Adsorption of Malachite Green from Aqueous Phase by Tea Stalk Powder: Parameters, Kinetic, Isothermal, and Thermodynamic Studies

Xiyao Liu,[a] Yilin Wu,[b] Wenchang Zhao,[a] Zhuanrong Wu,[c] Hua Han,[a] Zhenbang Xie,[a] Murat Yilmaz,[d] and Tzu-Hsing Ko [a,]*

Decolorization of malachite green (MG) from the aqueous phase was investigated using tea stalk powder. The adsorption efficiency decreased with the initial MG concentration, ionic strength of the solution, and heavy metal content. A suitable initial MG concentration of up to 200 mg/L can be accepted because adsorption efficiency of more than 95% is achieved. Various adsorption kinetic models were used to fit the experimental data, and the data obtained was best explained by the pseudo second-order model. The adsorption capacities calculated with the pseudo second-order model at different initial MG concentrations ranging from 24.27 to 158.7 mg/g were very close to the experimental data. The Langmuir isotherm fitted well, and the thermodynamic investigation showed that the adsorption of MG by tea stalk powder was feasible, endothermic, and spontaneous. The regeneration/adsorption experiments indicated that the tea stalk powder remained more than 95% of efficiency after six cycles using NaOH as desorbent and thus could be used many times. In conclusion, tea stalk has considerable potential as a cost-effective adsorbent for the removal of MG.

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Keywords: Malachite green; Tea stalk, kinetic; Isotherm analysis; Regeneration/adsorption cycle

*Contact information: a: Fujian Provincial Key Laboratory of Featured Biochemical and Chemical Materials, Fujian Province University Key Laboratory of Green Energy and Environment Catalysis, College of Chemistry and Materials, Ningde Normal University, Ningde city, China; b: College of Horticulture and Forestry Sciences, Huazhong Agriculture University, Wuhan city, Hubei, China; c: South China Botanical Garden, Chinese Academy of Sciences, Guangzhou city, Guangdong, China; d: Department of Chemistry and Chemical Processing Technologies, Bahçe Vocational School, Osmaniye Korkut Ata University, Osmaniye 80000, Türkiye; *Corresponding author:hsingko@gmail.com*

INTRODUCTION

Synthetic dyes are an important part of people's daily lives and are used in various fields. Approximately 12% of synthetic dyes are lost during manufacturing and processing, and 20% of the color produced is discharged into water bodies through industrial effluents, posing a threat to humans and the environment (Xu *et al*. 2009; Dou *et al*. 2012; Kumar and Kumar 2015). Malachite green is a cationic triphenylmethane dye that is widely used as an ectoparasitic, fungicide, food dye, food additive, medical disinfectant, and industrial dye. Malachite green is highly cytotoxic, affects the immune and reproductive systems, and has carcinogenic properties for mammalian cells, aquatic life, and many other organisms. Wastewater containing dyes is relatively difficult to treat because of the possible coexistence of cationic and anionic dyes, even with other compounds such as metals and NaCl. They are resistant to aerobic digestion and stable to light, heat, and oxidizing agents (Ullah *et al*. 2022). Therefore, solving the dye-induced pollution problem is increasingly crucial.

Numerous physical, chemical, and biological decolorization technologies have been used in recent decades, including coagulation, advanced oxidation and catalytic, membrane separation, biodegradation, and adsorption (Sun *et al.* 2011; Zuorro and Lavecchia 2014; Daâssi *et al.* 2014; Lau *et al.* 2015; Xu and Shao 2016). Among these existing techniques, adsorption is an acceptable method because it is inexpensive, easy to handle, and widely applicable. From the aspect of resource reuse, more attention is paid to waste and related materials that can be used as adsorbents for dye removal. Agricultural wastes as biosorbents for dye removal are potential materials because they are naturally available, renewable, non-toxic, easily converted, and can be processed without reprocessing. MG has a three-benzene ring structure compound with a molecular formula of $C_{23}H_{25}ClN_2$ (Fig. 1) and a molecular weight of 364.9 g/mol. Some reports have proposed the possible adsorption mechanisms between MG and solid adsorbent, including hydrogen bonding, electrostatic attraction, and π-π interactions (Abate *et al.* 2020). These interactions are mostly associated with the negatively charged carboxylate groups of lignocellulosic materials. Therefore, most agricultural wastes belong to lignocellulosic and have development potential for dye removal. Zhao *et al.* (2023) used kiwi peel as a biosorbent for the removal of MG. Their experimental results revealed a larger amount of $-NO_2$ and C-N functional groups on the surface of kiwi peels, and the maximum capacity of MG was reported as 580.61 mg/g based on Langmuir model simulation (Zhao *et al.* 2023). Alene and co-workers (2021) prepared the modified adsorbent by a physicochemical activation process from Gibto (*Lupinus albus*) seed peel waste. The specific surface area of the modified adsorbent was 1703 m^2/g, and the amine (N-H) functional groups, the C-H group of the alkane, and the carbonyl/carboxyl (C=O) groups were determined by FTIR. They suggested that the possible adsorption mechanism was due to electrostatic attraction and hydrogen bonding (Alene *et al.* 2021). For these reasons, the use of agricultural wastes for dye removal is still a hot topic today. In recent years, some agricultural wastes such as ginger waste (Ahmad and Kumar 2010), clove leaves (Sudarni *et al.* 2021) groundnut shells (Krishnasamy *et al.* 2022), rice husks (You *et al.* 2022), and orange peels (Guiza 2017) have been reported.

Tea is the second most consumed beverage in the world after water, and the annual production of tea is estimated to be more than 5.1 million tons in 2013, with China accounting for 36% of the total production (Azapagic *et al.* 2016; Indira *et al.* 2018). Tea stalks are one of the by-products of tea production, and many of them are directly discarded. Undoubtedly, tea stalks are widely regarded as undesirable material and most of them are collected at the local city's incinerator in China. Although using tea stalks to adsorb pollutants is not a perfect treatment, it is an intermediate solution for tea farmers, as tea stalk production is a big problem for them. Before tea stalks were used as adsorbents for dyes, the extracts of tea stalks, such as tea polyphenol, caffeine and polysaccharides, can be leached and collected for the synthesis of nano-metals. After extraction, the solid tea stalks could be used for the adsorption of dye. The authors have presented further work on the green synthesis of nano-Ce using waste tea leaf and tea stalk as well as its application for the degradation of dyes (Liu *et al.* 2021).

