Hindawi
Journal of Chemistry
Volume 2020, Article ID 5431046, 13 pages
https://doi.org/10.1155/2020/5431046

Research Article

Adsorption of Dye by Waste Black Tea Powder: Parameters, Kinetic, Equilibrium, and Thermodynamic Studies

Dongyi Lin,[1] Fan Wu,[1,2] Yuqun Hu,[1] Tingzhong Zhang,[1] Chengshun Liu,[1] Qiangda Hu,[1] Yunfei Hu,[1] Zhihui Xue,[1] Hua Han,[1] and Tzu-Hsing Ko[1]

[1]*Anxi College of Tea Science, Fujian Agriculture and Forestry University, Fuzhou City, Fujian Province, China*
[2]*College of Horticulture, South China Agricultural University, Guangzhou City, Guangdong Province, China*

Correspondence should be addressed to Tzu-Hsing Ko; hsingko@gmail.com

Received 20 November 2019; Accepted 7 January 2020; Published 8 February 2020

Academic Editor: José Morillo

Waste black tea powder was used as a potential adsorbent to remove methylene blue (MB) from aqueous solution. Several operating factors in adsorption of MB onto waste black tea powder were investigated, including contact time, initial MB concentration, solution pH, adsorption temperature, and dosage of waste black tea powder. Experimental results revealed that the adsorption efficiency increased with contact time and solution pH values and decreased with initial MB concentration and adsorption temperature. The equilibrium time was estimated to be around 60 min. The maximum adsorption capacity and the highest adsorption efficiency were 302.63 $mg{\cdot}g^{-1}$ and 100%, respectively. In kinetic study, pseudo-first-order and pseudo-second-order kinetic models, intraparticle diffusion model, and Boyd and Elovich models were employed to analyze the adsorption behavior and the adsorption mechanism. It was found that the pseudo-second-order kinetic model was suitable to describe the adsorption process, and the calculated equilibrium adsorption capacity was well close to the experimental data for different initial MB concentrations. The internal diffusion was not the only rate-controlling step, and the existence of boundary effect was observed in this study. From isotherm analysis, the equilibrium data were well represented by the Langmuir model, rather than Freundlich, Dubinin–Redushckevich, or Temkin models. The nonlinear fitting for various isotherm models implied that the adsorption behavior between MB and waste black tea powder was complication. Thermodynamic parameters including changes in Gibb's free energy, enthalpy, and entropy suggested that adsorption of MB onto waste black tea powder was a spontaneous and exothermic process. The multiple regeneration/adsorption experiments indicated that the used black tea powder efficiently remained more than 75% after five cycles using NaOH as a regenerative reagent and thus be used for many times. Therefore, as a low-cost and easily available material, waste black tea powder could be applied in wastewater treatment.

1. Introduction

Synthetic dyes are extensively used in various fields such as textile, printing, and decoration [1]. Due to its toxicity, stability, high chroma, and high concentration, synthetic dyes detrimentally affect aquatic lives and human beings [2]. Studies have proven that textile wastewater can reduce the level of dissolved oxygen and inhibit the reproduction of aquatic organisms if it enters a water body [3, 4]. Synthesis of dyes results in increased incidence of noncommunicable diseases, such as hormone disruptions, asthma and allergies, and chronic lung diseases, and contributes to occupational diseases, such as chronic kidney disease of multifactorial origins [5].

Methylene blue (MB) can be used in several applications, such as a vital component in the textile industry, an adjuvant in clinical practice or a disinfectant in fishery [6–8]. Notably, in the process of dying, MB utilization is only 5%, whereas 95% is wasted. MB, being nonbiodegradable, is a popular pollutant in water. If chronically overexposed to MB, a person may present dizziness, headaches, tremors, and mental confusion [7]. These phenomena have caused public concerns and attracted relevant exploration. Numerous effective treatment techniques, including ultrasonic assisted adsorption, enzymatic treatment, various oxidants, and adsorption, have been exploited [9–12]. However, several problems emerge in the promotion and production of these methods. Energy costs, inconvenience, small-scale, incontinuity, and noncomprehensiveness are some of the limitations of these methods.

Adsorption is considered to be a desirable approach because of its low cost, ease of operation, and excellent performance. Adsorbents can be made from ordinary and common substances, such as natural clay and orange peel [13, 14]. In recent years, agricultural waste has received considerable attention. These byproducts are rich in organic substances, which is a breeding ground for bacteria. Inadequate disposal of such waste can cause serious pollution and nuisance. The cost of waste processing reduces the already meager agricultural profits [15]. Therefore, the usage of waste materials should be explored. Tea has been recognized as the second most commonly consumed beverage in the world, and the annual output of tea is estimated more than 4 million tons [16, 17]. In China, it is undoubt that a huge amount of wasted tea was produced during production or consumption, leading to the serious environmental problem. It is believed that the waste tea is an asset when it is appropriately treated and reused. Therefore, the aim of the present work is to explore the potential of waste black tea as useful adsorbents for removal of MB from aqueous solution. Effective parameters including contact time, initial MB concentration, dosage of black tea, pH value, and temperature on the removal efficiency were experimentally investigated. The equilibrium isotherms were determined by several models to understand the mechanism of MB, and some kinetic models were used to fit the experimental data.

2. Materials and Methods

2.1. Tea Sample Preparation. The black tea samples used in this study were collected from Anxi county, Fujian province. To acquire the desired black tea samples for adsorption experiments, black tea samples were decocted by distilled water at 373 K for several times to remove pigments and unwanted chemical substances. After decoction, black tea samples were flushed with distilled water and dried in an oven at 343 K for 24 h. The dried black tea samples were crushed with an agate and were passed through an 80 mesh sieve. The black tea samples were stored in a glass desiccator for the adsorption experiments. The content of carbon, nitrogen, and hydrogen for waste black tea used in this study was measured to be $52.12 \pm 1.23\%$, $2.45 \pm 0.01\%$, and $1.18 \pm 0.01\%$ based on the elemental analysis. The water content and ash content were $6.66 \pm 0.05\%$ and $2.66 \pm 0.12\%$, respectively.

2.2. Chemicals. Methylene blue (MB) was obtained from Tianjin Zhiyuan Chemical Reagents Factory (Tianjin, China). The pH value of the MB solution was adjusted with HCl (Sinopharm Chemical Reagent Company) and NaOH (Sinopharm Chemical Reagent Company).

2.3. Equipment. The thermo-controlled shaker was used to promote the adsorption interaction between MB and black tea powder. The shaker also controlled the adsorption temperature. A centrifuge, purchased from Eppendorf, Germany, was applied to separate the black tea powder from the solution, and the supernatant was obtained for further analysis. A UV-visible spectrophotometer, supplied by Shimadzu Corporation, Japan, was used to determine the absorption value of the MB solution, and the maximum absorption wavelength of the MB solution was 664 nm. The concentration of MB solution was obtained by substituting the absorbance value into the prepared standard curve.

2.4. Batch Experiments. Five factors were tested in this study, namely, the contact time, initial MB concentration, solution pH, adsorption temperature, and waste black tea powder dosage. In these factor experiments, every conical flask (100 mL) was filled with 50 mL MB solution with different concentrations. After preheating for 30 min, the adsorption reaction was allowed to proceed for some time at a certain temperature. Then, the mixed samples were centrifuged at 4500 rpm for 5 min, and the supernatants were obtained. Using a UV-visible spectrophotometer at 664 nm, the concentration of residual MB was detected. Adsorption efficiency and adsorption capacity were calculated using the following equations:

$$\text{adsorption capacity}\,(Q) = \frac{(C_o - C_t)V}{m},$$
$$\text{adsorption efficiency}\,(E) = \frac{(C_o - C_t)}{C_o} \times 100\%, \quad (1)$$

where C_o is the initial concentration of MB and C_t is the concentration of MB at time t (min). m (g) is the weight of tea powder, and V (mL) is the volume of the MB solution. Repeated trials were performed for accuracy as average values were used for further analysis.

2.5. Isotherm Adsorption Experiments. In each conical flask, 0.2 g of black tea powder and 50 mL of the MB solution with a certain concentration were mixed in the thermostatic oscillator at 288–323 K. When reactions reached equilibrium, the mixtures were centrifuged, and then supernatant solutions were tested. Adsorption capacity and adsorption efficiency obtained were fitted with four adsorption models to analyze the adsorption behavior in experiments.

