

Research Article

Adsorption of basic blue41 dye on modified tea waste: optimization and kinetic studies

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ABSTRACT

Colored dye effluents raise a major threat to the surrounding ecosystem. Many of the dyes are extremely toxic. The aim of this study was to determine the equilibrium and kinetics adsorption of basic blue 41 dye (BB41) from wastewater by modified tea waste as a natural adsorbent. The target adsorbent was prepared in laboratory conditions and pulverized by ASTM standard sieves. The composition and physicochemical properties of modified tea waste (MTW) determined by utilization of various technique such as FTIR, SEM, EDS, BET, and XRD. The initial concentrations of BB41 were selected in the range of 25 and 100 mg.L⁻¹. The experimental data were fitted with Langmuir and Freundlich isotherm models. The experimental adsorption isotherm was in good concordance with Langmuir model ($r^2 = 0.98$). Based on the Langmuir isotherm the maximum amount of adsorption (q_m) was found to be 48.78 mg.g⁻¹. Increase of the adsorbent dose led to increase of the dye removal efficiency. Furthermore, increase of the solution pH up to 9 led to the improvement of dye adsorption. The maximum adsorption of dye was observed at pH 9. The kinetic studies showed that the adsorption of basic blue 41 on modified tea waste was complied with pseudo-second order kinetic ($r^2 > 0.99$) for all concentration.

Key word: Basic blue 41, Tea waste adsorbent, Adsorption removal, kinetic.

INTRODUCTION

There are many kinds of synthetic dyes appearing in the effluent of industries such as textiles, paper, leather, and plastics. The textile industry consumes a huge amount of water in during its different process especially during dyeing and finishing processes. The discharge of colored wastewater from these industries may exhibit a toxic hazard to environment. Dyes are known pollutants that not only affecting aesthetic merit but also reducing light

penetration and photosynthesis, and they are carcinogenic for human health [1]. The dye components are hardly degradable by conventional physicochemical or biological methods [2]. The degradation of synthetic dyes becomes highly difficult as the textile dyes are continually being replaced with modern dyes, that resistant to photochemical, chemical, and biological degradation [3]. Since a very small amount of dye in water is highly visible and can

be toxic to creatures in water, the removal of dye from wastewater becomes environmentally important [4]. The most commonly used methods for color removal include chemical treatment, adsorption, reverse osmosis, and solvent extractions [5]. Among these, the adsorption have been shown to be a reasonable technique to treat industries colored effluents [6]. The most used adsorbent for dye removal is activated carbon however it is considered to be ineffectual due to its difficult and high cost generation [4]. Many adsorbents such as zeolite, chitosan, and husk etc., are widely used in literatures.

Owing to high porosity and specific sorption characteristics, a wide range of agricultural wastes have been used as adsorbent for removal of various pollutants such as dyes, heavy metal, organic, and inorganic materials from water and wastewater [7]. The removal of soluble and suspended contaminants from aqueous solution by agricultural waste or natural adsorbent has been extensively studied by many researchers [8]. Numerous agricultural waste have been used as a natural adsorbent such as rice husk, corn cobs, coir dust, barks, and tea waste [9, 10]. Literatures on tea waste introduce it as a low-cost adsorbent with a good capacity in removal of organic and inorganic pollutants [11]. The presence of structural hydroxyl protons, carboxylic protons, and lactone protons in tea waste is responsible for its ion-exchange behavior and it could be a good adsorbent [12]. Tea consumption is part of the Iranian culture, so a huge amount of tea waste is being produced in tea industries and consumer of tea.

In addition, tea waste takes a long time for biodegradation. The tea wastes ashes can obtain by incineration that is not a pollutant rather it could be used as an adsorbent. Hence, tea waste is a cost effective adsorbent. The aim of this work is adsorption removal of basic blue 41 (BB41) by modified tea waste (MTW) obtained from Ahvaz province, as a cost effective and natural adsorbent from aqueous solution. The effect of operational parameters such as pH, adsorbent dosage, dye concentration, and contact time on the adsorption process was

surveyed. The adsorption isotherm models and kinetic study of the process were investigated.

Experimental

Materials and instruments

The basic blue 41 (BB41) with molecular formula $C_{20}H_{26}N_4O_6S_2$ and molecular weight 482.57 g/M (with purity of $\geq 99\%$ and solubility of 40 g.L^{-1} in $20 \text{ }^\circ\text{C}$) was obtained from Alvan Sabet company. Other chemical materials were purchased from Merck Ltd. Spent tea waste was collected from houses in Ahvaz, Iran.

A digital microprocessor-based moisture analyzer (Mettler LP16) was used for determination of moisture and ash content of the MTW based on ASTM D2866-11. Elemental composition of the adsorbent was determined by a CHNOS-Rapid Elemental Analytical Instrument (Elementer, Germany). A nitrogen adsorption/desorption apparatus (Quantachrome, 2000, NOVA) based on Brunauer-Emmett-Teller (BET) theory was used to measure the specific surface area of the adsorbent. Other properties of the adsorbent such as bulk density and particle size of samples were characterized by Gay-Lussac pycnometer and sieve analysis, respectively. The pH zero point of charge (pH_{pzc}) of the adsorbent was found based on Prado Cechinel, et al procedure [13]. The adsorbent was also characterized by a BRUKER's Vertex 70 infrared spectrometer for the Fourier transform infrared (FTIR) spectroscopy analysis. A Philips XL-20 Scanning Electron Microscope (SEM) (Philips Co., The Netherlands) was used to determine the surface morphologies of MTW. The crystal phases of the particles were evaluated by X-ray diffractometer (XRD, Philips Xpert, Netherlands). A UV-Vis spectrophotometer (PerkinElmer, Lambda Bio40, USA) was used to determine the concentration of the samples.

Preparation of the adsorbent

Preparation and modification of spent tea waste adsorbent was performed according to below method. Briefly, the solid tea waste was provided from households in Iran. It was first washed by distilled water several times until remove impurities. Subsequently, it was boiled

with deionized water at 100 °C for several times to remove the extra color. The samples were dried at 65 °C for 24 hours. The dried MTW was ground and sieved to obtain selected nominal particle size fractions. To make activation on surface of spent tea decolorized spent tea leaves were taken in H₂SO₄ solution and agitated for several min. The samples were washed several times to reach the neutral pH in filtered water. Washing spent tea with H₂SO₄ make increase of active groups on surfaces of tea leaves and prevents the stain production due to tannin existing in tea leaves as well as COD. After drying at 105 °C, modified tea waste (MTW) was ground and sieved to obtain selected nominal particle size fractions and particles between 250 and 100 µm diameter sizes were chosen according to the ASTM Method (American Society for Testing and Material) [14]. MTW particles were dried in the oven at 80–85 °C for 2 h and then stored in plastic bags for next use.

Procedure

In this study, different parameters were examined such as contact time, pH, and adsorbent dose. The adsorption of BB41 from aqueous solution on MTW was performed using batch technique. All the experiments were carried out at 25 °C. For the determination of adsorption isotherms, 50ml of dye solution of known initial concentration was shaken with a certain amount of the adsorbent (8 g/L) on a shaker at 25 °C. The pH was adjusted to 9, either using HCl or NaOH. Initial dye concentrations were changed in the range of 20 mg/L to 200mg/L. At various time intervals, samples were taken and allowed to settle and further centrifuged at 3000 rpm for 10 min. The concentration of the residual dye was measured using UV–Vis spectrophotometer at the maximum wavelength of 530 nm. The obtained data were used to calculate the adsorption capacity of the adsorbent. Several observations were made at different time intervals, to determine adsorption equilibrium and the maximum removal of the dye. The amount of adsorbed dye (q_e) and efficiency (%) of MTW were calculated by the following equations:

$$q_e = [(C_0 - C_e) / M] \times V \quad (\text{Eq. 1})$$

where V is the volume of the solution (L) and M is the mass of adsorbent (g). The dye removal percentage can be calculated as follows:

$$\% \text{ Removal} = [(C_0 - C_t) / C_0] \times 100 \quad (\text{Eq. 2})$$

where C₀ and C_e (mg/L) are the liquid-phase concentrations of dye at initial and equilibrium, respectively.

RESULTS AND DISCUSSION

Characterizations of MTW

Physicochemical features of the MTW based on the CHNOS–Rapid Elemental Analytical Instrument (Elementer, Germany) are shown in table 1. As shown in the table, the specific surface area of the MTW analyzed by nitrogen adsorption/desorption apparatus and (BET) model was found to be 285.5 m²/g. The SEM image of MTW was demonstrated in Fig. 2. According to the Figure the MTW has an unequal and a more porous structure. This can be related to the impurities removal from the spent tea surface during the acid washing process. So, acid washing process increases both the porosity and the active surface of MTW. This results can be approved by the high specific surface area of MTW (285.5 m²/g) than raw spent tea (21 m²/g) [15]. EDS spectrum of MTW adsorbent was shown in fig. 3. As can be seen from the figure, the presence of carbon, nitrogen, oxygen, and calcium elements with the weight percent of 63.39, 5.12, 30.82, and 0.65 respectively, were approved. The composition of the MTW was surveyed by XRD method. Fig. 4 shows XRD spectrum of the MTW. The XRD pattern approved amorphous phase for the MTW adsorbent.

Fig. 5 illustrates the FTIR spectrum of the MTW before and after adsorption of BB41. The FTIR spectroscopic characteristics are presented in Table 2. The bands around 3420 cm⁻¹ indicated the presence of bonded –OH groups [16, 17]. The bonds observed at about 2913 cm⁻¹ could be assigned to the aliphatic C–H group [17]. The bonds at 1660 cm⁻¹ and 1440 cm⁻¹ can be attributed to the C=O stretching modes and Symmetric bending of CH₃, respectively. Also

the peak at about 1050 cm^{-1} is attributed to S=O stretching mode. According to Fig. 5 and Table 2, the spectra show several absorption peaks, representing the multipart nature of the MTW. The results of the spectral analysis before and after BB41 adsorption shows not significant

changes in the bonded –OH groups, secondary amine group, C=O stretching of ether group and symmetric bending of CH_3 of the MTW showing that the adsorption process may be physicochemical in nature.

Table 1. Physicochemical features of MTW

Parameters	Values	Elemental analysis (%)	
Moisture content (%)	3.72 ± 0.4	C	57.5 ± 1.1
Water soluble compounds (%)	1.2 ± 0.3	H	7.3 ± 0.5
Insoluble compounds (%)	95.1 ± 0.4	N	0.4
Volatile fraction (%)	64.3 ± 2.9	O	30.3 ± 0.9
Ash content (%)	30.9 ± 2.7	S	4.5 ± 0.3
pH_{pzc}	5.0 ± 0.2		
Bulk density (kg/m^3)	258		
Particle size (μm)	100–250		
BET surface area (m^2/g)	285.5		

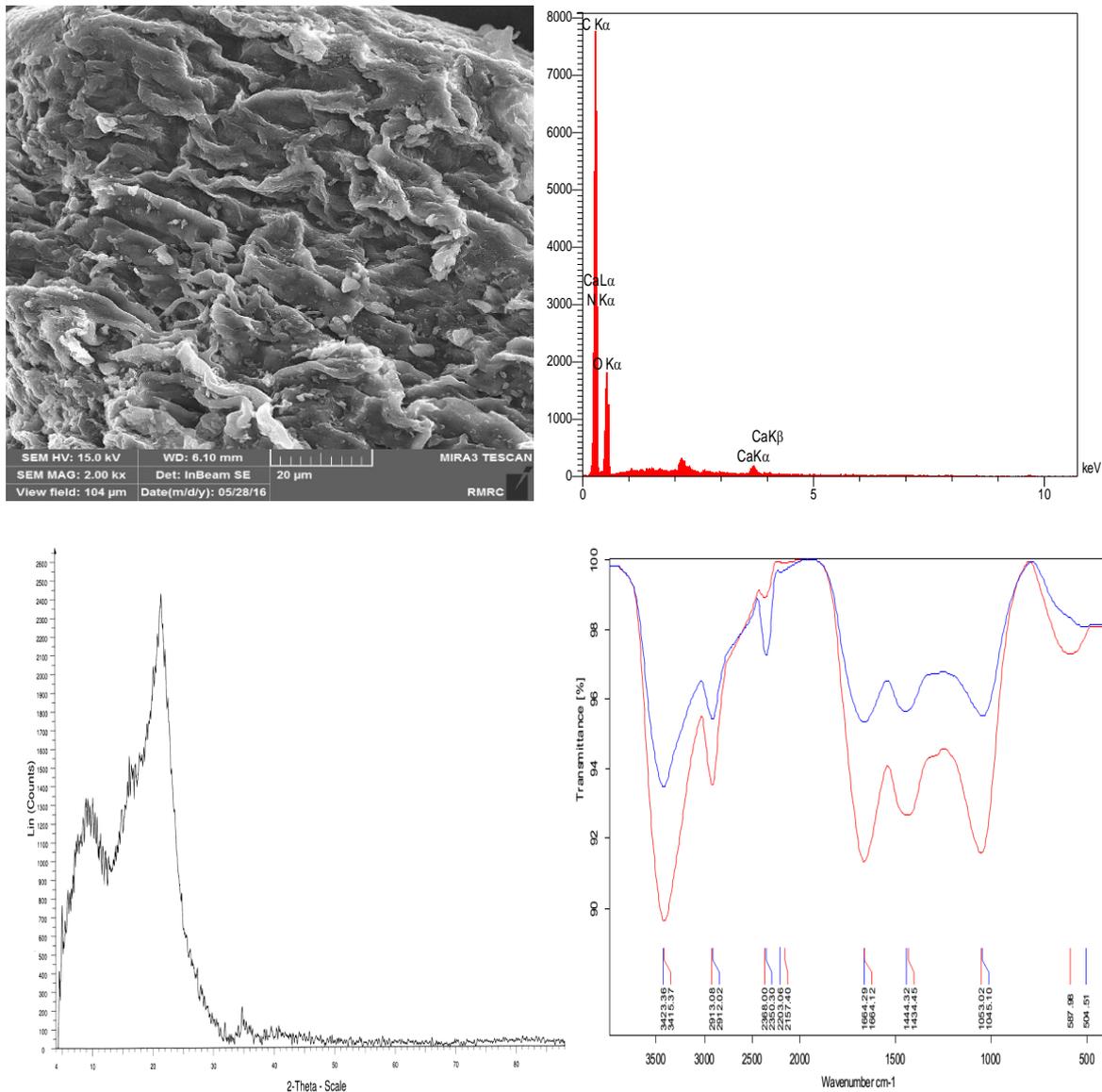


Figure 1. SEM, EDS, XRD, and FTIR spectra of MTW

Table 2. The FTIR spectral characteristics of MTW before and after BB41 adsorption