The objective of this study was to evaluate the potential of tea stalks as effective biosorbents for the adsorption of malachite green (MG) from the aqueous phase. A number of operating parameters, including initial MG concentration, tea stalk powder loading, ionic strength of the MG solution, operating temperature, heavy metal content , and pH of the solution were experimentally studied to determine adsorption efficiency. The equilibrium isotherms were determined with different models to understand the mechanism of MG and some kinetic models were used to fit the experimental data.

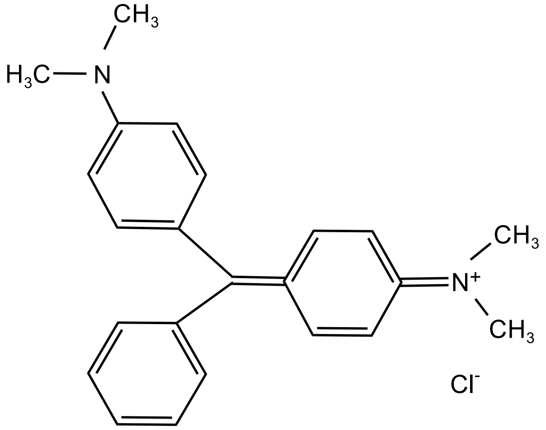

Fig. 1. The Chemical structure of malachite green (MG)

EXPERIMENTAL

Materials

All chemical reagents used in the study (malachite green, NaOH, $CuSO_4$, $ZnSO_4$, and $FeSO_4$) were of analytical grade and purchased from Sigma-Aldrich Trading Co., Ltd. (Shanghai, China). Tea samples including green tea, black tea, dark tea, oolong tea, and tea stalk were collected from the local market in Anxi county, Fujian province (Tiecha tea trading company). The BET surface area of the tea powders was 8.23 m^2/g (green tea), 2.67 m^2/g (black tea), 7.76 m^2/g (dark tea), 5.45 m^2/g (oolong tea), and 15.43 m^2/g (tea stalk). The oolong tea and tea stalk (by-product) samples are cultivated (*Camellia sinensis* var. Tieguanyin, five years old) in Mount Wuliang located in Fujian providence. The fresh tea shoots were plucked from tea trees on October 20, 2022, and manufactured by the steps of weathering, de-enzyme (also called fixation), rolling, and baking.

Tea stalks must be separated from the tea because they are undesired material for commercial tea. Based on the elemental analysis, the content of carbon, nitrogen, and hydrogen for tea stalk used in this study was 44.3%, 2.55%, and 4.41%. The water content and ash content were 4.84% and 3.80%, respectively. The contents of tea polyphenols, tea polysaccharides, and caffeine were 9.23%, 1.16%, and 1.87%, respectively. The main functional groups of the tea stalk were assigned to the bonded-OH groups (3454 cm^{-1}), aliphatic C-H group (2932 cm^{-1}), C=O stretching (1636 cm^{-1}), C-H bending (1385 cm^{-1}), C-O-C of polysaccharides (1150 cm^{-1}), and C-O-H stretching (1062 cm^{-1}). To obtain the desired tea powder samples for the adsorption experiments, the tea samples were boiled several times with distilled water at 373 K to remove the pigments. After treatment, tea samples were washed with distilled water and dried in an oven at 353 K for 24 h. The dry tea samples were crushed with agate and passed through an 80-mesh sieve. The tea powder samples were stored in a glass desiccator for the adsorption experiments.

Equipment

A thermo-controlled shaker was used to promote the adsorption interaction between MG and tea stalk powder. The shaker also controlled the adsorption temperature. A centrifuge from Eppendorf, Germany, was used to separate the tea stalk powder from the solution, and the supernatant was obtained for further analysis. A UV spectrophotometer, supplied by Shimadzu Corporation, Japan, was used to determine the absorbance value of the MG solution. The maximum absorption wavelength of the MG solution was 617 nm. The concentration of the MG solution was determined by substituting the absorbance value into the prepared standard curve.

Adsorption Experiments

The factors tested were the initial MG concentration (50, 100, 150, 200, 250, 300 and 400 mg/L of concentration), the tea stalk powder loading (0.8, 1, 2, 4, and 8 g/L), the ionic strength of the solution (0, 1, 2, 4, 6, 8, and 10% NaCl), operating temperature (283, 298, 308, and 318 K), and metal ion content (50 mg/L of $Cu^{2+,}$ Zn^{2+}, and Fe^{2+}), and the pH of the solution (3.0 to 9.0). The tea stalk powder loading was expressed by the ratio between the weight of the tea stalk powder and the volume of the solution (denoted as RM). The batch adsorption experiments were conducted in 100 mL conical flasks with 50 mL of MG solution at 298 K, 1 g/L of the tea stalk powder loading, and the pH of the solution was adjusted to 6.7±0.1 by adding a small quantity of HCl and NaOH. For the metal ion experiments, $CuSO_4$, $ZnSO_4$, and $FeSO_4$ hydrates were used to prepare the MG solution with a metal ion concentration of 50 mg/L. All the adsorption experiments were carried out in the thermo-controlled shaker (uncertainty of ± 0.5 K) with a shaking speed of 200 rpm. After adsorption, the solution was centrifuged at 5000 rpm for 5 min, and the supernatant was analyzed by UV spectrophotometer to determine the concentration of MG. Adsorption efficiency and adsorption capacity were calculated as follows,

$$\text{Adsorption capacity } (Q) = \frac{(C_o - C_t)\,V}{m} \tag{1}$$

$$\text{Adsorption efficiency } (E) = \frac{(C_o - C_t)}{C_o} \times 100\% \tag{2}$$

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

Isothermal Adsorption Experiments

In each Erlenmeyer flask, 0.1 g of tea stalk powder and 50 mL of the MG solution were mixed at a specific concentration in the thermostatic oscillator at 283 to 318 K. When reactions reached equilibrium, the mixtures were centrifuged, and the supernatant was examined. The determined adsorption capacity and adsorption efficiency were fitted with isotherm adsorption models to analyze the adsorption behavior in the experiments.