2.6. Kinetic Studies. In this study, an MB solution containing 0.2 g of black tea powder with an initial concentration of $1000\ \text{mg}\cdot\text{L}^{-1}$ was selected as the reaction system. The system was reacted at the ambient temperature of 298 K for 60 min. The absorption value of the solution was determined, and the MB concentration was calculated. Data analysis was conducted according to the methods described previously. Different kinetic models were used for fitting the mechanism of action.

2.7. Pseudo-First-Order and Pseudo-Second-Order Kinetic Models. Pseudo-first-order and pseudo-second-order kinetic models were widely used to analyze the transient behavior in adsorption process. In the pseudo-first-order kinetic model, the adsorption rate is assumed to linearly decrease as the removal efficiency increases. In the pseudo-second-order kinetic model, the interaction between adsorbate and adsorbent, such as electron sharing and exchange, plays a decisive role in the reaction rate [18]. This denotes that the adsorption proceeds with the nature of chemisorption. The pseudo-first-order and pseudo-second-order equation in a linear form can be expressed as follows:

$$\ln\left(Q_e - Q_t\right) = \ln\left(Q_e\right) - \frac{K_{pf}}{2.303}t, \tag{2}$$

where K_{pf} is the constant of the pseudo-first-order rate, Q_e is the amount of MB adsorbed at equilibrium, and Q_t is the amount of MB adsorbed at equilibrium at time t (min). That is,

$$\frac{t}{Q_t} = \frac{1}{K_{ps}Q_e^2} + \frac{1}{Q_e}t, \tag{3}$$

where K_{ps} is the constant of the pseudo-second-order rate, Q_e and Q_t are the amounts of MB adsorbed at equilibrium and at time t (min), respectively.

2.8. Intraparticle Diffusion Model. To determine the potential adsorption mechanism, the intraparticle diffusion model was selected for further study. In the intraparticle diffusion model, it is assumed that the internal diffusion is the only rate-controlling step when the linear regression curve of Q_t versus $t^{0.5}$ passed the origin [19]. The parameters of this model are calculated as follows:

$$Q_t = K_{id}t^{0.5} + C, \tag{4}$$

where Q_t is the amount of MB adsorbed at equilibrium at time t, K_{id} is the intraparticle diffusion rate constant, and C is the intercept, which represents the effect of the boundary layer on molecule diffusion.

2.9. Boyd and Elovich Models. The Boyd model, a theoretical model originally developed for ion exchange kinetics, was found to be applicable to adsorption systems, mostly to determine the rate-controlling step [20]. The Boyd model allows calculating the effective diffusion coefficient, provided the Boyd plot passes through the origin:

$$F = 1 - \frac{6}{\pi^2}\sum_{n-1}^{\infty}\frac{1}{n^2}e^{-n^2 B_t}. \tag{5}$$

Here, F is the ratio of adsorption amount at time t to the adsorption amount at equilibrium, that is, $F = Q_t/Q_e$, and B_t is a numerical function of F. When $F > 0.85$, the relationship between F and B_t can be expressed using the following equation:

$$B_t = 0.4977 - \ln(1 - F). \tag{6}$$

The Elovich model is mainly applicable for systems in which the adsorbent surface is heterogeneous and is often valid for chemisorption kinetics, such as electron exchange in the liquid phase [18]. Generally, the Elovich model can be expressed as follows:

$$Q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln(t), \tag{7}$$

where Q_t is the amount of MB adsorbed at any time t, α is the initial sorption rate, whereas β represents the surface coverage extent and the activation of energy for chemisorption. The value of $1/\beta$ illustrates the available amount of adsorption sites; therefore, $(1/\beta)\ln(\alpha\beta)$ reflects the adsorption capacity when $\ln t = 0$.

2.10. Adsorption Isotherm. The applicability of Langmuir, Freundlich, Dubinin-Redushckevich (D-R), and Temkin isotherm models was tested for MB adsorption onto waste black tea powder. The best fitting model was determined by the regression correlation coefficient.

Based on the assumption that intermolecular forces decrease rapidly with distance, the Langmuir model describes the uniform adsorption sites and single molecule layer in adsorption [21]. Rather than changing with the surface coverage, its adsorption energy is constant [22]. The Freundlich model, an empirical equation, is mainly applied to the adsorption of heterogeneous surface and multilayer physical adsorption systems [23]. It is assumed that strong binding sites are occupied in priority, and the binding strength declines with the increasing degree of site occupation. The D–R isotherm is an empirical model for the adsorption of subcritical vapors onto micropore solids [24]. The Temkin model is used to explain chemisorption of the heterogeneous surface and is used in the premise that adsorption heat decreases linearly with coverage because of the adsorbent-adsorbate interactions [25]. Mathematical expressions of the four models are presented as follows.

2.10.1. Langmuir Isotherm Model

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{Q_m K_L}, \tag{8}$$

where Q_e is the amount of MB adsorbed at equilibrium, Q_m is the maximum adsorption capacity, C_e is the concentration of MB at equilibrium, and K_L is the Langmuir constant that relates to the adsorption capacity and adsorption efficiency. Dimensionless equilibrium parameter R_L estimates whether the Langmuir isotherm is favorable:

$$R_L = \frac{1}{1 + K_L C_o}, \tag{9}$$

where C_o is the initial concentration of MB, and if $0 < R_L < 1$, the adsorption process is generally considered to be favorable; if $R_L > 1$, the adsorption is unfavorable; if $R_L = 1$, then the adsorption process is linear; and if $R_L = 0$, the adsorption is irreversible.

2.10.2. Freundlich Isotherm Model

$$\ln Q_e = \ln K_F + \frac{1}{n}\ln C_e, \quad (10)$$

where K_F is the Freundlich constant and n is heterogeneity factor, related to adsorption capacity and adsorption intensity, respectively.

2.10.3. Dubinin–Redushckevich (D–R) Isotherm Model.

$$\ln Q_e = \ln Q_m - K_D \varepsilon^2, \quad (11)$$

where K_D indicates the coefficient related to the adsorption-free energy and ε is the Polanyi potential that can be calculated using the following equation:

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right), \quad (12)$$

where R is the gas constant and T (K) is the absolute temperature.

The Temkin isotherm model is expressed as follows:

$$Q_e = \frac{RT}{B_T}\ln\left(A_T C_e\right), \quad (13)$$

where B_T is the Temkin constant related to the heat of sorption and A_T is the Temkin constant denoting the Temkin isotherm equilibrium binding.

2.11. Determination the Point of Zero Charge (pH_{pzc}) of Waste Black Tea Powder. A volume of 50 mL NaCl (0.01 M) aqueous solution was added in flask as an electrolyte. The initial pH value of aqueous solution ranging from 2.0 to 11.0 was prepared, and 0.1 gram of black tea powder was added in different initial pH solutions. The mixed solution was shaken at an agitation speed of 200 rpm for 120 min at 298 K. After shaking, black tea powder was filtered, and the final pH value was measured by pH meter.

2.12. Regeneration and Reusability. In the regeneration experiment, the used black tea powder was, respectively, regenerated by using 0.05 N NaOH and deionized water at a shaker for 60 min at 298 K. The treated black tea powder was separated from the suspension and washed with deionized water in an ultrasonic shaker for 60 min and repeated for three times. After ultrasonic treatment, the regenerated black tea powder was dried in an oven at 333 K.

3. Results and Discussion

3.1. Structural and Textural Characterization. The pore structural and crystal texture were examined by N_2 sorption measurement and XRD, as shown in Figure 1. The BET surface area is measured to be 0.738 $m^2 \cdot g^{-1}$ which is relatively lower than other common-used adsorbents [18, 21, 26]. The major pore size distribution of the black tea powder can be observed in the range of 1–3 nm and belongs to the smaller pore volume. The N_2 adsorption/desorption isotherm exhibits the type IV behavior, which is characteristic of mesoporous structure based on the IUPAC classification. In addition, the feature of hysteresis loop is found at $P/P_0 = 0.9$–1.0 and suggests to be related to the capillary condensation associated with ink-bottle-shaped pores. XRD pattern shows a broad peak at $2\theta = 20.2$, which is associated with the organic functional groups. It is speculated that the lignin and cellulose may be the possible chemical compounds because they are important compositions of tea ash. No sharp peaks were detected in the XRD pattern, indicating the major species present in black tea are in form of amorphous texture. The FTIR spectrum of waste black tea powder before and after adsorption of MB revealed that the major signal features of adsorbed black tea sample corresponded to the standard MB, indicating that the MB is significantly adsorbed on the surface of black tea and resulted in the disappearance of some functional groups for fresh black tea.

3.2. Effects of Reaction Parameters on MB Adsorption

3.2.1. Effect of Contact Time. The effect of contact time on the adsorption efficiency was estimated at a dosage of 4 $g \cdot L^{-1}$ within an initial MB concentration from 100 to 2200 $mg \cdot L^{-1}$. As depicted in Figure 2, the removal efficiency of MB onto waste black tea powder increased with contact time. A rapid increase in the adsorption efficiency was observed at the first 20 min, whereas a slow rate of increase occurred as the reaction progressed. A reasonable explanation can be the surplus activated sites on the surface of adsorbents and the required diffusion time for MB molecules from the liquid to solid phase [27]. In the contact time of 60–120 min, limited increase in the adsorption efficiency was observed, which could be attributed to surface saturation with MB molecules.

3.2.2. Effect of Initial MB Concentration. The effects of the initial MB concentration on the adsorption efficiency and adsorption capacity were investigated at 298 K, a dosage of 4 $g \cdot L^{-1}$, and a contact time of 120 min. As illustrated in Figure 3, the adsorption efficiency decreased with initial MB concentration. The highest adsorption efficiency was determined to be 100% at an MB concentration of 100 $mg \cdot L^{-1}$ and decreased to 55% at 2200 $mg \cdot L^{-1}$. The results could be ascribed to sufficient active sites at a low initial MB concentration, but the constant active sites were difficult to bind the increasing MB molecules from the bulk phase. Besides, with the increase of dye concentration, the repulsion between cations of dye may increase, resulting in declining adsorption efficiency [28]. On the contrary, the initial MB concentration provides stronger driving force to overcome the resistance of mass transfer between the aqueous phase and black tea powder. Therefore, an increase in initial MB concentration enhances the adsorption capacity of MB. The adsorption capacity of MB increased from 24.98 to 302.63 $mg \cdot g^{-1}$ as the initial MB concentration increased from 100 to 2200 $mg \cdot L^{-1}$.

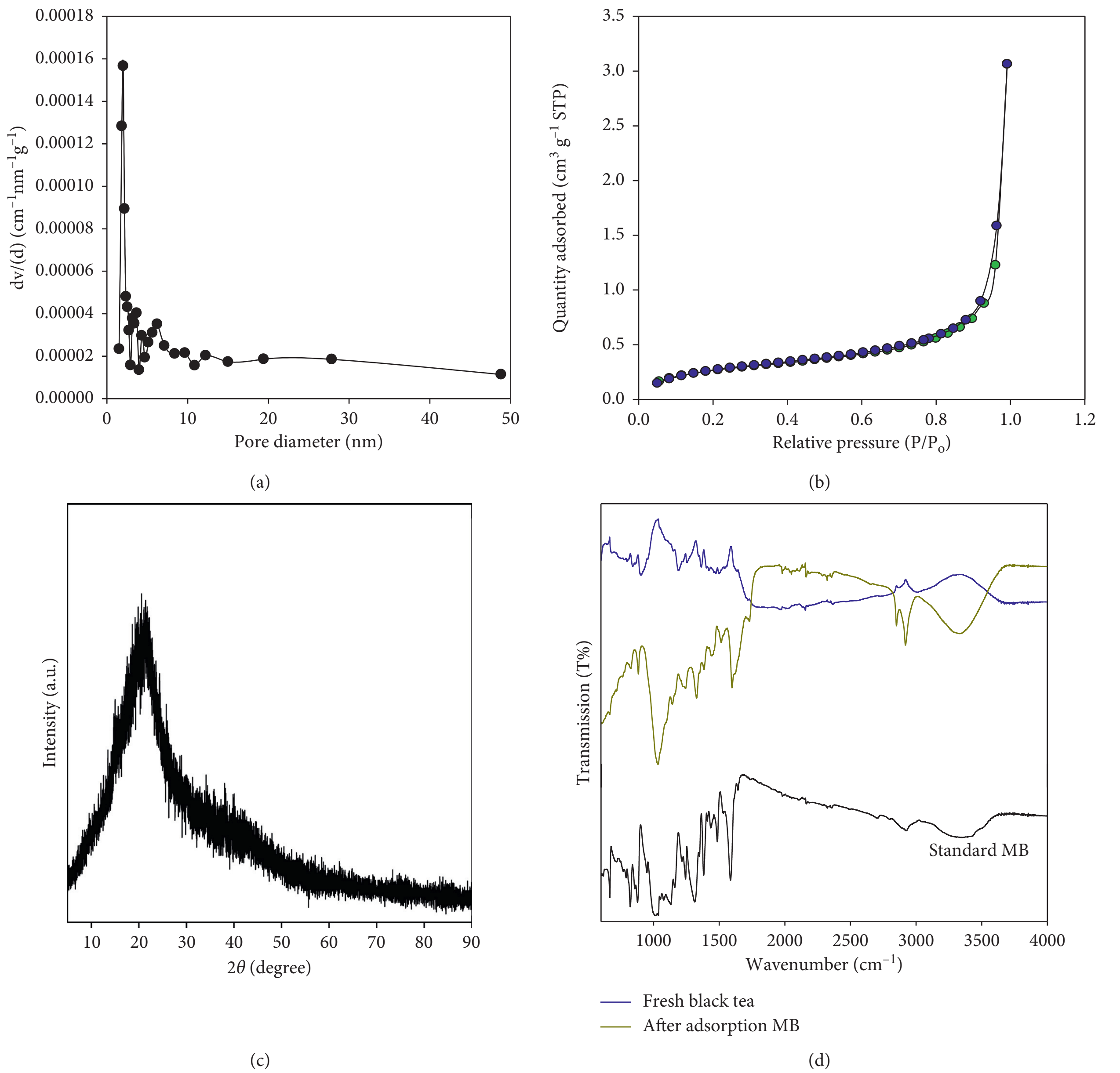


Figure 1: (a) Pore size distribution and (b) N_2 adsorption/desorption isotherms. (c) XRD pattern of waste black tea powder and (d) FTIR spectrum of black tea before and after adsorption of MB in this study.

3.2.3. Effect of the Aqueous Phase pH Value. The effect of the aqueous phase pH value was evaluated at the condition of an initial MB concentration of 1000 mg·L^{-1} and a dosage of 4 g·L^{-1}. Accompanied by the increase of aqueous phase pH values, the adsorption efficiency increased as depicted in Figure 4(a). The increase in pH from 3 to 11 caused the growth beyond 26% in the adsorption efficiency. The effects of aqueous phase pH might be related to the dissociation of the functional groups and changes in charge on the surface of waste black tea powder and the aqueous chemistry of MB molecules [29]. To further understand the point of zero charge of black tea powder, pH_{pzc} is determined in Figure 4(b). pH_{pzc} of black tea powder is estimated around 5.55 ± 0.21, and the surface charges are toward the negative charge when pH is greater than 11, whereas when the pH is lower than 4, the surface of the black tea powder becomes positively charged. On the contrary, MB is a cationic dye with positively charged ions in aqueous solution. The concentration of H^+ ion increases with decreasing pH value, causing a competition for active sites of MB between H^+ ion and cationic groups on MB. Therefore, the adsorption efficiency of MB onto black tea declines.

3.2.4. Effect of Adsorption Temperature. To understand the effects of adsorption temperature, a series of temperatures ranging from 288–323 K were investigated at different initial MB concentrations and the dosage of 4 g·L^{-1}. Experimental