IR peaks	Frequencies (cm^{-1})			Assignment	Reference
	Before adsorption	After adsorption	Differences		
1	3415	3423	+8	Bonded -OH groups	[17, 18]
2	2913	2912	+1	aliphatic C-H stretch	[17]
3	2853	2853	0	aliphatic C-H stretch	[19]
4	1719	1719	0	carbonyl stretch of carboxyl	[16]
5	2368	2350	-18	P-H stretch	[20]
6	2157	2203	+46	C≡C stretch	[20]
7	1664	1664	0	C=O stretching	[21]
8	1434	1444	+10	Symmetric bending of CH_3	[22]
9	1053	1045	-8	S=O stretch	[20]
10	587	504	-83	C-CN bending	[20]

Effect of contact time and dye concentration

The effect of contact time for the adsorption of BB41 on MTW was studied for a period of 5 h for initial dye concentration of 25-100 mg/L at respective natural pH, as depicted in Fig. 6. The adsorption of BB41 was quite rapid in the initial contact time and then gradually increased with the prolongation of contact time. After 90 min of contact, no significant variation in dye adsorbed was shown. Based on these results, 90 min was taken as the equilibrium time in batch adsorption experiments. It was also found from Fig. 6 that the adsorption amount of BB41 in mass unit (mg/g) increases with increase in dye concentration, for example the q_e amount was found to be around 9.5 and 2.5 mg/g for dye concentration of 100 and 25 mg/L at 90 min, respectively. The high concentration of dye can increase the driven force in solution causing more adsorption on MTW surface [23]. In Nasuha et al. study, the adsorption capacity of rejected tea to remove methylene blue was minimum at pH 3, this increased up to 4 and remained nearly constant over the initial pH ranges of 4–8.[24]

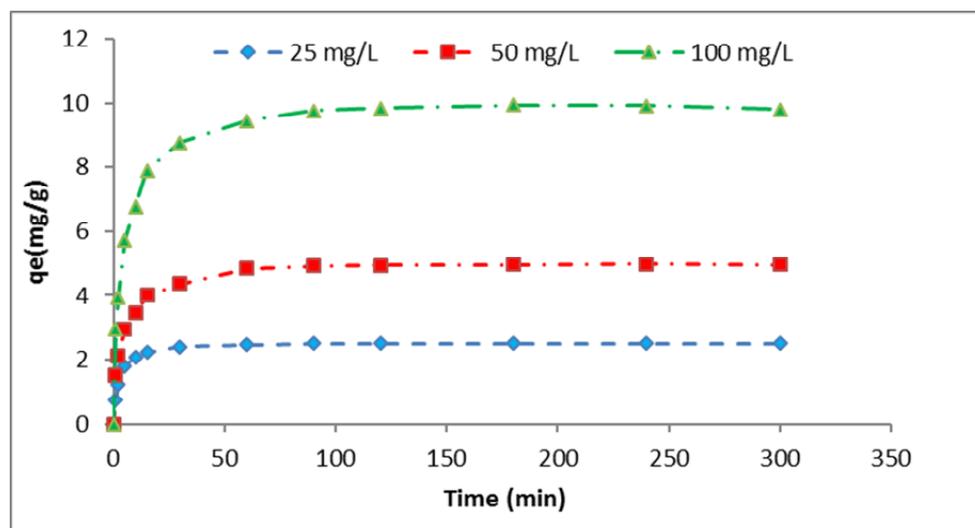


Figure 2. Effect of contact time and initial concentration on the amount of the dye adsorbed (pH=7.5, adsorbent dose=10 g.L^{-1})

Effect of pH

The removal efficiency of the dye as a function of pH is shown in Fig. 7. The adsorption of dyes by MTW was found to be a maximum in the basic pH of 9. The pH value of the dye solution plays an important role in the whole adsorption

process and particularly on the adsorption capacity. As shown in the figure, an increase in the removal was observed in the pH of 9 after that the adsorption, however, decreased with increasing the range of pH values. The pH_{pzc} value (the pH at the point of zero charge) of the

tea waste is found to be 5.0 ± 0.2 (table1). At $\text{pH} < \text{pH}_{\text{pzc}}$, tea waste surface may get positively charged due to the adsorption of H^+ . Amine groups become protonated at pH below pH_{pzc} . At lower pH, a possible protonation of the carboxyl groups might also occur. Thus a force of repulsion occurs between the dye cations and the adsorbent surface. In addition, at lower pH the concentrations of H^+ being high, they compete with the positively charged BB41 cations for vacant adsorption sites. Thus, at low pH, the adsorption is low. The reverse situation

occurs at $\text{pH} > \text{pH}_{\text{pzc}}$. At $\text{pH} > \text{pH}_{\text{pzc}}$, the surface of tea waste may get negatively charged due to adsorption of OH^- , and the carboxyl groups of the tea waste may get deprotonated producing negatively charged adsorption sites. However, the adsorption decreases at pH value higher than 9 again. May be another phenomenon occur (ion exchange or chelation for example) in higher pH. Similar results were reported in the previous literature [16].

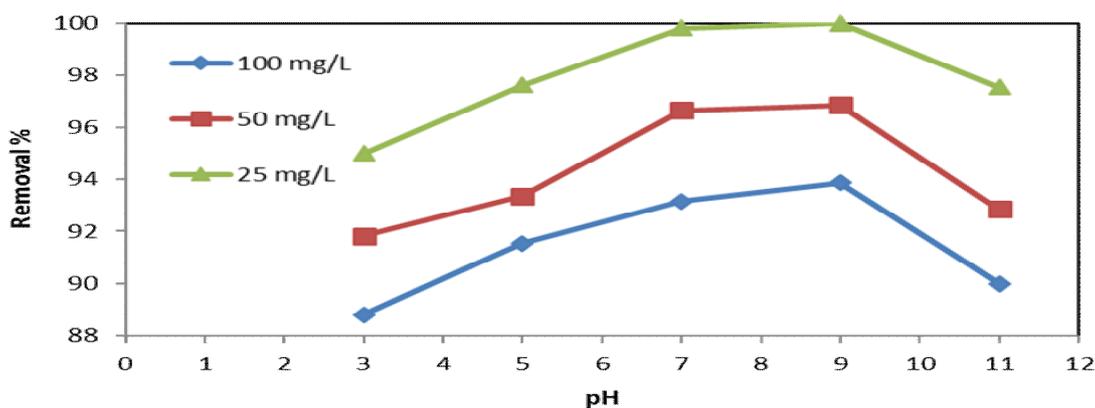


Figure 3. Effect of pH on the dye adsorption ($t = 90$ min)

Effect of adsorbent dosage

The study of adsorbent dosage for removal of BB41 from aqueous solution was carried out at different adsorbent doses (0.1 – 8 g/L) using a 25 mg/L of the dyes (Fig. 8). It was observed that percentage of dye removal was increased with increasing adsorbent dosage from 0.1 to 8 g/L. However, no significant changes were observed

after adsorbent dose of 5 in removal of dye according to fig.8. The removal percentage of dye increasing with adsorbent dosage could be attributed to increase in the adsorbent surface areas, augmenting the number of MTW sites available for adsorption, as already reported [25].

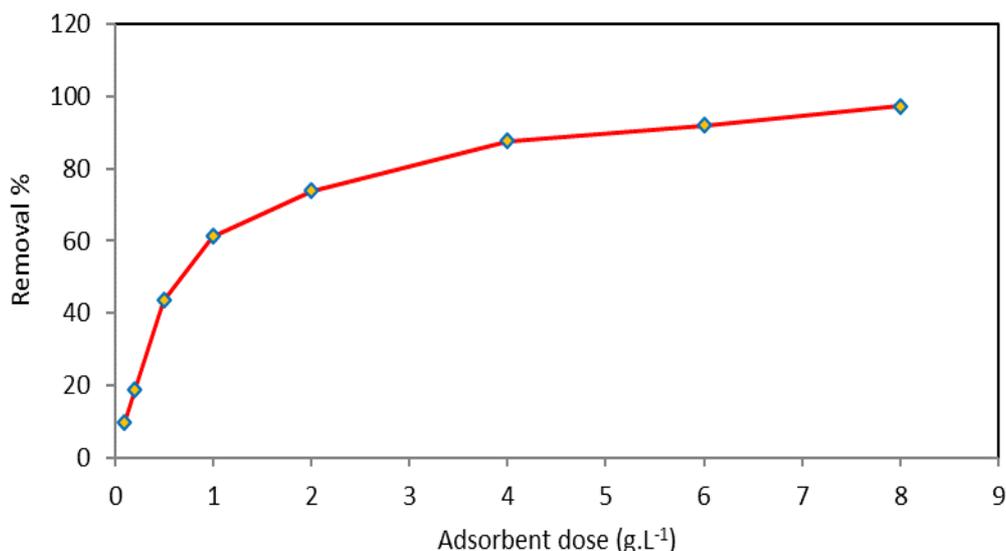


Figure 4. Effect of adsorbent dose on the dye adsorption ($t = 90$ min, $\text{pH}=7.5$)