Kinetic Studies

An MG solution with a RM of 1 g/L in different initial concentrations of MG was selected as the reaction system. The system was reacted at 298 K for 60 min. The absorption value of the solution was determined, and the MG concentration was calculated. Data analysis was conducted to fit the mechanism of the reaction for different kinetic models.

Pseudo First-order and Pseudo Second-order Kinetic Models

The pseudo-first order and second order kinetic models were generally used to fit the kinetic data. The pseudo first-order model can be described by the following linear form (Azizian 2004; Hubbe *et al.* 2019):

$$ln\left(Q_e - Q_t \right) = ln\left(Q_e \right) - \frac{K_{pf}}{2.303} t \tag{3}$$

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

The pseudo-second order kinetic model is based on the sorption capacity of the solid phase and can be expressed in linear form as shown follows (Ho 2006b):

$$\frac{t}{Q_t} = \frac{1}{K_{ps} Q_e^2} + \frac{1}{Q_e} t \tag{4}$$

where K_{ps} is the constant of the pseudo second-order rate.

Intraparticle Diffusion Model

To determine the possible adsorption mechanism, the intraparticle diffusion model was selected for further investigation. In the intraparticle diffusion model, it is assumed that internal diffusion is the only rate-controlling step when the linear regression curve of Q_t versus $t^{0.5}$ passes the origin (Weber and Morris 1963; Li *et al.* 2018). The parameters of this model are calculated as follows,

$$Q_t = K_{id} t^{0.5} + C \tag{5}$$

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

Boyd and Elovich Models

The Boyd model, a theoretical model originally developed for the kinetics of ion exchange, has been shown to be applicable to adsorption systems, particularly for determining the rate-controlling step (Viegas *et al.* 2014). The Boyd model can be used to calculate the effective diffusion coefficient, provided that the Boyd plot passes through the origin, as follows,

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

where F is the ratio between the amount of adsorption at time t and the amount of adsorption at equilibrium, i.e., $F = Q_t / Q_e$, B_t is a numerical function of F. When $F > 0.85$, the relationship between F and B_t can be expressed by Eq. 7.

$$B_t = 0.4977 - ln(1 - F) \tag{7}$$

The Elovich model is mainly applicable to systems where the surface of the adsorbent is heterogeneous and applies to chemisorption kinetics, *e.g.*, electron exchange in the liquid phase (Viegas *et al.* 2014). In general, the Elovich model can be expressed as follows,

$$Q_t = \frac{1}{\beta} ln (\alpha \beta) + \frac{1}{\beta} ln (t) \tag{8}$$

where Q_t is the amount of MG adsorbed at any time t, α is the initial adsorption rate, while

β is the surface coverage extent and activation 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 $t = 0$.

Adsorption Isotherm

Four well-known adsorption isotherm models, including the Langmuir, Freundlich, Dubinin-Radushckevich (D-R), and Temkin, were used to investigate the adsorption behavior of MG onto tea stalk. The Langmuir model is used to elucidate the equilibrium between adsorbent and adsorbate, as well as the monolayer adsorption is proposed in this model (Altıntıg *et al.* 2017). The Freundlich model describes the surface heterogeneity of adsorbents and adsorption energy exponentially decreases with active sites occupation. The physical monolayer and multilayer adsorption can be described by the Freundlich isotherm model (Ali *et al.* 2018). The D-R isotherm assumes the pores distribution of an adsorbent following the Gaussian energy distribution, which is a valuable model to distinguish chemisorption or physisorption (Ahmad *et al.* 2015). The Temkin isotherm is explicitly used to consider the indirect interaction between adsorbents and adsorbates. In this model, the heat of adsorption is a function of the temperature of all molecules in the surface layer and presumes that the heat of adsorption decreases linearly rather than logarithmically with coverage. The Temkin isotherm is reasonable for the intermediate concentration range (Ge *et al.* 2016). The mathematical expressions of the four models are presented below.

Langmuir isotherm model

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{Q_m K_L} \tag{9}$$

In Eq. 9, Q_e is the amount of MG adsorbed at equilibrium, Q_m is the maximum adsorption capacity, C_e is the concentration of MG at equilibrium, K_L is the Langmuir constant that relates to adsorption capacity and adsorption efficiency. Dimensionless equilibrium parameter R_L estimates whether the Langmuir isotherm is favorable,

$$R_L = \frac{1}{1 + K_L C_o} \tag{10}$$

where C_o is the initial concentration of MG, 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.

Freundlich isotherm model

$$\ln Q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{11}$$

In Eq. 11, K_F is the Freundlich constant, and n is heterogeneity factor, related to adsorption capacity and adsorption intensity, respectively.

Dubinin-Radushckevich (D-R) isotherm model

$$\ln Q_e = \ln Q_m - K_D\, \varepsilon^2 \tag{12}$$

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,

$$\varepsilon = RT\ ln\ (1 + \frac{1}{C_e}) \tag{13}$$

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

The Temkin isotherm model is expressed as follows:

$$Q_e = \frac{RT}{B_T}\ ln(A_T\ C_e) \tag{14}$$

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.

Adsorption Thermodynamics

To explore the spontaneous condition for adsorption of MG onto tea stalks, the thermodynamic parameters were calculated based on the different temperature and the MG concentration of 300 mg/L at 60 min. The change in Gibb's free energy, enthalpy, and entropy are determined using the following equations:

$$\triangle G^0 = R\ T\ ln\ K \tag{15}$$

$$ln\ K = -\frac{\Delta H^0}{R\ T} + \frac{\Delta S^0}{R} \tag{16}$$

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 changes in 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 $1/T$.