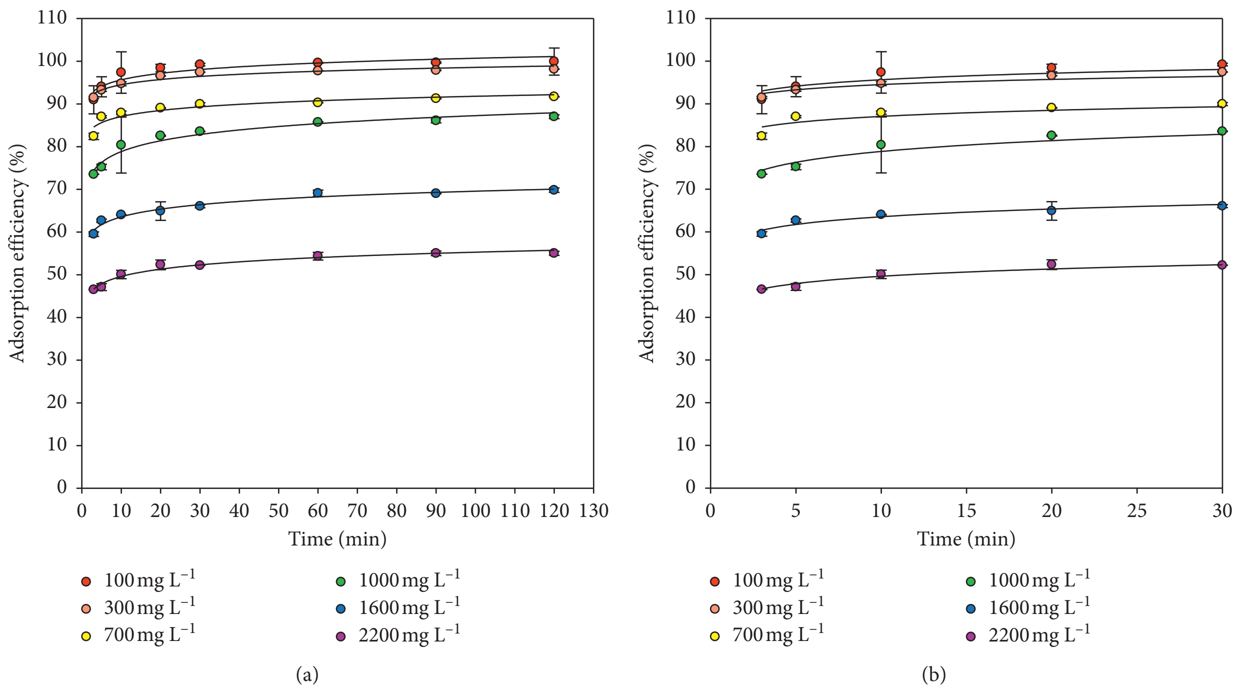


Figure 2: Effects of contact time on adsorption efficiency for various MB concentrations: (a) the whole process and (b) the first 20 min.

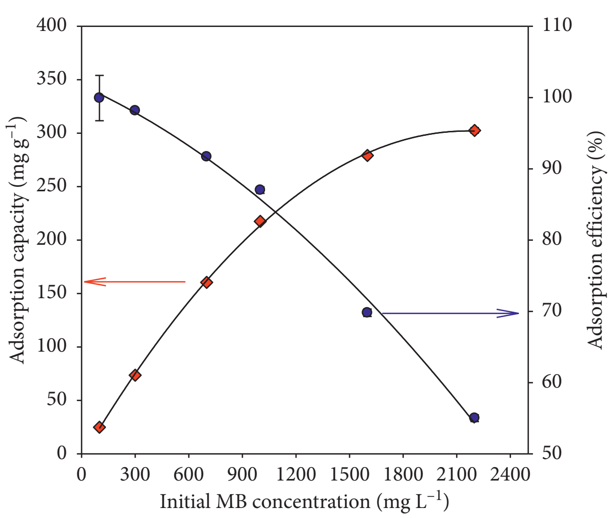
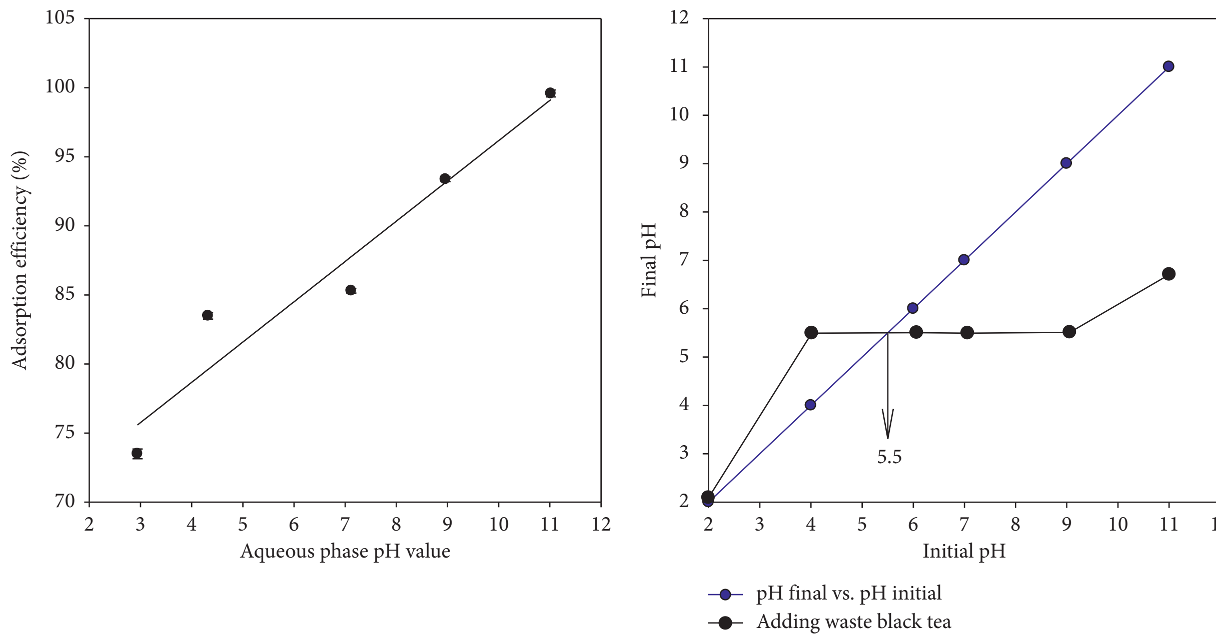


Figure 3: Effect of initial MB concentration on adsorption efficiency.

results are depicted in Figure 5. Adsorption efficiency slightly decreased with the adsorption temperature, which confirmed physical adsorption. This tendency indicated that the lower the adsorption temperature, the higher the treatment effect and suggested that the adsorption between MB and black tea powder was an exothermic process. A similar phenomenon occurred in the investigation of MB adsorption onto maize silk powder as well as methyl orange adsorption onto spent tea leaves [30].

3.2.5. Effect of Waste Black Tea Powder Dosage. Figure 6 shows the plot between adsorption efficiency and dosage of black tea powder. As shown, fitting curves at different initial MB concentrations proved that adsorption efficiency increased with the dosage of black tea powder, and the highest adsorption efficiency was achieved at 10 g·L^{-1}. This was due to the increased surface area and availability of more adsorption sites that was on account of the greater adsorption efficiency [31]. However, a negligible further increase was observed when the concentration of the dosage of black tea powder exceeded 4 g·L^{-1}. A reasonable explanation could be that under high adsorbent concentration, abundant active sites remained vacant when MB molecules were almost removed. For the consideration of treatment effect and practical benefit, the dosage of 4 g·L^{-1} probably was the suitable choice at the initial MB concentrations of 300–700 mg·L^{-1}.

3.3. Adsorption Kinetic Studies. Adsorption kinetics elucidations provide important information regarding adsorption rate and relevant coefficients for pilot scale design in the future. The fitting results obtained from pseudo-first order and pseudo-second-order models are summarized in Table 1. The correlation coefficient values (R^2) for the pseudo-second-order are more than 0.99 at different MB concentrations, which are greater than those obtained from the pseudo-first-order model. Moreover, a large difference in maximum adsorption capacities (Q_{cal}) between the experiment and calculation was found. The Q_{cal} values calculated from the pseudo-second-order model are 25.06, 161.29, and 277.78 mg·g^{-1} for different MB concentrations, which are much close to the experimental values (Q_{exp}). These findings supported the applicability of the pseudo-second-order kinetic model and indicated that chemical reactions of valence



(a) (b)

Figure 4: (a) Effect of aqueous phase pH values on the MB adsorption efficiency and (b) the point of zero charge for waste black tea.

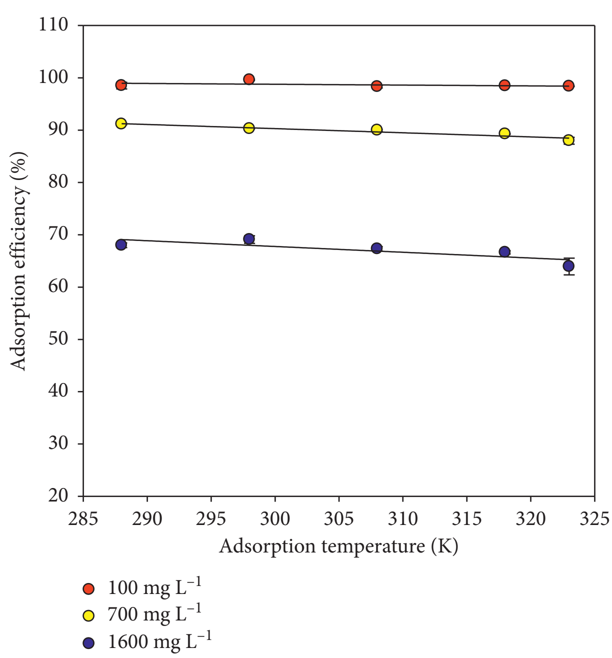


Figure 5: Effect of adsorption temperature on adsorption efficiency.