Adsorption kinetic

The kinetic adsorption data was processed to understand the dynamics of adsorption process in terms of the order of rate constant. Kinetic data were treated with the pseudo-first-order kinetic model [26]. The differential equation is the following:

$$(dq_t / dt) = k_1 (q_e - q_t) \tag{Eq. 3}$$

where q_e and q_t refer to the amount of dye adsorbed (mg/g) at equilibrium and at any time, t (min), respectively, and k_1 is the equilibrium rate constant of pseudo-first-order sorption (min^{-1}). Integrating Eq. (3) for the boundary conditions $t = 0$ to t and $q_t = 0$ to q_t , gives:

$$\text{Log } q_e / (q_e - q_t) = k_1 / 2.303t \tag{Eq. 4}$$

Which is the integrated rate law for a pseudo-first-order reaction. Eq. (4) can be rearranged to obtain a linear form:

$$\log (q_e - q_t) = \log q_e - (k_1 / 2.303)t \tag{Eq. 5}$$

Values of the rate constant, k_1 , equilibrium adsorption capacity, q_e , and the correlation coefficient, r^2 , were calculated from the plots of $\log (q_e - q_t)$ versus t (Fig. 9) for three dye concentration. Although the correlation coefficients for concentration of 25, 50 and 100 mg/L are found to be 0.95, 0.86 and 0.65, respectively, however the calculated equilibrium adsorption capacities do not agree with experimental values (Table 3). This indicates that adsorption of BB41 onto MTW is not an ideal pseudo-first-order reaction.

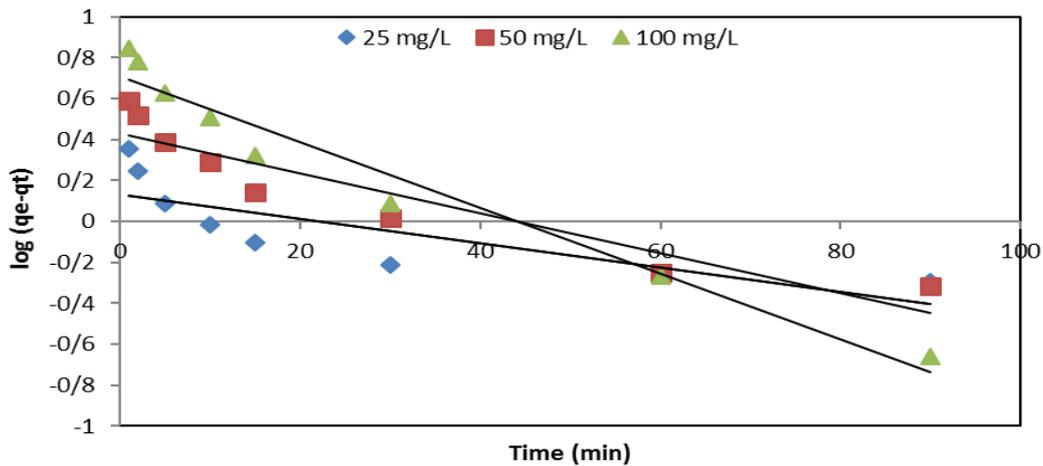


Figure 5. Pseudo-first order kinetics for dye adsorption onto MTW (Adsorbent dose = 10 g.L⁻¹, pH = 7.5)

Kinetic data were further treated with the pseudo-second order kinetic model. The differential equation is the following:

$$(dq_t / dt) = k_2 (q_e - q_t)^2 \tag{Eq. 6}$$

where k_2 is the equilibrium rate constant of pseudo-second order adsorption (g/mg.min). Integrating Eq. (6) for the boundary condition $t = 0$ to t and $q_t = 0$ to q_t , gives:

$$1/q_e - qt = 1/q_e + k_2t \tag{Eq. 7}$$

Which is the integrated rate law for a pseudo-second-order reaction. Eq. (7) can be rearranged to obtain a linear form:

$$t/q_e = 1/(k_2q_e^2) + (1/q_e)t \tag{Eq. 8}$$

If pseudo-second-order kinetics is applicable, the plot of t/q_t versus t should show a linear relationship. The linear plots of t/q_t versus t show a good agreement of experimental data with the pseudo-second-order kinetic model for all dye concentration (Fig.10). The correlation coefficients (r^2) for the second-order kinetic model are higher than 0.99.

The second order rate constant, k_2 , and the equilibrium adsorption capacity, q_e , were calculated from the intercept and slope of the plots of t/q_t versus t . The calculated q_e values agree very well with the experimental data (Table3). These indicate that the adsorption of

BB41 on MTW obeys pseudo-second-order kinetic model. In Uddin et al. study the sorption was analyzed using pseudo-first-order and pseudo-second order kinetic models for methylene blue adsorption by tea waste and the sorption kinetics was found to follow a pseudo-second order kinetic model [16]. Li et al.

reported similar findings for the adsorption of methyl violet on Pu-erh tea powder [27]. Similar phenomenon was observed for the adsorption of radionuclide Tl-201 on fibrous waste tea [28], and also in adsorption of Orange-G and Methyl Violet dyes on bagasse fly ash [29].

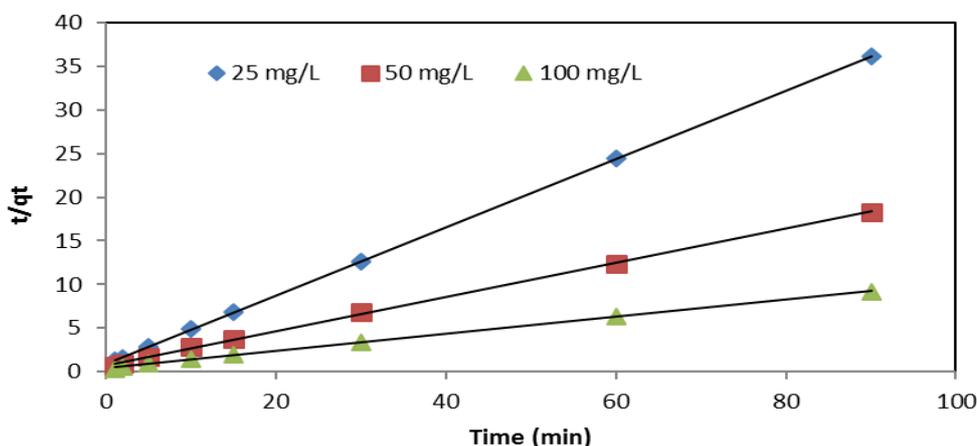


Figure 6. Pseudo-second order kinetics for dye adsorption onto MTW (Adsorbent dose = 10 g.L⁻¹, pH = 7.5)

Table 3. Pseudo-first and pseudo-second order adsorption rate constants and the calculated and experimental q_e for the adsorption of BB41 on MTW

kinetic models	experimental	pseudo first order			pseudo second order		
concentration	$q_{e\text{ exp}}$ (mg/g)	k_1 (min ⁻¹)	$q_{e\text{ cal}}$ (mg/g)	r^2	k_2 (g mg ⁻¹ min ⁻¹)	$q_{e\text{ cal}}$ (mg/g)	r^2
25 mg/L	3	0.013	1.36	0.95	0.17	2.55	1
50 mg/L	5.4	0.022	2.7	0.86	0.053	5.09	0.99
100 mg/L	10	0.037	5.1	0.65	0.001	10.12	0.99

Adsorption isotherms

Two important isotherms are selected in this study, which are namely the Langmuir and Freundlich isotherms [30, 31]. The Langmuir adsorption isotherm assumes that adsorption occurs at specific homogenous sites within the adsorbent and has found successful application in many adsorption studies of monolayer adsorption [30]. The linear form of the Langmuir isotherm equation is written by the following equation:

$$1/q_e = 1/(q_m K_1 C_e) + (1/q_m) \quad (\text{Eq. 9})$$

where q_e is the equilibrium dye concentration on the adsorbent (mg/g), C_e is the equilibrium dye concentration in the solution (mg/L), q_m is the

monolayer adsorption capacity of the adsorbent (mg/g), and K_1 is the Langmuir adsorption constant (L/mg) and related to the free energy of adsorption. Values of q_m and K_1 were calculated from the intercept and slope of the linear plots (Fig.11), respectively, and are presented in Table 4. From the table it is evident that the maximum dye sorption capacity of MTW (q_m) and the r^2 value are 48.72 mg/g and 0.97 at 25 °C, respectively. The r^2 of the Langmuir isotherm was greater than that of the Freundlich isotherm for the adsorption of dye. This implies that the Langmuir model better depicts the adsorption of BB41 on MTW than the Freundlich model. Some investigations of dye adsorption using several adsorbents have been conducted. Nasuha et al. reported similar r^2 for

adsorption of methylene blue by Rejected tea based on Langmuir isotherm. They found the q_m was to be 147 mg/g [24].

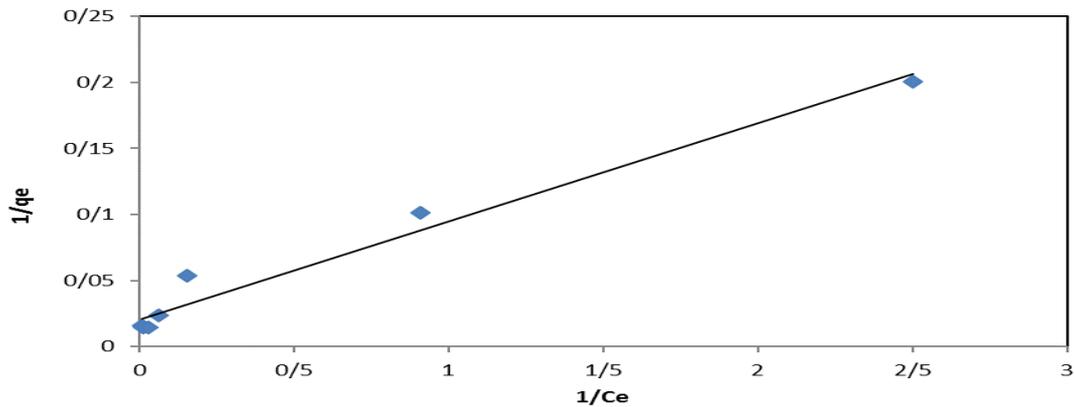


Figure 7. Langmuir adsorption isotherm of dye onto MTW

The Freundlich isotherm is an empirical equation employed to describe heterogeneous systems. A linear form of the Freundlich equation is

$$\log q_e = \log k_f + (1/n)\log C_e \quad (\text{Eq. 10})$$

Where K_f (L/g) and n (dimensionless) are the Freundlich adsorption isotherm constants, being

indicative of the extent of the adsorption and the degree of nonlinearity between solution concentration and adsorption, respectively. The plots of $\log q_e$ against $\log C_e$ for the adsorption of BB41 on MTW (Fig. 12) were employed to generate the intercept value of K_f and the slope of $1/n$ [32, 33].

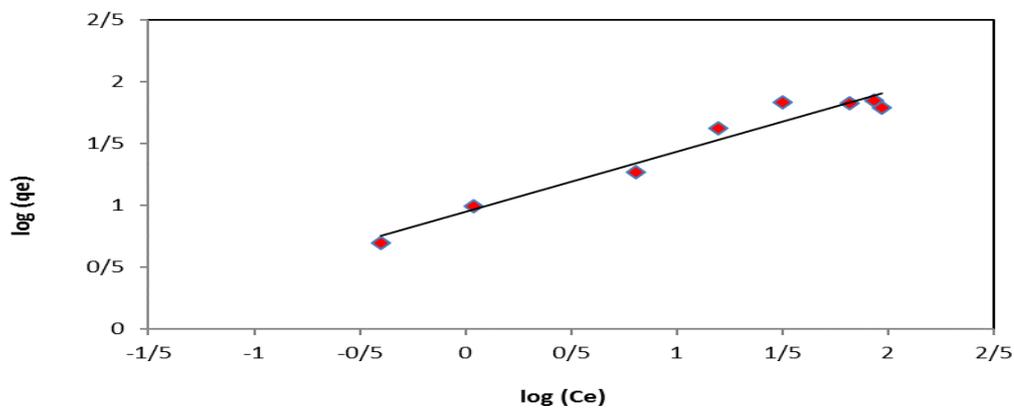


Figure 8. Freundlich adsorption isotherm of dye onto MTW

The essential attributes of the dimensionless separation factor (R_L) can be written as:

$$R_L = 1/(1 + C_0 K_1) \quad (\text{Eq. 11})$$

Where C_0 is the highest initial dye concentration (mg/L). The values of R_L calculated as above equation are incorporated in Table 4. As the R_L values lie between 0 and 1, the adsorption

process is favorable [2]. Further, the R_L values for the adsorption of BB41 are between 0.018 and 0.15 and therefore, its adsorption is favorable. Other researcher for removal of dye reported same results by tea waste leaf that indicates tea waste is promising adsorbent for removal of dye.

Table 4. The isotherms parameters and correlation coefficients for BB41 adsorption onto MTW

T (°C)	Langmuir				Freundlich		
	q_m (mg/g)	K_l (L/mg)	r^2	R_L	n	k_f (mg/g)	r^2
25	48.78	0.27	0.97	0.018~0.15	2.05	8.81	0.95

One of the Freundlich constants KF indicates the adsorption capacity of the adsorbent. The other Freundlich constants n is a measure of the deviation from linearity of the adsorption. If a value for n is equal to unity the adsorption is linear. If a value for n is below to unity, this implies that adsorption process is chemical, but a value for n is above to unity, adsorption is favorable a physical process. The highest value of n at equilibrium is 2.05 at 25 °C, represents favorable adsorption at low temperature and therefore this would seem to suggest that physical, which is referred the adsorption bond becomes weak and conducted with Van Der Waals forces, rather than chemical adsorption is dominant when it is used for adsorbing BB41 [34, 35].

CONCLUSIONS

In this study, MTW was produced and tested as a low cost adsorbent for the removal of BB41. The effects of adsorbent dosage, initial pH, contact time, and initial dye concentration on the removal of BB41 was investigated through batch experiments. The experimental results showed that MTW prepared was a suitable adsorbent for removal of BB41 from aqueous solution. In batch studies, the removal percentage increased with an increase of contact time and MTW dose and decreased with an increase in solute concentration. Removal of BB41 was high at the pH 9. The pH and contact time were obtained to be pH 9 and 90 min, respectively. Isotherm modeling revealed that the Langmuir equation could better describe the adsorption of dye on the MTW as compared to other models. Kinetic data were appropriately fitted with the pseudo-second-order adsorption rates. Because of the high specific surface area indicated favorable adsorption behavior for BB41. MTW is a non-toxic material and can be provided in a simple and cost-effective way for simple application. These unique features present MTW as a low cost, promising and feasible alternative for dye removal.

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