Regeneration and Reusability

The used tea stalk powder was regenerated using a 0.05 N NaOH solution on a shaker for one h at room temperature. The treated tea stalk powder was collected from the suspension and then washed with 50 mL of distilled water in an ultrasonic shaker for one h and repeated three times. After ultrasonic treatment, the regenerated tea stalk powder was dried in an oven at 333 K. After regeneration process, the wastewater containing NaOH were collected and released to the wastewater treatment plant for further purification. The amount of wastewater containing NaOH is relatively small compared to the other wastewater coming from the industrial areas. The increase in salinity coming from the release of NaOH is controllable when they are collected to wastewater treatment plant.

RESULTS AND DISCUSSION

Screening of Various Types of Used Tea Powder for MG Adsorption

To evaluate the adsorption potential for MG, different types of waste tea powder were pretested. The adsorption efficiency after 30 min for all tea powder samples exceeded 90%, which is an acceptable for MG adsorption (Fig. 2a). The adsorption efficiency at steady-state is in the order of tea stalk > dark tea ≈ green tea > oolong tea > black tea. The adsorption efficiency increased rapidly and reached steady-state within 10 min for the tea stalk powder; more than 90% of the adsorption efficiency was achieved at a contact time of 2 min. This can be attributed to the difference in surface area of the tea powder. The tea stalk powder has a larger surface area among the test tea samples. The MG molecules are easily diffused to the surface of the tea sample due to the larger surface area. A relatively slow increase in adsorption efficiency was observed for green tea, which is probably due to the stronger mass transfer resistance within the pore structure of green tea. Based on these results, the tea stalk powder was the best material and was selected as a candidate for further testing.

Effect of Initial MG Concentration

The effect of initial MG concentration on adsorption efficiency and capacity was investigated at 298 K, tea stalk powder loading of 1 g/L, and contact time of 60 min with initial concentration of MG ranging from 50 to 400 mg/L. The adsorption efficiency remained stable at 96% within 50 to 200 mg/L and appeared to decrease when the initial MG concentration was controlled to 250 mg/L (Fig. 2b). The absorption capacity was proportional to the initial MG concentration with a linear increase from 24.34 to 158.30 mg/g. These observations are in agreement with previous reports, where the initial concentration of the dye had a positive effect on the adsorption capacity (Lin *et al.* 2020; Hu *et al.* 2019). The driving force created by the high initial concentration may have overcome the hindrance of MG adsorption between the liquid and solid phases (Cheng *et al.* 2008). Thus, the acceptable initial MG concentration can be controlled up to 250 mg/L because more than 90% of adsorption efficiency and 100 mg/g capacity were achieved.

Effect of Tea Stalk Powder Loading

The relationship between tea stalk powder loading, adsorption efficiency, and capacity was investigated (Fig. 2c). The adsorption efficiency of MG increased from 84.2% to 96.8%, while the adsorption capacity decreased from 105.35 to 12.05 mg/g when the tea stalk powder loading increased from 0.4 to 8 g/L. The adsorption efficiency remained at least 91% with a capacity of 91.45 mg/g when the tea stalk powder loading is 1 g/L, which is a suitable choice under the experimental conditions. Considering the treatment effect and practical benefit, the tea stalk powder loading of 1 g/L was judged to be the suitable choice.

Effect of Ionic Strength

Wastewater contains a large amount of inorganic salt, which acts as a barrier to adsorption. A series of different NaCl concentrations were investigated under different MG concentrations. The adsorption efficiency decreased slightly from 97 to 94% and remained stable for an MG concentration of 50 mg/L (Fig. 2d). No further serious deactivation of adsorption efficiency was observed. For 100 mg/L, the adsorption efficiency decreased from 96 to 93% and remained constant with increasing NaCl addition from 0 to 2%, and gradually decreased to about 89%. The addition of NaCl causes the competition between MG molecule and NaCl on active sites of tea stalk, as well as the adsorption efficiency of MG decreased. In addition, the salt may shield the electrostatic interaction of the surface of MG molecule and tea stalk powder because of directional moves of anions and cations due to electrostatic. This result suggests that the tea stalk powder is an acceptable adsorbent for MG when the concentration of MG is controlled to less than 100 mg/L since an adsorption efficiency of about 90% is achieved in a NaCl range of 0 to 8%.

Effect of Operating Temperature

Temperature affects adsorption efficiency and can help answer the question of whether physisorption or chemisorption occurs during the reaction. The adsorption experiments were carried out at 283, 298, 308, and 318 K under different MG concentrations. A slight increase in adsorption efficiency with temperatures was observed for the cases of 50 and 100 mg/L (Fig. 2e). In contrast, there was a noticeable increase in adsorption efficiency with temperature for the case of 300 mg/L. The adsorption efficiency increased from 77 to 90% when the temperature is increased from 283 to 318 K. The plausible reasons for this result could be that the kinetic energy of MG increased at a higher temperature, thereby enhancing the collision frequency between the active sites due to the decreasing viscosity of the aqueous solution. Based on the above results, the adsorption between MG and tea stalk powder is an endothermic process.

The Effect of Metal Ions

Wastewater contains trace metals such as Cu^{2+}, Zn^{2+}, Fe^{2+}, *etc*., which leads to a competitive adsorption effect for the whole reaction. To understand the effect of metal ions on the removal behavior, an effluent containing Cu^{2+}, Zn^{2+}, and Fe^{2+} was studied. The adsorption efficiency decreased with the addition of metal ions (Fig. 2f). The adsorption efficiency decreased to 86.4%, 90.7%, and 90.8% at the equilibrium phase with the addition of Cu^{2+}, Zn^{2+}, and Fe^{2+}, respectively. No difference was observed between Zn^{2+} and Fe^{2+}, while the addition of Cu^{2+} had the worst effect on adsorption efficiency.

This result can be attributed to the competition between metal ions and MG on the surface of the tea stalk. This competition decreases the adsorption efficiency. Moreover, the hydration radius is defined as the radius of the ion and the closely bound water molecules. The ions with larger size and smaller charge hold the water molecules less tightly and therefore have a smaller atomic radius. The hydrated radii for Cu^{2+}, Zn^{2+}, and Fe^{2+} are 0.419, 0.43, and 0.428 nm, respectively. The smaller atomic radius can diffuse more easily into the internal pore structure of the adsorbent, and causes a competitive reaction with other species. The wastewater containing Cu^{2+} shows the worst performance due to its smaller atomic radius and greater electronegativity.

The Effect of pH of the solution

To understand the effect of pH on adsorption efficiency, a series of experiments were conducted in a pH range from 3.0 to 9.0 and the point of zero charge of tea stalk was also investigated. The adsorption efficiency showed a remarkable increase with pH from 3.0 to 7.0 and remains constant above 7.0 (Fig. 2g). Similar results have been reported for the adsorption of MG by rice husk, pine cone, and *Catha edulis* stem (Chowdhury *et al.* 2011; Abate *et al.* 2020; Kavci 2021). MG is a cationic dye and the number of negatively charged sites on the adsorbent increases with pH, resulting in further enhancement of the electrostatic interaction between the cationic MG molecules and the tea stalk. Moreover, the point of zero charge of the tea stalk is determined at 6.7 (Fig. 2h), indicating that the surface charges are potentially negatively charged at pH higher than 6.7. Therefore, the effect of pH on the adsorption of MG in this study reveals that the adsorption efficiency remains constant in the pH range from 7.0 to 9.0, which is consistent with the point of zero charge of the tea stalk.

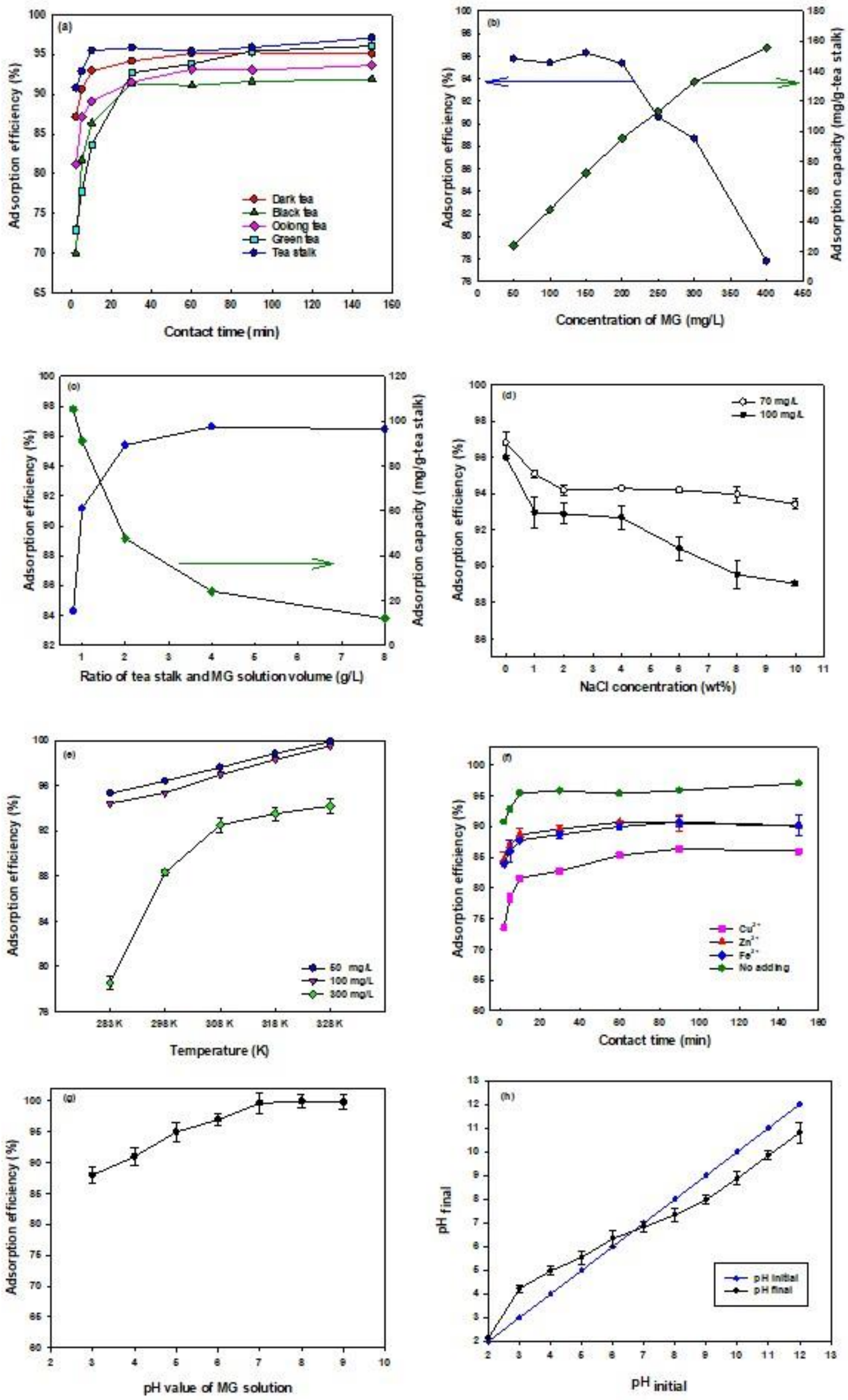

Fig. 2. A preliminary screen of various types of tea powder and other operating parameters for the removal of MG from the aqueous phase in this study (a) types of tea powder, (b) concentration of MG, (c) tea stalks loading, (d) ionic strength, (e) operating temperature, (f) metal ions, (g) pH of solution, and (h) point of the charge

Adsorption Kinetics

Typical adsorption kinetic models, including pseudo first-order, pseudo second-order, intraparticle diffusion, Elovich, Bangham, and Boyd models were used to understand the adsorption behavior between MG and tea stalk powder, as shown in Fig. 3 and Table 1. Note that the R^2 values for the pseudo first-order model at different concentrations of MG ranged from 0.80 to 0.98, while the R^2 values for the second-order model are better than 0.99. The Q_{max} values derived from the pseudo second-order model were very close to the experimental values (Q_{exp}), indicating that the pseudo second-order model is more suitable. These results support the applicability of the pseudo second-order kinetic model.

The fitting result of the Elovich model was better than that of the pseudo first-order, and the R^2 was larger with increasing MG concentration, suggesting that the Elovich model is more appropriate for describing higher MG concentrations. The value of α (initial adsorption constant) was higher than β (desorption constant), indicating that the overall reaction in this study is centered on the adsorption process.

This also explains why the initial adsorption efficiency of MG onto tea stalk powder was high and the adsorption rate decreased with contact time. Although the above kinetic models provide some important insights, they do not shed light on the diffusion mechanism and rate-controlling steps associated with the adsorption phenomena. Therefore, the intraparticle diffusion, Bangham, and Boyd models were applied to determine whether diffusion was the rate-limiting step.

The intraparticle diffusion model presented three stages (Fig. 3e). The first stage represents the transport of MG molecules from the bulk solution to the external surface of the tea stalk powder by diffusion through the boundary layer; the adsorption capacity increased rapidly due to more available sites on the surface. The second stage showed a slower adsorption rate of MG compared to the first stage. It is due to the available sites on the external surface were saturated (Da’Na *et al.* 2011). In the third stage, the adsorption reached equilibrium.

The slopes of the first stage were higher than those of the second stage, which means that the mass transfer resistance between the external boundary layer film of the liquid and the adsorbent was relatively lower, causing the rapid adsorption rate in the first stage. Moreover, the intercepting lines of three stages did not go through the origin. This illustrated that internal pore diffusion was not the only rate-controlling step and some other mechanisms along with the intraparticle diffusion are probably involved (Cheung *et al.* 2007; Du *et al.* 2014).

To determine whether surface diffusion or pore diffusion is the critical step in the adsorption of MG, the Bangham and Boyd kinetic model was applied to define the actual rate-controlling step in the adsorption process. The Bangham model can be used to determine whether pore diffusion is the only rate-controlling step. The fitting results show that all the plots tend to a straight line with R^2 of 0.89-0.97, which is an acceptable fit and illustrates that pore diffusion is not the only rate-controlling step. The plots of the Boyd model also tend toward a linear line, but do not pass through the origin for all concentrations of MG. This suggests that the adsorption rate of MG onto tea stalk powder was mainly governed by surface diffusion.

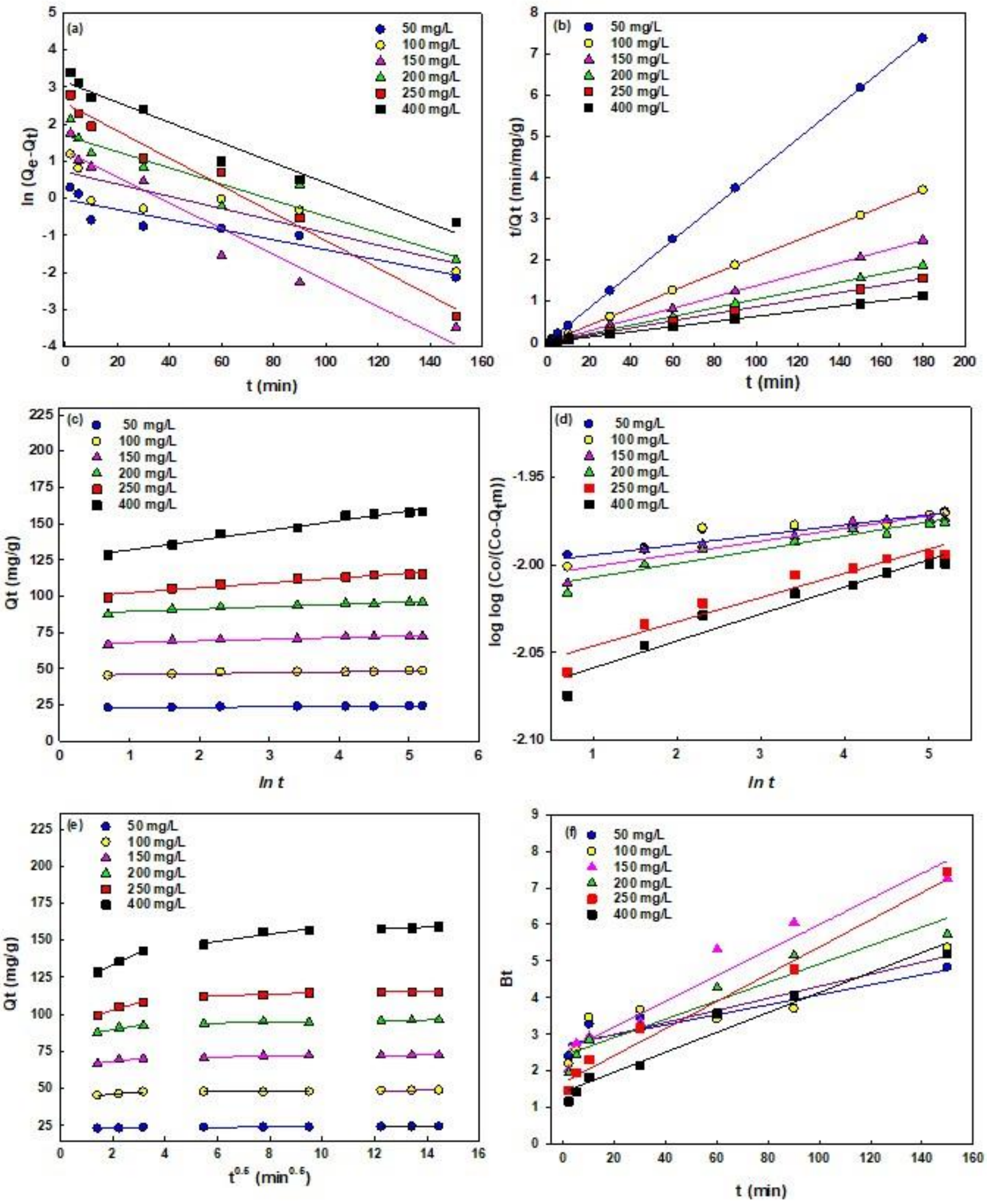

Fig. 3. Fitting plots of (a) pseudo-first-order model, (b) pseudo-second-order model, (c) Elovich model, (d) Bangham model, (e) intraparticle-diffusion model, and (f) Boyd model for the adsorption of MG onto tea stalk powder

Table 1. Kinetic Parameters of MG Adsorption by Tea Stalk Powder at Different Concentrations

MG Concentration (mg/L)	Pseudo-first-order				Pseudo-second-order			Elovich			Bangham	Intraparticle diffusion First stage			Intraparticle diffusion Second stage		
	Q_{exp} (mg/g)	K_1 (1/min)	R^2	Q_{max} (mg/g)	K_2 (1/min)	R^2	Q_{max} (mg/g)	α	β	R^2	R^2	K_{id}	R^2	C	K_{id}	R^2	C
50	23.39	0.01	0.87	0.97	0.12	0.99	24.27	$2.42*10^{7}$	3.88	0.90	0.89	0.45	0.95	22.36	0.05	0.88	23.58
100	48.67	0.02	0.80	2.04	0.06	0.99	48.54	$3.51*10^{19}$	1.63	0.82	0.81	1.35	0.99	43.46	0.10	0.61	47.18
150	72.44	0.04	0.95	3.57	0.04	0.99	72.46	$1.29*10^{29}$	0.82	0.91	0.90	1.92	0.82	64.45	0.21	0.68	70.11
200	96.18	0.02	0.89	5.44	0.02	0.99	96.15	$2.35*10^{38}$	0.59	0.92	0.91	2.84	0.95	84.14	0.27	0.72	92.62
250	115.26	0.04	0.98	12.93	0.01	0.99	114.9	$2.48*10^{43}$	0.28	0.95	0.94	5.26	0.94	92.29	0.45	0.94	109.90
300	136.77	0.05	0.87	28.25	0.01	0.99	136.9	$2.84*10^{50}$	0.22	0.95	0.94	7.22	0.97	105.70	0.80	0.98	127.20
400	158.30	0.03	0.96	22.95	0.01	0.99	158.7	$9.57*10^{54}$	0.14	0.98	0.97	8.35	0.99	116.70	1.46	0.75	141.60

Table 2. Isothermal Fittings for the MG Adsorption onto Tea Stalk Powder

Temp. (K)	Q_{exp} (mg/g)	Langmuir			Freundlich			Dubinin-Radushkevich			Temkin		
		Q_{max} (mg/g)	R_L	R^2	n	K_F	R^2	B	Q_{max} (mg/g)	R^2	B_T	A_T	R^2
283	115.92	123.31	0.03-0.16	0.99	2.39	19.79	0.95	1.97	91.90	0.88	87.38	1.10	0.99
298	133.12	138.73	0.04-0.21	0.99	1.71	16.85	0.98	1.67	102.21	0.86	62.07	0.80	0.99
308	135.85	139.57	0.02-0.12	0.99	1.94	24.26	0.99	0.61	100.14	0.83	71.69	1.51	0.99
318	136.16	141.62	0.02-0.14	0.99	1.83	22.21	0.07	0.84	108.53	0.89	69.08	1.24	0.99

Adsorption Isotherm Studies

Four adsorption isothermal models were used to fit the experimental data at different temperatures, and the results are summarized in Table 2. The Langmuir and Temkin models showed the best fit with an R^2 value of 0.99 within the specified temperatures. The good fit of the Langmuir model reflects that monolayer coverage of MG onto tea stalk powder may be one of the main adsorption mechanisms. Moreover, all R_L values are between zero and one at different temperatures, indicating that the adsorption of MG onto the surface of the tea stalk powder is a favorable process. The maximum capacities estimated by Langmuir are very close to the experimental values at all temperatures. Higher R^2 values were also obtained for the Temkin model, suggesting that the electrostatic interaction may play a crucial role during the adsorption process. The Freundlich isotherm model shows moderate fits to the experimental data. For the D-R model, the calculated maximum adsorption capacities differed obviously from the experimental results compared to the Langmuir model and the R^2 values were relatively lower than the other models, implying the D-R model was not applicable in this study. In sum, the Langmuir isotherm model is suitable to describe the adsorption behavior of MG onto tea stalk powder.

Thermodynamics Studies

The calculated thermodynamic parameters at 300 mg/L of MG and different temperatures are shown in Table 3. The ΔG values were determined to be negative between -1.22 and -4.52 KJ/mol for different temperatures, which shows that the interaction between MG and tea stalk powder is a favorable and feasible adsorption process that proceeded spontaneously with an endothermic reaction over the temperature ranges of 283-318 K in this study. This result is consistent with the effect of operating temperature, where the adsorption efficiency increased with temperature. Similarly, the positive value of ΔS signifies the increase in disorder at the interface of MG and tea stalk powder.

Table 3. Thermodynamic Parameters of MG Adsorption onto Tea Stalk Powder

Temperature (K)	△G (kJ/mol)	△H (kJ/mol)	△S (J/mol/K)
283	-1.22	25.86	96.75
298	-3.45		
308	-4.14		
318	-4.52		

Regeneration Cycle Investigation

In addition to better adsorption efficiency and higher adsorption capacity, the extent of regenerability is also important to evaluate the quality of the adsorbent for practical applications. To investigate the regenerability of the tea stalk, six regeneration/adsorption cycles were performed (Fig. 4). After regeneration, excellent regeneration performance was observed. The removal efficiency remained constant (more than 95%) and no further deactivation is observed (Fig. 4a). The adsorption efficiency even was greater than 99% for the fifth cycle (Fig. 4b). This result is similar to a previous study, in which the adsorption efficiency of methylene blue was about 97% after six regeneration cycles under the same conditions with using tea stalk powder as an adsorbent (Lee *et al.* 2019).

The color of MG solution was clearly distinguishable after different regeneration/adsorption cycles (Fig. 4c). The explanation for the excellent regeneration performance of the tea stalk powder can be attributed to the complete desorption of MG from the surface of the tea stalk powder when NaOH solution was used as the desorbent. Moreover, it is reported that the surface and pore structure of the tea stalk powder is changed by the regeneration process, and the adsorption sites on the tea stalk powder are more active and difficult to collapse and clog (Daneshvar *et al.* 2017).

