



Kinetic modeling of methylene blue adsorption onto acid-activated spent tea: A comparison between linear and non-linear regression analysis

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Original Article

Abstract

The kinetic study of methylene blue (MB) adsorption using acid-activated spent tea (AASST) as an adsorbent from aqueous solution with the aim of comparing linear and non-linear regression analysis methods was performed at varying initial MB concentrations (10-100 mg/l). Hence, spent tea leaves, which were activated using concentrated sulfuric acid, were prepared. The physicochemical characteristics of the prepared adsorbent were also measured. In addition, a scanning electron microscope (SEM) and Fourier transform infrared spectroscopy (FTIR) instruments were employed to determine the size, morphology, and functional groups of AASST. Furthermore, the influence of different particle sizes of adsorbent on the adsorptive removal efficiency of MB was evaluated. The obtained data on MB adsorption were fitted using 4 kinetic models, namely pseudo first-order, pseudo second-order, Elovich, and intraparticle diffusion (I-D). The results of kinetic investigations showed that pseudo second-order kinetic model compared to the other applied models, with significant coefficient of determination ($r^2 > 0.98$), could best fit the experimental data of MB adsorption. In addition, among all linear forms of the pseudo second-order model, form 1 could better fit the MB adsorption data. Additionally, by comparing the performance of both linear and non-linear forms of the pseudo second-order kinetic model, it can be postulated that non-linear regression analysis could be more appropriate than the linear approach for kinetic study of MB adsorption onto the AASST adsorbent. Ultimately, based on the results of particle size experiments, the smaller the size of the adsorbent particles, the higher the adsorption efficiency of MB will be.

KEYWORDS: Adsorption, Kinetic, Linear and Non-Linear Models, Methylene Blue, Spent Tea

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Introduction

Removal of toxic compounds from soil and water resources has always been one of the most paramount concerns of environmentalists. Dyes

are colored substances and are found in the wastewater of several industries, such as textile, leather, paper, and plastic.¹ The discharge of such wastewater into the water resources will cause a wide range of problems, like harmful influence on photosynthesis and enhancement of the chemical oxygen demand (COD).² Until now, numerous conventional

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techniques, such as oxidation or ozonation,^{3,4} coagulation and flocculation,⁵ reduction,⁶ and membrane separation,⁷ have been employed to treat water polluted with MB or other colored compounds. These processes are apparently costly and have several operational difficulties, due to which they are not able to effectively eliminate large concentrations of MB from industrial and agricultural effluents. Therefore, the application of a cost-effective and highly efficient remediation technique is prescribed.

Among all treatment techniques, adsorption is recommended as a well-known and popular approach for removal of dyes due, in essence, to its operational simplicity, economic benefits, and insensitive nature toward poisonous substances. Based on existing literature, some agricultural waste products, such as wheat husk,^{8,9} rice husk,^{10,11} pomelo (*Citrus grandis*) peel,¹² and *Posidonia oceanica* (L.) fibres,¹³ as well as some cheap materials, like sawdust,¹⁴ perlite and clay,^{15,16} fly ash,¹⁷ and natural zeolite,¹⁸ were extensively investigated as alternative adsorbents for MB removal.

Tea plantation farms are widely visible in Northern Iran. Dried and smashed leaves of tea bushes have largely been consumed as one of the most popular beverages among Iranians. The remaining spent tea materials of tea production process are not practical and are either stored or disposed as waste. Hence, the management and utilization of these enormous wastes in the environmental context is a critical necessity. Until today, spent tea leaves have been used for remediation of a large number of environmental pollutants. Amarasinghe and Williams reported that the application of spent tea materials in the removal of copper and lead showed fruitful results.¹⁹ In another research, Wasewar et al. stated that tea factory waste materials, during batch experiment studies, could easily remove high concentrations of zinc from aqueous solution.²⁰ In the present study, spent tea materials were treated with concentrated sulfuric acid in order to increase their capacity to

adsorb MB from aqueous media.

To design a batch sorption system, the determination of kinetics reaction is a crucial point because through kinetic data, information on the rate of adsorbate uptake onto the adsorbent surfaces and factors influencing reaction rate are obtained.²¹ Generally, the most commonly used kinetic models to express the processes between liquid and solid surfaces are pseudo first-order and pseudo second-order models. Although some studies have revealed that pseudo first-order model can best fit the experimental data of contaminants adsorption,²² a research has confirmed the lack of ability of the corresponding model to predict the theoretical adsorption capacity of adsorbents.²³ In recent years, pseudo second-order model has been commonly used as it best expresses the kinetic reaction of some pollutants in a series of batch experiments. However, the linear form of the pseudo second-order model proposed by Blanchard et al. results in lackluster performance in the prediction of the adsorption capacity of pollutants.²³ Therefore, an analysis of the performance and ability of both linear and non-linear forms of kinetic models in predicting kinetic parameters is vital.

Even though MB adsorption using spent tea has been performed previously, to the best of our knowledge, no comparative study of non-linear and linear kinetic approaches of MB adsorption onto acid-activated spent tea (AAST) has been performed. Therefore, the objectives of the present paper are synthesis and characterization of AAST, and comparison of kinetic model efficiency and obtained kinetic parameters of MB adsorption onto AAST using both non-linear and linear methods.

Materials and Methods

MB ($C_{16}H_{18}ClN_3S \cdot 3H_2O$) (Figure 1), concentrated hydrochloric acid, sulfuric acid, and sodium hydroxide were purchased from Merck & Co. (Kenilworth, NJ, USA). All reagents were

analytical grades. The stock solution of MB was prepared by dissolving a segment of MB into 1000 mL of distilled water, then, diluting to reach MB solutions with desirable concentrations. Furthermore, the solutions were kept in a dry environment at 4 °C.

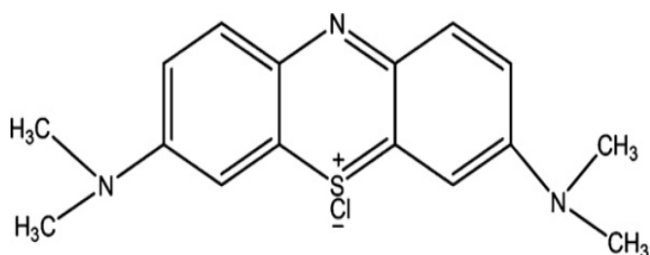


Figure 1. The structure of methylene blue

To prepare the adsorbent, spent tea material of household tea waste were employed. Initially, tea leaves were washed completely with distilled water to remove all chemical or physical impurities. Then, spent tea was decolorized through boiling in distilled water at 100 °C, and, subsequently, kept and dried in an electric oven at 65 °C. Then, the resulted spent tea was activated through immersion in a strong sulfuric acid solution followed by a few minutes of vigorous shaking. Then, they were washed with distilled water to reach a pH of 7. The principal objective of acid washing of adsorbent was the activation of the adsorbent surfaces through the creation of numerous pores on the internal and external surfaces in order to increase the ability of adsorbent to remove MB. In the next step, obtained AAST materials were oven dried at 105 °C, and then, passed through a range of steel sieves. In accordance with the ASTM Method, only particles between 100 and 250 µm in diameter mesh size were used throughout the study, apart from studying the effect of adsorbent particle size. Finally, AAST was dried at 80-85 °C for about 2 hours, and then, kept in plastic bags in a dry environment until the beginning of the batch experiments.

Initially, the moisture and ash content, chemical composition, water soluble and insoluble substances, and the volatile fraction of

the adsorbent were determined. To find the morphological features of AAST, a scanning electron microscope (SEM) (Philips Co., Netherlands) was applied. Furthermore, Fourier transform infrared spectroscopy (FTIR) was used to find the surface functional groups of the AAST. The specific surface area of adsorbent was measured using adsorption/desorption technique using the Brunauer-Emmett-Teller (BET) method. Moreover, pH of zero point charge (pH_{ZPC}) of AAST was measured at varying pH values according to the Yargic et al. method.²⁴ In addition, the sieve and Gay-Lussac pycnometer methods were also applied to determine the size and bulk density of AAST, respectively.

In this research, kinetic study of MB adsorption onto AAST was carried out in a series of batch experiments at room temperature (25 ± 2 °C). Regarding batch experiments, 0.5 g of adsorbent was added to amber glass bottles containing various initial MB concentrations (10, 25, 50, and 100 mg/l) with optimum pH of 7.0. The optimum pH value of 7.0 of the batch experiments was obtained from similar previous experiments. In addition, both 0.1 M HCl and 0.1 M NaOH solutions were used to adjust the pH of MB solution. Then, the bottles were placed in a shaker and rotated vigorously with the intensity of 300 rpm for 1 to 300 minute time intervals. Subsequently, to separate the adsorbents from MB solutions, samples were centrifuged at 5000 rpm for around 5 minutes. The residual concentration of MB in solutions was measured using a UV-visible spectrophotometer (SPEKOL 2000, Analytik Jena, Germany) at its maximum MD absorbance wavelength of 665 nm. