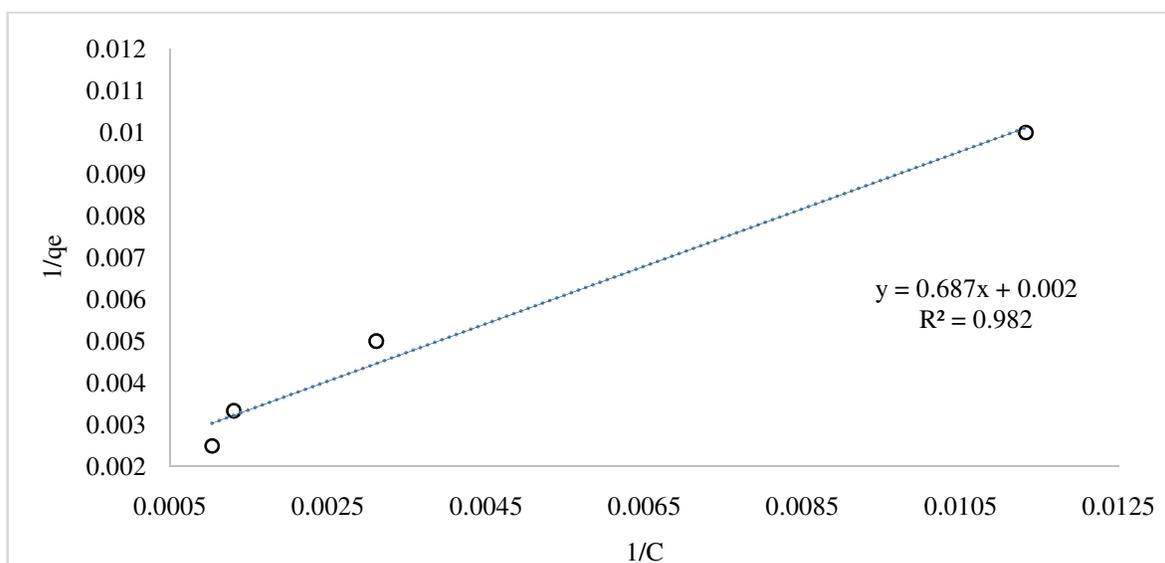


Figure-8: Linear plot of the Langmuir isotherm for MB adsorption on to TIWAC. (TIWAC= 0.001 g, MB 300 mg/L, agitation time 8 hr, pH 7, 30 ±2 °C).

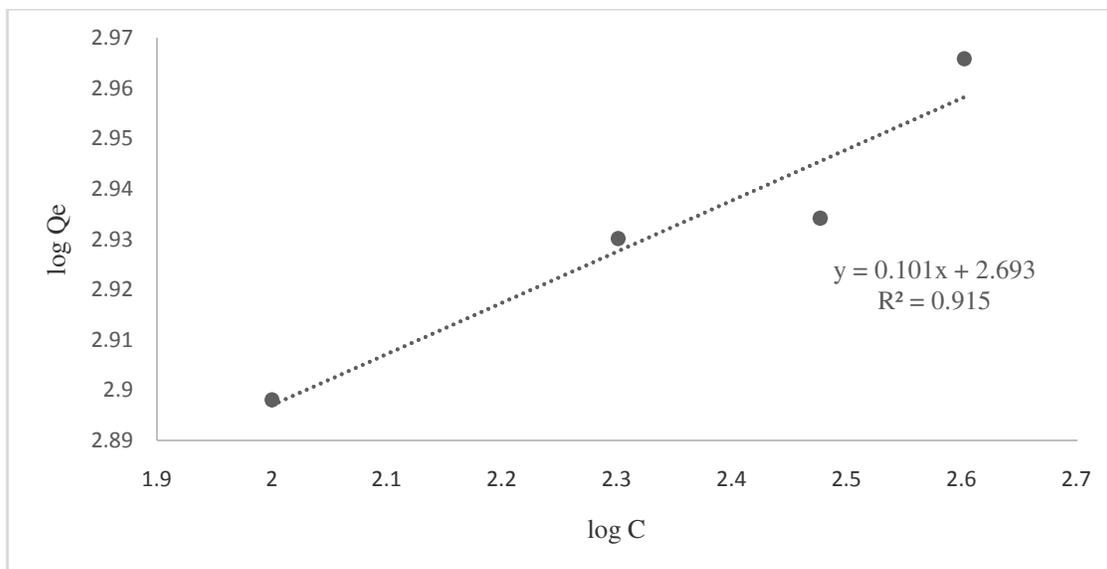


Figure-9: Linear plot of the Freundlich isotherm for MB adsorption to TIWAC. (TIWAC= 0.001 g, MB 300 mg/L, agitation time 8 hr, pH -7, 30 ±2 °C).