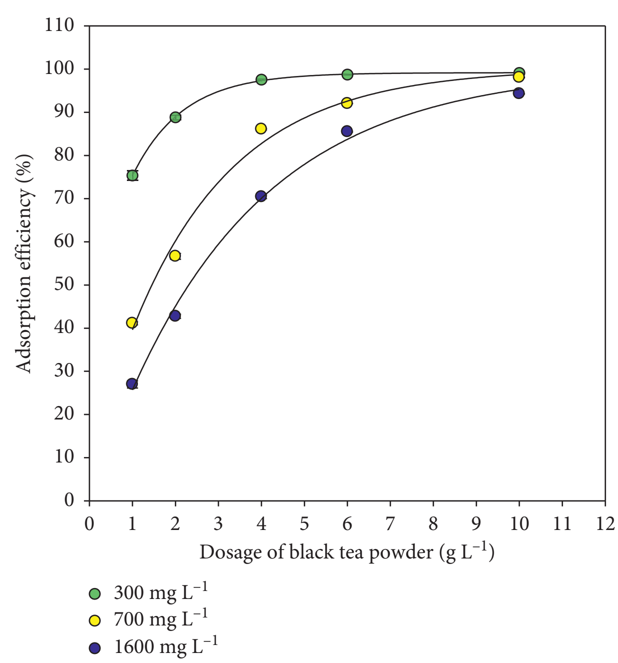


Figure 6: Effect of the dosage of waste black tea powder on adsorption efficiency.

electron forces between adsorbents and adsorbents were involved, which likely determined the rate of reaction. Studies on biological adsorbents have reported similar kinetic fitting results [22]. To further understand the possible kinetic mechanisms, the intraparticle diffusion, Boyd, and Elovich models were considered in this study. The fitting results of intraparticle diffusion, Boyd, and Elovich models for the adsorption of MB onto black tea powder are presented in Figure 7. Result of intraparticle diffusion model revealed that the internal diffusion was not the only rate-controlling step because all plots were neither essentially linear nor passed the origin over the whole process. This proved that some other mechanisms were involved in addition to intraparticle diffusion. Therefore, the diffusion mechanism was uncertain. The solute-surface interaction was restricted either on the surface or into the pores of the

Table 1: Fitting results for pseudo-first-order and pseudo-second-order kinetic models.

MB concentration ($mg{\cdot}L^{-1}$)	Pseudo-first-order model				Pseudo-second-order model		
	Q_{exp} ($mg{\cdot}g^{-1}$)	k_1 (min^{-1})	R^2	Q_{cal} ($mg{\cdot}g^{-1}$)	k_2 (min^{-1})	R^2	Q_{cal} ($mg{\cdot}g^{-1}$)
100	24.98	0.06	0.90	1.49	0.13	0.99	25.06
700	160.49	0.06	0.94	10.60	0.01	0.99	161.29
1600	279.23	0.07	0.96	36.90	0.01	0.99	277.78

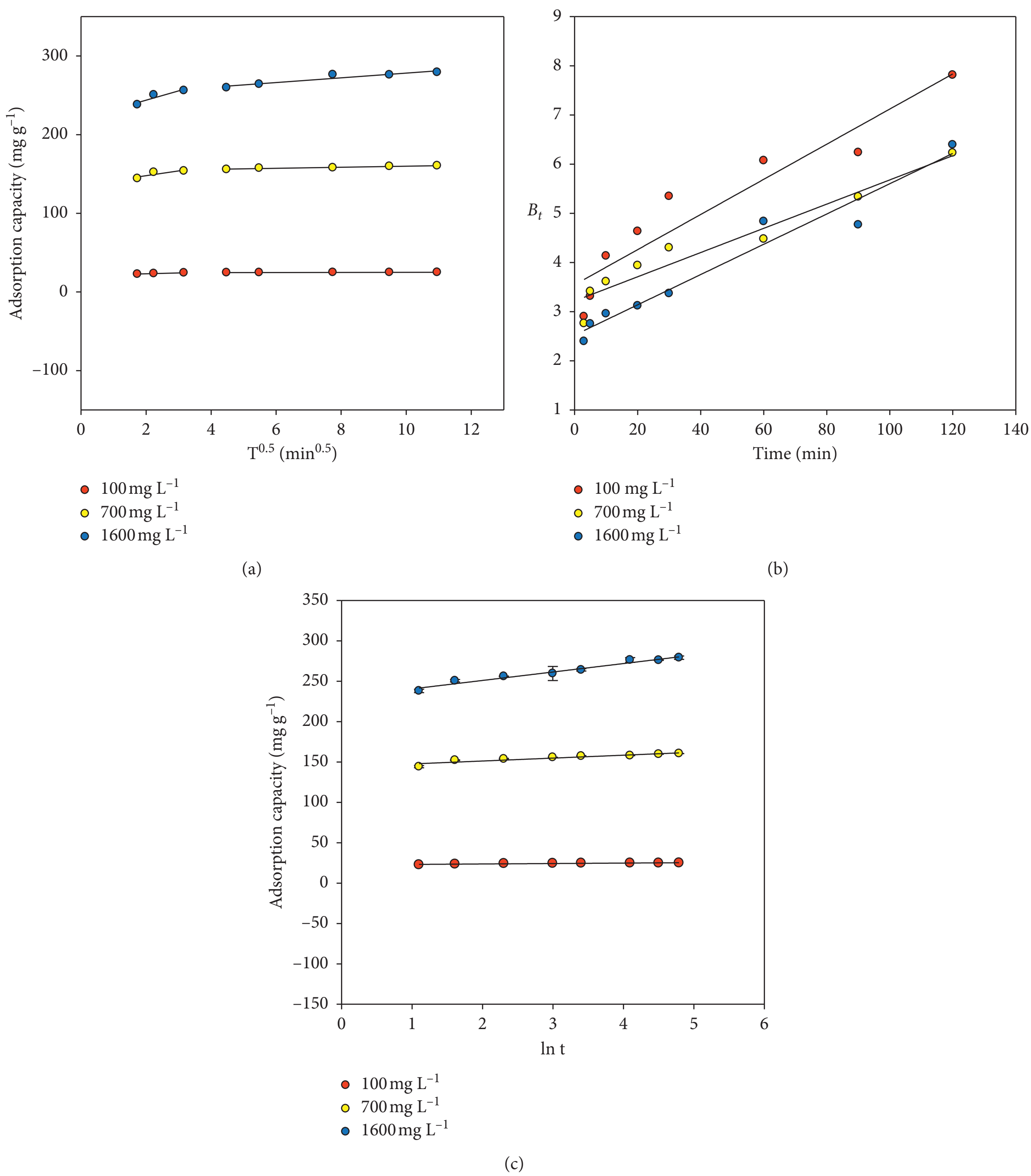


Figure 7: Fitting plots of (a) intraparticle diffusion model (b) Boyd model, and (c) Elovich model for adsorption of MB onto black tea powder.

adsorbent [32]. As shown in Figure 7(a), the adsorption of MB onto black tea powder can be divided into two steps. In the external surface adsorption stage, the first step, a rapid increase in adsorption capacity was observed, whereas in the second stage, a gradual proceed was observed in which the intraparticle diffusion was rate-limited. In addition, the existence of boundary effect was obtained. The experimental data were further analyzed by the Boyd model to determine the actual rate-controlling step in this study. As depicted in Figure 7(b), three fitting curves exhibited a linear trend, although none of these passed through the origin. Therefore, the existence of boundary effect was obtained. This supported the findings in the intraparticle diffusion model study to some extent. The linear regression correlation coefficients at 100, 700, and 1600 $mg{\cdot}L^{-1}$ were 0.90, 0.94, and 0.95, respectively, which were not highly favorable. To avoid irregularity that can occur in practice, the Elovich model was used to fit the adsorption data as shown in Figure 7(c). At different initial MB concentrations, the calculated regression correlation coefficients were all inferior to those of pseudo-second-order kinetic model, denoting the insufficiency of Elovich model for describing the relationship between MB and tea powder. Figure 8 shows the nonlinear fitting for pseudo-second-order model, intraparticle diffusion model, Boyd model, and Elovich model. Plots of these models were conform to the experimental plot among which the pseudo-second-order model fitted best. This finding suggested that chemical adsorption was more suitable to explain the mechanisms of adsorption of MB onto black tea powder, rather than physical adsorption. Furthermore, the adsorption behaviors were complex and comprehensive, such as ion exchange and multirate-controlling steps.