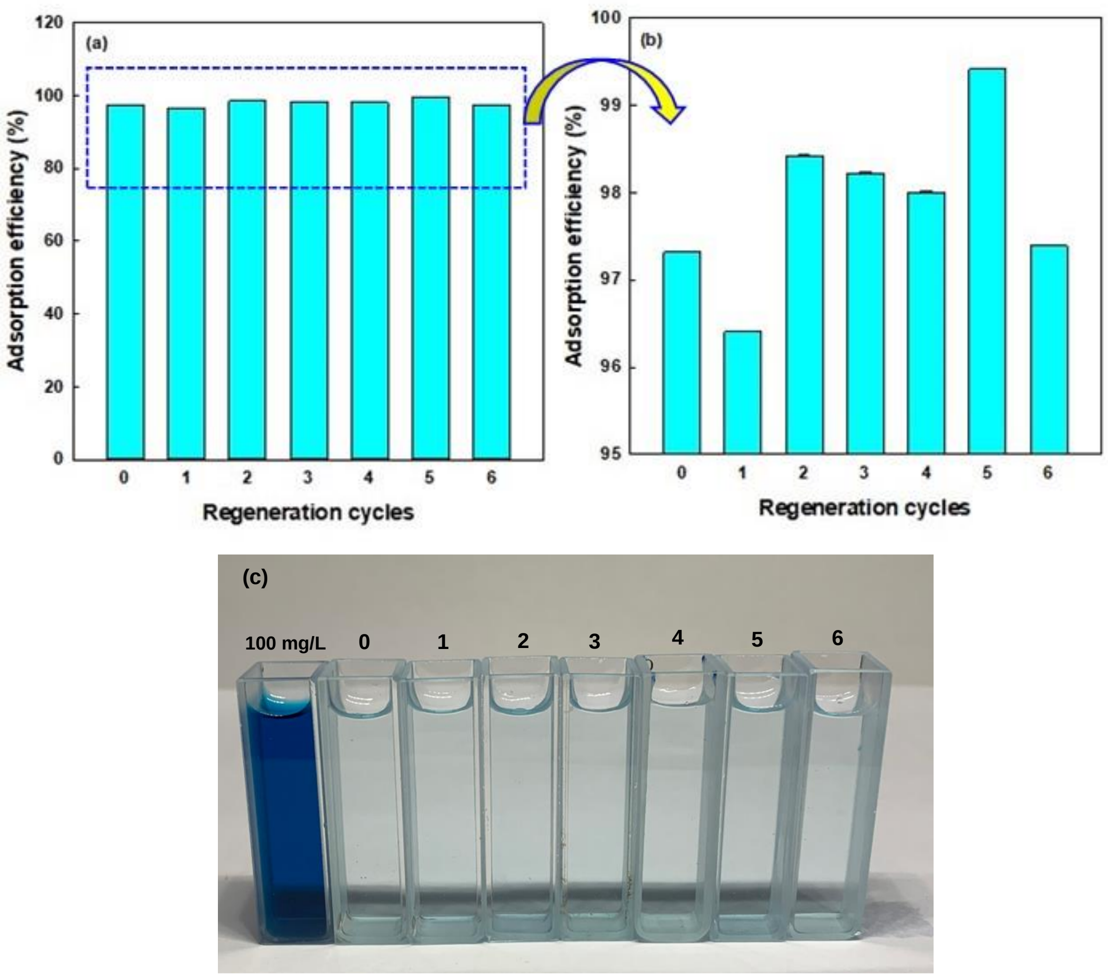

Fig. 4. Regeneration and recyclability test for the adsorption of MG (a), the interval 95% to 100% (b), and the color of MG solution before and after regeneration/adsorption cycles (c)

Comparison with Other Adsorbents

Table 4 shows the comparison of the maximum adsorption capacity of MG on various adsorbents. Note that the tea stalk had a larger adsorption capacity among the reported adsorbents. On the basis of a series of experimental performances, the tea stalk is a potential and suitable adsorbent for the removal of MG. Moreover, it is believed that the tea stalk can be modified using a physical or chemical treatment to improve its adsorption affinity with different dyes and increase the adsorption capacity.

Table 4. Comparison of Adsorption Capacity of MG with other Reported Natural Adsorbents

Adsorbent	Adsorption Capacity of MG (mg/g)	Reference
Seashell powder	42.33	(Chowdhury and Saha 2010)
Degreased coffee bean	55.30	(Baek *et al*. 2010)
Mango seed husks	47.90	(Franca *et al.* 2010)
Rattan sawdust	28.50	(Hameed and El-Khaiary 2008)
Neem sawdust	58.10	(Khattria and Singh 2009)
Treated ginger waste	84.03	(Ahmad and Kumar 2010)
Wood apple shell	34.56	(Sartape *et al.* 2017)
Walnut shell	90.80	(Dahri *et al.* 2014)
Tea stalk	133.50	this study

CONCLUSIONS

1. This study demonstrated the applicability of tea stalks as a sustainable biosorbent for the removal of malachite green (MG) from an aqueous solution. The results of batch experiments showed that the adsorption efficiency of MG was affected by the initial MG concentration, tea stalk powder loading, ionic strength of the solution, operating temperature, and heavy metal content.
2. The kinetic study suggested that the pseudo second-order model fitted well and is the optimal adsorption model to describe the adsorption of MG onto tea stalk powder. Adsorption isotherm results exhibited that the adsorption of MG fitted well to the Langmuir model. The adsorption capacity could be predicted in the range of 123.3 to 141.6 mg/g when the temperature was controlled at 283 to 318 K.
3. The thermodynamic investigation showed that the adsorption of MG by tea stalks was feasible, endothermic, and spontaneous in nature. The results of regeneration/adsorption experiments indicated that the tea stalks powder remained more than 95% of efficiency after six cycles using NaOH as a desorbent and thus be used for many times.

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