According to the values of the correlation coefficient (R^2) it can be concluded that the Langmuir isotherm has been best fitted than Freundlich model for MB adsorption onto TIWAC (Table- 3).

Table-3: Constants of Langmuir and Freundlich isotherms for MB adsorption onto TIWAC (TIWAC= 0.001 g, MB 300 mg/L, agitation time 8 hr, pH =7, 30 ±2 °C).

Langmuir isotherm			Freundlich isotherm		
q_0 (mg/g)	b (L/mg)	R^2	k	n	R^2
303.03	0.032	0.9824	97.84	0.371	0.9158

Adsorption kinetic studies: Pseudo-first-order and pseudo-second order kinetic models were tested to understand the adsorption mechanism of MB onto TIWAC. The equation for the pseudo-first-order kinetic model is given as in equation (7)²⁵,

$$\log(q_e - q) = \log q_e - k_1/2.303 t \quad (7)$$

Where q_e is the amount of dye adsorbed (mg/g) at equilibrium and q is the amount of dye adsorbed (mg/g) at any time, t (min). k_1 is the equilibrium rate constant of pseudo-first-order sorption (min^{-1})²⁵.

The plots of $\log (q_e - q)$ versus t of 200 mg/L and 300 mg/L of MB samples (Figure-10) were used to calculate the rate constant (k_1), adsorption capacity at the equilibrium (q_e), and the correlation coefficient (R^2). The pseudo-second-order kinetic model equation is given as in equation (8),

$$\frac{1}{q} = \frac{1}{q_e} + \frac{1}{k_2 q_e^2 t} \quad (8)$$

Where, k_2 refers to the rate constant at the equilibrium for the pseudo second-order adsorption process. The plot of $1/q$ vs $1/t$ is shown in Figure-11.

According to the graphs, the values of R^2 for the pseudo-first-order kinetic model was significantly higher than the R^2 values for the pseudo-second order model (Figure-10 and Figure-11) for the two concentrations studied; 200 mg/L and 300 mg/L of initial MB concentrations. This indicates that the adsorption kinetics of MB adsorption onto TIWAC are satisfactorily described by pseudo-first order kinetic model.

Fixed bed column experiments: In order to study the practical usability of the adsorbent TIWAC in industrial applications of wastewater treatment processes, as a preliminary step, bench-scale fixed bed column experiments were conducted. The performance of fixed-bed columns are generally described by breakthrough curves.

A column packed with TIWAC (6.0 cm) was eluted with MB solution (500 mg/g, 500 mL) at flow rates of 10 mL/min and 2 mL/min. As the MB solution enters the column packed with TIWAC, the adsorbate get adsorbed filling some active adsorption sites at the first few layers of the adsorbent. When the adsorbent near the entrance get saturated with the adsorbate, the adsorbate penetrates further in to the column before all the adsorbate removed. Therefore, as the time goes on the active adsorption sites shift down through the column. The break through point occurs when the adsorbate's concentration leaving the column is similar to the initial concentration of the adsorbate. The length of unused bed (LUB) is given by equation (9),

$$LUB = \frac{z}{T_s} (T_s - T_b) \quad (9)$$

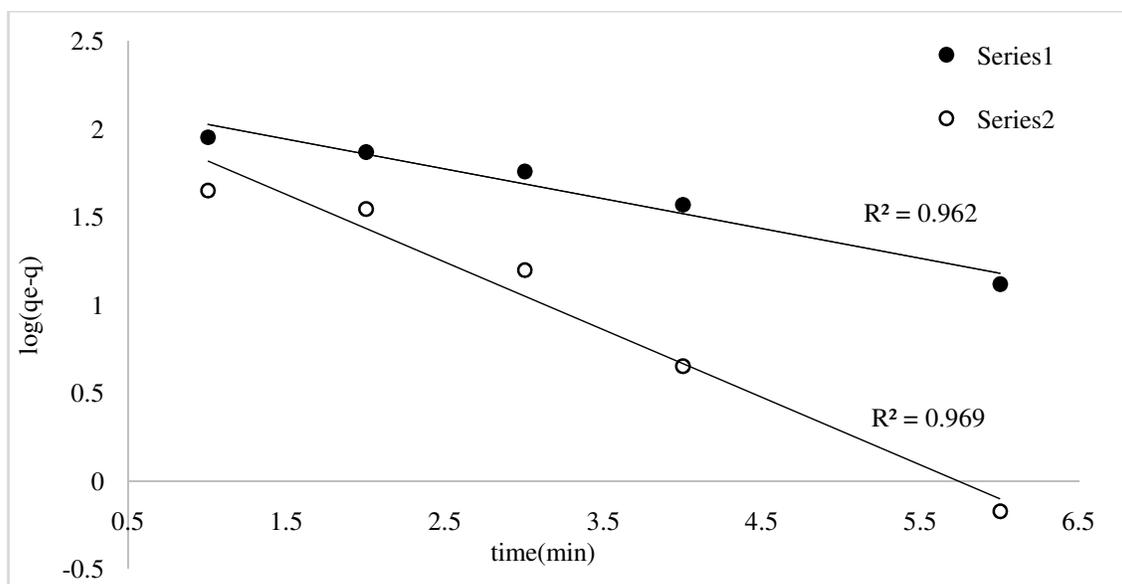


Figure-10: Pseudo first order kinetics of MB adsorption on to TIWAC. (TIWAC=0.001 g, MB 300 mg/L and 200 mg/L, agitation time 8 hr, pH 7, 30 ± 2 °C).

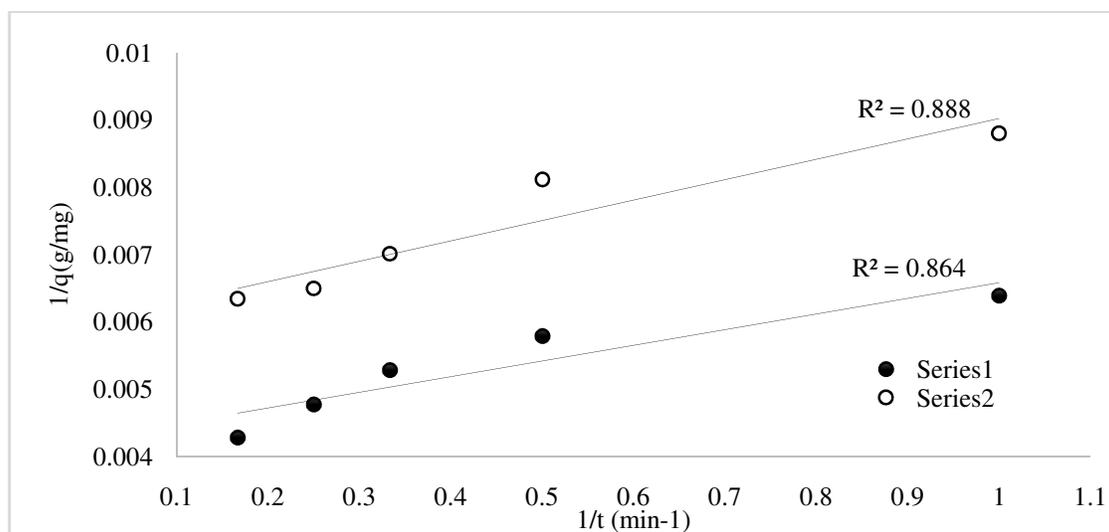


Figure-11: Pseudo- second order kinetics of MB adsorption on to TIWAC. (TIWAC=0.001 g, MB 300 mg/L, agitation time 8 hr, pH 7, 30 ± 2 °C).

The bed capacity (BC) is given by equation (10),

$$BC = G (C_0 - C^*) T_s \quad (10)$$

The adsorption capacity of adsorbate at equilibrium is given by equation (11),

$$q_{eq} = \frac{(C_0 - C^*)V}{W} \quad (11)$$

Where, Z is the bed height, C* is the concentration of the adsorbate leaving the bed initially, T_s is the time required for full bed exhaustion, T_b is the breakthrough time (the point where outlet concentration starts to increase), G is the solution rate

(L/min), C₀ is the inlet adsorbate concentration, W is the mass of the dry adsorbent and V is the volume of the solution.

According to the breakthrough curve (Figure-12), the T_b was achieved after 80 minutes when the elution rate was 2 mL/min and T_b was 50 minutes when the elution rate was 10 mL/min. (Table-4). The results revealed that the earlier breakthrough time was reached when the flow rate was increased. Similarly, the reduction of q_e was observed as the flow rate was increased (Table-4). The highest bed adsorption capacity was obtained (65.75 mg/g) at the flow rate of 2 mL/min under the operational conditions. The enhancement of MB uptake at lower flow rates is probably due to the availability of sufficient contact time for adsorbate to interact with the adsorbent TIWAC.

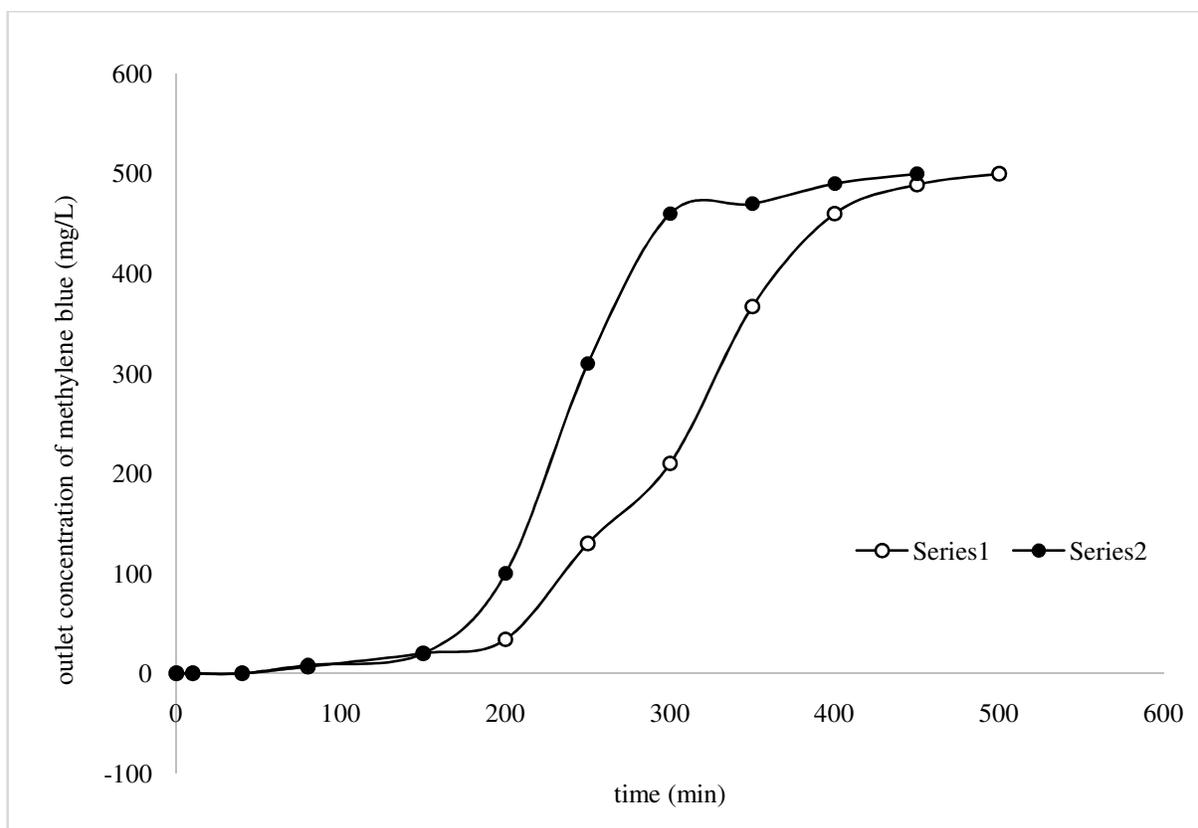


Figure-12: Break through curve for adsorption of MB (500 mg/L, 500 mL, bed height 6.0 cm, TIWAC dosage 1.2 g, flow rate-2mL/min [series 1], 10 mL/min [series 2]).

Compared to the maximum adsorption capacity obtained from isotherm experiments ($q_0 = 303.3$ mg/g) the adsorption capacities (q_e) of columns are lower. The main reason for the lowered q_e value would be due to the poor interaction between the adsorbate molecules and adsorbents in columns compared to that in the batch experiments. In addition, liquid channeling in columns may also result in poor adsorbent-dye interaction and less residence time²⁶.

The results further revealed that the LUB values were less than 85% for both elution rates. The low values for bed capacity (BC) and higher LUB might be due to the low column height and higher elution rates used in this experiment. It is also important to note that other factors such as adsorbate concentration, flow rate, adsorbent dosage used and particle size of the adsorbent may also affect the performance of fixed bed columns. By suitable optimization of these parameters, more effective fixed bed column can be obtained. Further, it can be concluded that the performance of the fixed bed column could be enhanced by reducing the flow rate.

Comparison of TIWAC with commercially available granular AC for the adsorption of MB: A bench-scale fixed-bed column experiment was conducted to compare the performance of a column packed with TIWAC with a column filled with commercially available granular activated carbon for

MB removal at flow rate 10 mL/min. The break through curves for MB adsorption onto two adsorbents are shown in the Figure-13.

Table-4: Results of MB adsorption in column with 6.0 cm height, TIWAC-1.2 g, 10 mL/min and 2 mL/min flow rate and MB (500 mg/L, 500 ml).

T_s	T_b	Z (cm)	G (ml/min)	LUB (cm)	BC (mg)	q_e (mg/g)
450	80	6	2	4.93	78.91	65.75
350	50	6	10	5.14	49.16	40.90

When looking at the shapes of the break through curves, the shape of the commercial GAC curve was quite similar to the ideal shape of the break through curve. Also, it was evident that, T_b was achieved after 50 minutes when the columns were packed with TIWAC and commercial activated carbon and column packed with TIWAC have a very closer LUB value to the commercial activated carbon (Table-5). Therefore, it can be concluded that TIWAC can be used for commercial applications for wastewater purification by further optimizing the bed parameters including adsorbent dosage, flow rate and the height of the bed.

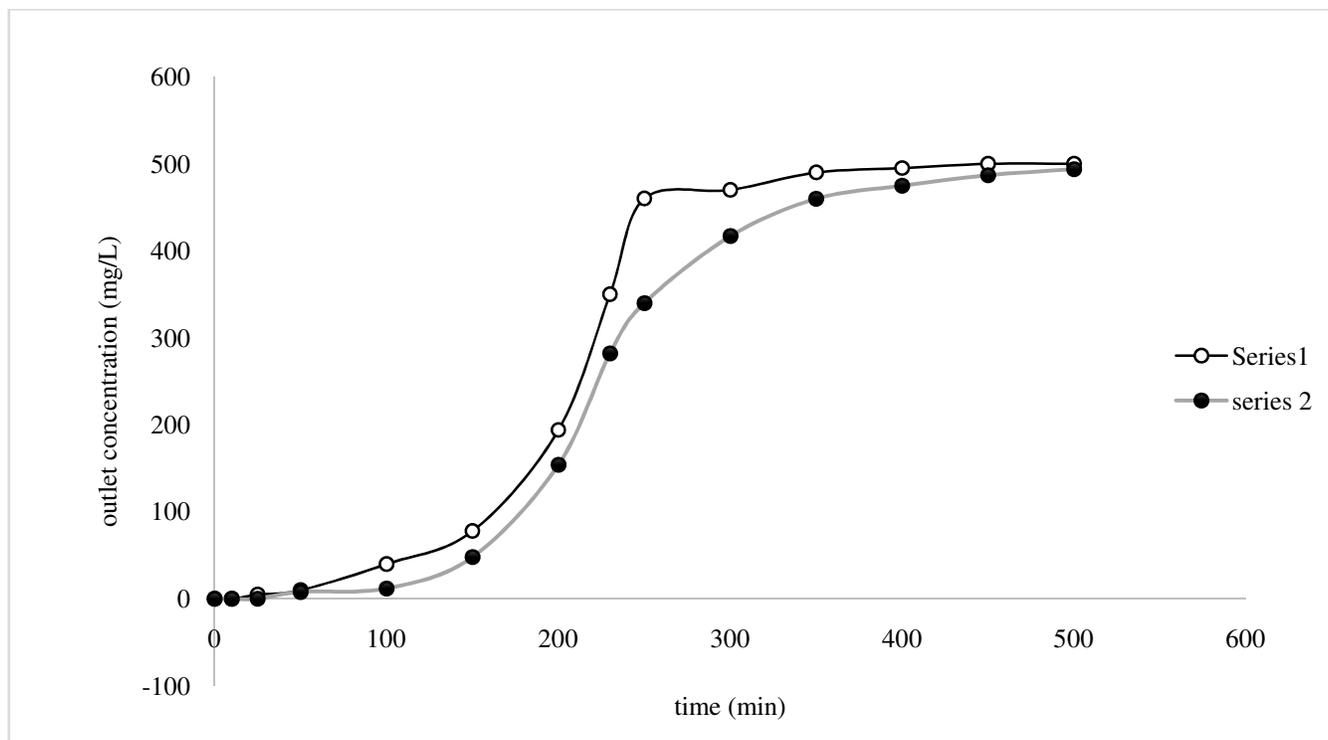


Figure-13: Break through curve for adsorption of MB on to TIWAC [series 1] and commercial activated carbon [series 2] (MB - 500 mg/L, 500 mL, bed height 6.0 cm, TIWAC dosage 1.2 g.).

Table-5: Results on adsorption of MB in fixed bed column with 6.0 cm height, 10 mL/min flow rate.

	T _s (min)	T _b (min)	Z (cm)	G (ml/min)	LUB (cm)	BC (mg)
TIWAC	350	50	6.0	10	5.14	49.16
Commercial granular activated carbon	450	50	6.0	10	5.33	24.25

Conclusion

The results revealed that the activated carbon made using tea factory waste could be used as a low-cost, efficient bio-adsorbent for removal of MB from aqueous solutions. The adsorbent dose, agitation time, pH of the solution and initial dye concentration affect the MB adsorption onto TIWAC. It has been observed that the experimental data fitted more accurately to the Langmuir model for the selected concentrations of MB. The experimental data fit well with the pseudo-first-order kinetic model.

According to the results obtained from fixed bed column experiments the breakthrough time, LUB and BC for the elution rate of 10 mL/min were 50 min, 5.14 cm and 49.16 mg respectively. At the elution rate of 2 mL/min, breakthrough time, LUB and BC were 80 min, 4.93 cm and 78.91 mg respectively. Also, the results obtained by the experiment reveals that the MB removal efficiency of TIWAC could be further enhanced by optimizing parameters such as flow rate, particle size, and the height of the bed of the column.

References

1. Ratna and Padhi B.S. (2012). Pollution due to synthetic dyes toxicity & carcinogenicity studies and remediation. *Int. J. Environ. Sci.*, 3(3), 940-955.
2. Sarasa J., Roche M.P., Ormad M.P., Gimeno E., Puig A. and Ovelleiro J.L. (1998). Treatment of a wastewater resulting from dyes manufacturing with ozone and chemical coagulation. *Water Research*, 32(9), 2721-2727.
3. Robinson T., Chandran B. and Nigam P. (2002). Removal of dyes from a synthetic textile dye effluent by biosorption on apple pomace and wheat straw. *Water Res.*, 36, 2824-2830.
4. Robinson T., McMullan G., Marchant R. and Nigam P. (2001). Remediation of dyes in textile effluent: A critical review on current treatment technologies with a proposed alternative. *Bioresour. Technol.*, 77(3), 247-255.
5. Panizza M., Barbucci A., Ricotti R. and Cerisola G. (2007). Electrochemical degradation of methylene blue. *Sep. Purif. Technol.*, 54(3), 382-387.

6. Tsai W.T. (2001). Adsorption of acid dye onto activated carbons prepared from agricultural waste bagasse by ZnCl₂ activation. *Chemosphere*, 45(1), 51-58.
7. Ganewatta G. and Edwards G.W. (2000). The Sri Lanka Tea Industry: Economic Issues and Government Policies. School of Business La Trobe University Bundoora, Victoria, Australia.
8. Wijerathna D.M.C.B., Lee K., Koide T., Jinadasa K.B.S.N., Kawamoto K., Iijima S., Herath G.B.B., Kalpage C.S. and Mangalika L. (2013). Solid waste generation, characteristics and management within the households in Sri Lankan urban areas. University of Moratuwa, Sri Lanka.
9. Sugumaran P., Susan V.P., Ravichandran P. and Seshadri S. (2012). Production and Characterization of Activated Carbon from Banana Empty Fruit Bunch and Delonix regia Fruit Pod. *J. Sustain. Energy Environ.*, 3, 125-132.
10. Yang K. (2010). Preparation of high surface area activated carbon from coconut shells using microwave heating. *Bioresour. Technol.*, 101, 6163-6169.
11. Yalcin M. and Arol A.I. (2002). Gold cyanide adsorption characteristics of activated carbon of non-coconut shell origin. *Hydrometallurgy*, 63(2), 201-206.
12. Caturla F., Molina-Sabio M. and Rodríguez-Reinoso F. (1991). Preparation of activated carbon by chemical activation with ZnCl₂. *Carbon N.Y.*, 29(7), 999-1007.
13. Robert A.M. (2011). Encyclopedia of Analytical Chemistry, A Practical Approach. John Wiley & Sons Ltd, Chichester. 10815-10837. ISBN: 978-0-470-97333-2.
14. Thomas B.N., George S.C. and Shell C.O. (2015). Production of Activated Carbon from Natural Sources. Abstract Trends in Green Chemistry Preparation of Activated Carbon from Preparation of Activated Carbon from Bamboo Chips Preparation of Activated Carbon from Cherry Stones. *iMedPub Journals*, 6, 1-5.
15. Rahman M.A., Amin S.R. and Alam A.S. (2012). Removal of methylene blue from waste water using activated carbon prepared from rice husk. *Dhaka University Journal of Science*, 60(2), 185-189.
16. Khodaie M., Ghasemi N., Moradi B. and Rahimi M. (2013). Removal of Methylene Blue from Wastewater by Adsorption onto ZnCl₂ Activated Corn Husk Carbon Equilibrium Studies. *J. Chem.*, 6.
17. Öktem Y., Soyly S. and Aytan N. (2013). The adsorption of methylene blue from aqueous solution by using waste potato peels; equilibrium and kinetic studies. *J Sci Ind Res.*, 71, 817-821.
18. Dąbrowski A., Podkościelny P., Hubicki Z. and Barczak M. (2005). Adsorption of phenolic compounds by activated carbon - A critical review. *Chemosphere*, 58, 1049-1070.
19. Tan I.A.W., Hameed B.H. and Ahmad A.L. (2007). Equilibrium and kinetic studies on basic dye adsorption by oil palm fibre activated carbon. *Chem. Eng. J.*, 127, 111-119.
20. Hameed B.H., Ahmad A.A. and Aziz N. (2007). Isotherms, kinetics and thermodynamics of acid dye adsorption on activated palm ash. *Chem. Eng. J.*, 133, 195-203.
21. Malik P.K. (2004). Dye removal from wastewater using activated carbon developed from sawdust: adsorption equilibrium and kinetics. *Waste Manag.*, 113, 81-88.
22. Annadurai G., Juang R.S. and Lee D.J. (2002). Use of cellulose-based wastes for adsorption of dyes from aqueous solutions. *J. Hazard. Mater.*, 92, 263-274.
23. Namasivayam C. and Kavitha D. (2002). Removal of Congo Red from water by adsorption onto activated carbon prepared from coir pith, an agricultural solid waste. *Dye. Pigment.*, 54, 47-58.
24. Hameed B.H., Salman J.M. and Ahmad A.L. (2009). Adsorption isotherm and kinetic modeling of 2, 4-D pesticide on activated carbon derived from date stones. *J. Hazard. Mater.*, 163, 121-126.
25. Febrianto J. (2009). Equilibrium and kinetic studies in adsorption of heavy metals using biosorbent: A summary of recent studies. *J. Hazard. Mater.*, 162, 616-645.
26. Han R., Wang Y., Zhao X., Wang Y., Xie F., Cheng J. and Tang M. (2009). Adsorption of methylene blue by phoenix tree leaf powder in a fixed-bed column: experiments and prediction of breakthrough curves. *Desalination*, 245(1-3), 284-297.
27. Kannan N. and Sundaram M.M. (2001). Kinetics and mechanism of removal of methylene blue by adsorption on various carbons—a comparative study. *Dye. Pigment.*, 51, 25-40.
28. Hameed B.H., Din A.M. and Ahmad A.L. (2007). Adsorption of methylene blue onto bamboo-based activated carbon: kinetics and equilibrium studies. *Journal of hazardous materials*, 141(3), 819-825.
29. Elmorsi T.M. (2011). Equilibrium isotherms and kinetic studies of removal of methylene blue dye by adsorption onto miswak leaves as a natural adsorbent. *Journal of Environmental Protection*, 2(06), 817. https://www.researchgate.net/publication/268261926_Equilibrium_Isotherms_and_Kinetic_Studies_of_Removal_of_Methylene_Blue_Dye_by_Adsorption_onto_Miswak_Leaves_as_a_Natural_Adsorbent/figures?lo=1 (Accessed 10/03/2018)