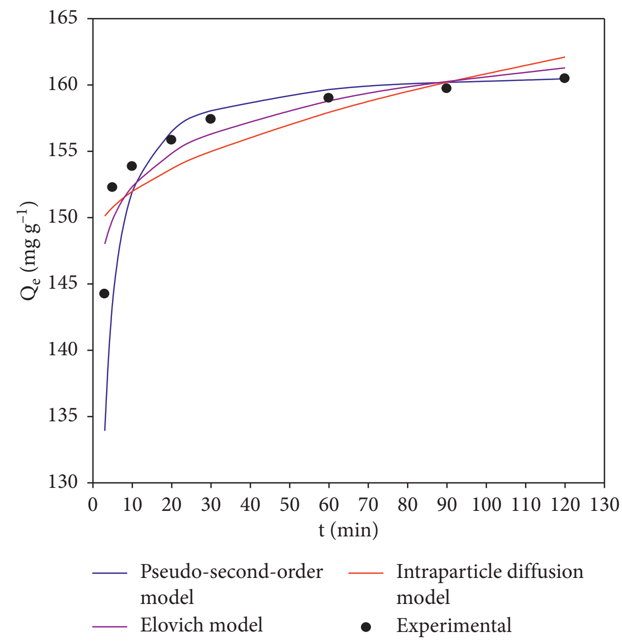


Figure 8: Nonlinear fitting plots of various kinetic models.

3.4. Adsorption Isotherm Studies. As depicted in Table 2, the Langmuir equation depicted the adsorption process satisfactorily. The R^2 value of 0.99 was achieved using the Langmuir model, which was higher than other three isotherm models. Moreover, the calculated $Q_{\max}$ value, 312.5 $mg{\cdot}g^{-1}$, was considerably close to the experimental value, 302.63 $mg{\cdot}g^{-1}$. In addition, the R_L values obtained from the Langmuir model were in the range of 0.01–0.25, which indicated that the adsorption of MB onto waste black tea powder was favorable [14]. Note that the R^2 value in the Freundlich isotherm model was 0.99, indicating a good degree of fit. In addition, the heterogeneity factor (n) was calculated to be 3.69. A reaction was classified as a favorable reaction if $1 < n < 10$ and confirmed that the adsorption was favorable. A combined analysis of the Langmuir and Freundlich isotherm models indicated that the adsorption of MB onto wasted black tea powder was a complex process that included physical absorption and chemical adsorption and monolayer absorption and multilayer adsorption. Similar results were reported in a study of MB adsorption onto neem leaf powder [33]. For the D–R model, the calculated maximum adsorption capacity was merely 194.40 $mg{\cdot}g^{-1}$, which did not concur with the experimental results. Furthermore, the R^2 value was relatively lower than other models, implying the D–R model was not applicable to describe the adsorption of MB onto waste black tea powder. The Temkin model appears to have a moderate fitting result in this study. This finding suggests that the electrostatic interaction is likely one of the mechanisms between waste black tea powder and MB. Figure 9 shows the nonlinear fittings for different isothermal models. Comparing to the experimental data and the calculated plots, Freundlich, Temkin, and Langmuir models matched well with the experimental plot at low equilibrium concentration, middle equilibrium concentration, and high equilibrium concentration, respectively. These fitting curves were close but not identical to the experimental data, indicating complex adsorption behaviors. The reaction mechanisms were speculated to include but not limited to π-π conjugation, hydrogen-bond interaction, and electrostatic interaction.

3.5. Thermodynamics Studies. To understand the spontaneous condition in this study, the thermodynamic parameters were calculated to validate the adsorption of MB onto waste black tea powder. The change in Gibb's free energy is used to determine the thermodynamic parameters shown in the following equations:

$$\Delta G^0 = RT \ln K,$$
$$\ln K = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R}, \qquad (14)$$

where ΔG^0 is the standard Gibbs free energy change of adsorption and R is the gas constant. T is the absolute temperature, and K is the rate constant of adsorption at the equilibrium state. The enthalpy (ΔH^0) and entropy (ΔS^0) can be exactly calculated from the slope and intercept of the linear straight by plotting $\ln K$ versus $1/T$. The calculated thermodynamic parameters are given in Table 3. The values

Table 2: Isotherm fittings for MB adsorption onto waste black tea powder.

Temperature (K)	Langmuir				Freundlich			Temkin			D–R	
	Q_{exp} ($mg{\cdot}g^{-1}$)	Q_{max} ($mg{\cdot}g^{-1}$)	R_L ($L{\cdot}mg^{-1}$)	R^2	n	K_f ($mg{\cdot}g^{-1}$)	R^2	A_T ($L{\cdot}g^{-1}$)	B_T ($KJ{\cdot}mol^{-1}$)	R^2	$Q_{D\text{-}R}$ ($mg{\cdot}g^{-1}$)	R^2
298	302.63	312.50	0.01–0.25	0.99	3.69	51.29	0.99	10.98	82.91	0.91	194.40	0.71

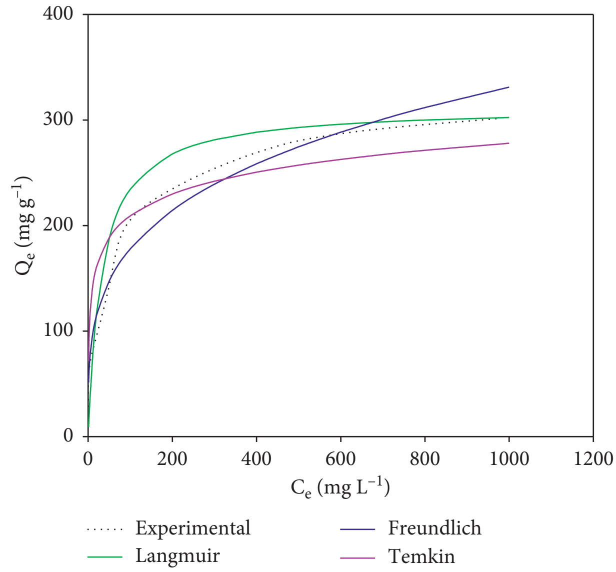


Figure 9: Nonlinear plots of isotherm models.

Table 3: Thermodynamic parameters for MB adsorption onto black tea powder.

Temperature (K)	$\triangle G^0$ ($kJ{\cdot}mol^{-1}$)	$\triangle H^0$ ($kJ{\cdot}mol^{-1}$)	$\triangle S^0$ ($J{\cdot}mol^{-1}{\cdot}K^{-1}$)
288	−5.59		
298	−5.95		
308	−5.62	−18.50	−18.09
318	−5.60		
323	−5.35		

of ΔG^0 were determined to be negatively ranged between −5.95 and −5.35 KJ/mol for different temperatures, demonstrating that the interaction between MB and waste black tea powder is a favorable and feasible adsorption process that was spontaneous and exothermic reaction ($\Delta H^0 = -18.5$ kJ/mol) over the temperature ranges of 298–323 K in this study. In addition, the negative ΔS^0 signifies the decrease in disorder at the adsorbent/aqueous phase solution interface during the adsorption process. This result is consistent with other reports obtained by Ge et al. and Kumar et al., in which their research showed the negative ΔS^0 value was calculated for adsorption of MB onto magnetic graph oxides and cashewnut shell [25, 34].

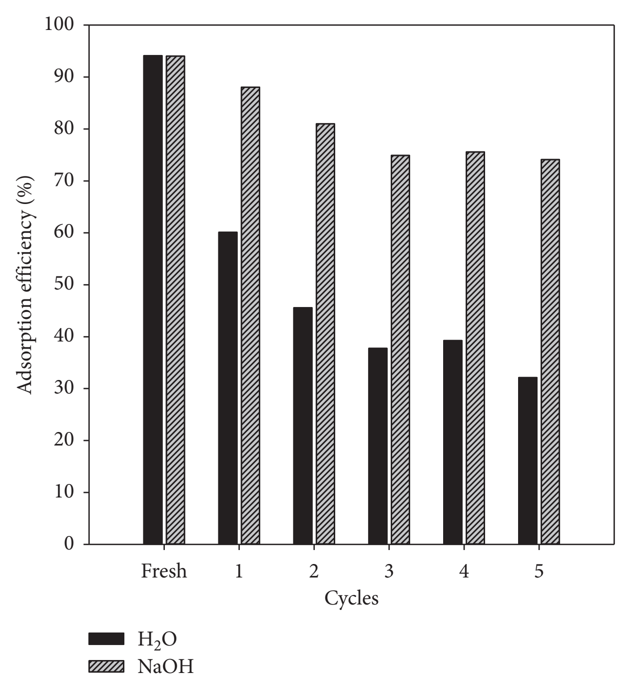


Figure 10: Regeneration and recyclability test for the adsorption of MB.

3.6. Regeneration Cycle Investigation. Regeneration and reuse of adsorbent is a critical parameter to evaluate the overall performance of adsorbent and practical applications. The adsorption efficiency of treated black tea powder is displayed in Figure 10. The adsorption efficiency decreased with regeneration cycles for H_2O and NaOH. It is evident that the used black tea powder regenerated by NaOH possesses better

Table 4: Comparison adsorption capacity of MB with different adsorbents.

Adsorbent	Adsorption capacity of MB ($mg \cdot g^{-1}$)	Reference
Raw Algerian kaolin	52.76	[38]
Mesoporous silica	65.70	[39]
Rice husk	28.50	[40]
Date palm leaves	58.10	[41]
Tea stem	103.09	[42]
Waste black tea powder	312.50	This study

adsorption efficiency, indicating that NaOH is a suitable reagent for regeneration process. After five cycles, adsorption efficiency of treated black tea powder decreased after the fifth regeneration process from about 94% to 75%, better than the result reported by other reports [35]. On the contrary, the adsorption efficiency dropped rapidly with regeneration cycles for H_2O. This implies that the interaction between tea powder and MB is relatively stronger, and desorption of MB is not easily to be reacted when H_2O was used as a regeneration reagent. The decrease in adsorption efficiency is likely attributed to some tea powder was dissolved into NaOH/H_2O and changed superficial structures of black tea powder and subsequently led to loss and blockage of adsorption sites [36, 37]. It is concluded that NaOH proves to be an acceptable desorbing agent, and used black tea powder is useful, inexpensive, ecofriendly, and competent adsorbent for dye control from the aqueous system on the basis of the regeneration results in this study.

3.7. Comparison with Other Adsorbents. Table 4 lists the comparison of maximum adsorption capacity of MB on various adsorbents. Note that the waste black tea shows a larger adsorption capacity among the reported adsorbents. On the basis of a series of experimental performances, the waste black tea powder is a potential and suitable adsorbent for removal of MB. In addition, it is believed that the waste black tea powder can be availably modified using physical or chemical treatment to enhance its adsorption affinity with different dyes and increase in adsorption capacity.

4. Conclusions

Waste black tea powder was prepared and applied to remove methylene blue (MB) from aqueous solution in a batch scale reactor. The adsorption efficiency increased with contact time, solution pH values, and waste black tea powder dosage. The maximum adsorption capacity was $302.63\ mg \cdot g^{-1}$, and the highest adsorption efficiency was 100%. From the kinetics and isotherm investigation, the pseudo-second-order model performed well at different initial MB concentrations, denoting the adsorption process of MB onto black tea was multistage chemisorption. The Langmuir model was appropriate to represent the equilibrium data, and the dimensionless equilibrium parameter (R_L) denoted that the adsorption was favorable. Thermodynamic investigation revealed the adsorption mechanism between MB and black tea powder was spontaneous and exothermic process. The multiple regeneration/adsorption experiment suggested that more than 75% efficiency could be achieved after five cycles. NaOH is a suitable desorbing agent for regeneration. Although waste black tea is a potential material for the removal of MB and some operating factors and their effects were carried out in a batch experiment, other reactor systems, such as a column mode reactor or continuous stirred tank reactor (CSTR), should be thoroughly considered in the future. In addition, some other isotherm models including Redlich–Peterson isotherm (combination of Langmuir–Freundlich model), Sip model, and Toth model could be considered for better understanding the possible adsorption behavior. Briefly, as elucidated in this research, waste black tea powder is a readily available and ecofriendly adsorbent for removing dye pollution.

Data Availability

The data generated and analyzed in this manuscript are available from the corresponding author upon request.

Disclosure

Fan Wu is the co-first author in this study.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Authors' Contributions

Dongyi Lin and Fan Wu contributed equally to this work. Fan Wu, Dongyi Lin, and Tzu-Hsing Ko conceived and designed the research and experiments. Yuqun Hu, Tingzhong Zhang, Chengshun Liu, and Qiangda Hu performed the experiments. Yufei Hu, Zhihui Xue, and Hua Han collected data, calculated experimental errors, and performed the model analysis. Dongyi Lin and Fan Wu wrote the paper, and Tzu-Hsing Ko revised the manuscript. All authors have read and approved the final manuscript.

Acknowledgments

This work was partially funded by the Construction of Modern Agricultural and Industrial Park for Anxi County, Fujian Province, Minister of Agriculture and Rural Affairs (KMD183003A), the Natural Science Foundation of Fujian Province of China (2019J01664), and the Educational and Scientific Program of Young Teacher, Department of Education, Fujian Province (JT180118). Special thanks are due to Mr. Yangshun Lin, Richun tea-industry limited company, for providing all black tea samples used in this study.

References

[1] Z. Cai, Y. Sun, W. Liu, F. Pan, P. Sun, and J. Fu, "An overview of nanomaterials applied for removing dyes from wastewater," *Environmental Science and Pollution Research*, vol. 24, no. 19, pp. 15882–15904, 2017.

[2] X. Sun, C. Wu, Y. Zhou, and W. Han, "Using DOM fraction method to investigate the mechanism of catalytic ozonation for real wastewater," *Chemical Engineering Journal*, vol. 369, pp. 100–108, 2019.

[3] L. Cundari, B. D. Afrah, D. I. Utami, and N. I. Matondang, "Adsorption model in removal of direct synthetic dyes in aqueous solution onto tea waste," *Journal of Physics: Conference Series*, vol. 1167, no. 1, pp. 12–46, 2019.

[4] N. J. Edokpayi, S. S. Ndlovu, and O. J. Odiyo, "Characterization of pulverized Marula seed husk and its potential for the sequestration of methylene blue from aqueous solution," *BMC Chemistry*, vol. 13, no. 1, p. 10, 2019.

[5] A. S. Wimalawansa and J. S. Wimalawansa, "Environmentally induced occupational diseases with emphasis on chronic kidney disease of multifactorial origin affecting tropical countries," *Annals of Occupational and Environmental Medicine*, vol. 28, no. 1, p. 33, 2016.

[6] B. Shanmugarajah, I. M. Chew, N. M. Mubarak, T. S. Choong, C. Yoo, and K. Tan, "Valorization of palm oil agro-waste into cellulose biosorbents for highly effective textile effluent remediation," *Journal of Cleaner Production*, vol. 210, pp. 697–709, 2019.

[7] L. Vutskits, A. Briner, P. Klauser et al., "Adverse effects of methylene blue on the central nervous system," *Anesthesiology*, vol. 108, no. 4, pp. 684–692, 2008.

[8] J. Rurr, J. Paiva, I. Lima, T. Alencar, C. Lage, and A. Leitão, "Microbiological decontamination of water: improving the solar disinfection technique (SODIS) with the use of nontoxic vital dye methylene blue," *Photochemistry and Photobiology*, vol. 95, no. 2, pp. 618–626, 2019.

[9] K. Indu, S. Priya, K. Vinit, K. S. Ashok, and U. Ahmad, "Superb sono-adsorption and energy storage potential of multifunctional Ag-Biochar composite," *Journal of Alloys and Compounds*, vol. 785, pp. 240–249, 2019.

[10] T. Chiong, S. Y. Lau, Z. H. Lek, B. Y. Koh, and M. K. Danquah, "Enzymatic treatment of methyl orange dye in synthetic wastewater by plant-based peroxidase enzymes," *Journal of Environmental Chemical Engineering*, vol. 4, no. 2, pp. 2500–2509, 2016.

[11] G. Kyzas and M. Kostoglou, "Green adsorbents for wastewaters: a critical review," *Materials*, vol. 7, no. 1, pp. 333–364, 2014.

[12] M. Malakootian, H. Hossaini, A. Asadipour, and M. Daneshkhah, "Preparation and characterization of modified sepiolite for the removal of acid green 20 from aqueous solutions: isotherm, kinetic and process optimization," *Applied Water Science*, vol. 8, no. 6, p. 174, 2018.

[13] S. Guiza and M. Bagane, "Equilibrium studies for the adsorption of dyes on natural clay," *Annnles de Chimie-Science des Materiaux*, vol. 29, no. 2, pp. 615–626, 2004.

[14] S. Guiza, "Biosorption of heavy metal from aqueous solution using cellulosic waste orange peel," *Ecological Engineering*, vol. 99, pp. 134–140, 2017.

[15] A. E. Kholif, M. M. Y. Elghandour, G. B. Rodríguez, O. A. Olafadehan, and A. Z. M. Salem, "Anaerobic ensiling of raw agricultural waste with a fibrolytic enzyme cocktail as a cleaner and sustainable biological product," *Journal of Cleaner Production*, vol. 142, pp. 2649–2655, 2017.

[16] D. Indira, B. Das, H. Bhawsar et al., "Investigation on the production of bioethanol from black tea waste biomass in the seawater-based system," *Bioresource Technology Reports*, vol. 4, pp. 209–213, 2018.

[17] A. Azapagic, J. Bore, B. Cheserek, S. Kamunya, and A. Elbehri, "The global warming potential of production and consumption of Kenyan tea," *Journal of Cleaner Production*, vol. 112, pp. 4031–4040, 2016.

[18] G. D. Akpen, M. I. Aho, and M. H. Mamwan, "Equilibrium and kinetics of colour adsorption from textile wastewater by a novel adsorbent," *Global Journal of Pure and Applied Sciences*, vol. 24, no. 1, pp. 61–67, 2018.

[19] Z. Li, G. Wang, K. Zhai, C. He, Q. Li, and P. Guo, "Methylene blue adsorption from aqueous solution by loofah sponge-based porous carbons," *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, vol. 538, pp. 28–35, 2018.

[20] R. M. C. Viegas, M. Campinas, H. Costa, and M. J. Rosa, "How do the HSDM and Boyd's model compare for estimating intraparticle diffusion coefficients in adsorption processes," *Adsorption*, vol. 20, no. 5-6, pp. 737–746, 2014.

[21] E. Altıntig, H. Altundag, M. Tuzen, and A. Sari, "Effective removal of methylene blue from aqueous solutions using magnetic loaded activated carbon as novel adsorbent," *Chemical Engineering Research and Design*, vol. 122, pp. 151–163, 2017.

[22] T. Smitha, T. Santhi, A. L. Prasad, and S. Manonmani, "Cucumis sativus used as adsorbent for the removal of dyes from aqueous solution," *Arabian Journal of Chemistry*, vol. 10, no. 1, pp. 244–251, 2012.

[23] A. Asmat, B. Muhammad, K. Romana, F. Robina, and S. Maria, "Ultrasound-assisted adsorption of phenol from aqueous solution by using spent black tea leaves," *Environmental Science and Pollution Research*, vol. 25, no. 23, pp. 22920–22930, 2018.

[24] M. A. Ahmad, N. Ahmad, and O. S. Bello, "Adsorption kinetic studies for the removal of synthetic dye using durian seed activated carbon," *Journal of Dispersion Science and Technology*, vol. 36, no. 5, pp. 670–684, 2015.

[25] H. Ge, C. Wang, S. Liu, and Z. Huang, "Synthesis of citric acid functionalized magnetic graphene oxide coated corn straw for methylene blue adsorption," *Bioresource Technology*, vol. 221, pp. 419–429, 2016.

[26] A. Ö6oss, Ö Ş oss, M. M. Küçük, and C. Saka, "Preparation and characterization of activated carbon from pine cone by microwave-induced $ZnCl_2$ activation and its effects on the adsorption of methylene blue," *Cellulose*, vol. 21, no. 4, pp. 2457–2467, 2014.

[27] F. H. Asaad and E. Hassan, "Production of activated carbons from waste carpets and its application in methylene blue adsorption: kinetic and thermodynamic studies," *Journal of Environmental Chemical Engineering*, vol. 5, no. 1, pp. 955–963, 2017.

[28] S. Guiza, M. Bagane, A. H. Al-Soudani, and H. B. Amore, "Adsorption of basic dyes onto natural clay," *Adsorption Science & Technology*, vol. 22, no. 3, pp. 245–255, 2004.

[29] J. Fu, Z. Chen, M. Wang et al., "Adsorption of methylene blue by a high-efficiency adsorbent (polydopamine microspheres): kinetics, isotherm, thermodynamics and mechanism analysis," *Chemical Engineering Journal*, vol. 259, pp. 53–61, 2015.

[30] S. M. Miraboutalebi, S. K. Nikouzad, M. Peydayesh, N. Allahgholi, L. Vafajoo, and G. McKay, "Methylene blue adsorption via maize silk powder: kinetic, equilibrium, thermodynamic studies and residual error analysis," *Process*

Safety and Environmental Protection, vol. 106, pp. 191–202, 2017.

[31] G. B. Oguntimein, "Biosorption of dye from textile wastewater effluent onto alkali treated dried sunflower seed hull and design of a batch adsorber," *Journal of Environmental Chemical Engineering*, vol. 3, no. 4, pp. 2647–2661, 2015.

[32] M. A. Islam, A. Benhouria, M. Asif, and B. H. Hameed, "Methylene blue adsorption on factory-rejected tea activated carbon prepared by conjunction of hydrothermal carbonization and sodium hydroxide activation processes," *Journal of the Taiwan Institute of Chemical Engineers*, vol. 52, pp. 57–64, 2015.

[33] K. Bhattacharyya and A. Sharma, "Kinetics and thermodynamics of methylene blue adsorption on neem (*Azadirachta indica*) leaf powder," *Dyes and Pigments*, vol. 65, no. 1, pp. 51–59, 2005.

[34] P. S. Kumar, S. Ramalingam, C. Senthamarai, M. Niranjanaa, P. Vijayalakshmi, and S. Sivanesan, "Adsorption of dye from aqueous solution by cashew nut shell: studies on equilibrium isotherm, kinetics and thermodynamics of interactions," *Desalination*, vol. 261, no. 1-2, pp. 52–60, 2010.

[35] A. Erdem, F. A. Ngwabebhoh, S. Çaebh, D. Bingöl, and U. Yildiz, "Fabrication and characterization of novel macroporous Jeffamine/diamino hexane cryogels for enhanced Cu(II) metal uptake: optimization, isotherms, kinetics and thermodynamic studies," *Chemical Engineering Research and Design*, vol. 117, pp. 122–138, 2017.

[36] L. Liu, S. Fan, and Y. Li, "Removal behavior of methylene blue from aqueous solution by tea waste: kinetics, isotherms and mechanism," *International Journal of Environmental Research and Public Health*, vol. 15, no. 7, p. 1321, 2018.

[37] E. Daneshvar, A. Vazirzadeh, A. Niazi, M. Kousha, M. Naushad, and A. Bhatnagar, "Desorption of methylene blue dye from brown macroalga: effects of operating parameters, isotherm study and kinetic modeling," *Journal of Cleaner Production*, vol. 152, pp. 443–453, 2017.

[38] L. Mouni, L. Belkhiri, J.-C. Bollinger et al., "Removal of methylene blue from aqueous solutions by adsorption on kaolin: kinetic and equilibrium studies," *Applied Clay Science*, vol. 153, pp. 38–45, 2018.

[39] J. L. Zhi, W. Z. Zhi, Y. S. Tian, X. S. Wen, and Y. C. Fu, "Enhanced adsorption of the cationic dyes in the spherical CuO/meso-silica nano composite and impact of solution chemistry," *Journal of Colloid and Interface Science*, vol. 485, pp. 192–200, 2017.

[40] K. R. P. Manoj, S. K. Krushnamurty, A. K. Mahammadunnisa, and C. S. Dayamani, "Preparation of activated carbons from bio-waste: effect of surface functional groups on methylene blue adsorption," *International Journal of Environmental Science and Technology*, vol. 12, no. 4, pp. 1363–1372, 2015.

[41] M. Gouamid, M. R. Ouahrani, and M. B. Bensaci, "Adsorption equilibrium, kinetics and thermodynamics of methylene blue from aqueous solutions using date palm leaves," *Energy Procedia*, vol. 36, pp. 898–907, 2013.

[42] T. C. Lee, S. Wang, Z. Huang et al., "Tea stem as a sorbent for removal of methylene blue from aqueous phase," *Advances in Materials Science and Engineering*, vol. 2019, Article ID 9723763, 15 pages, 2019.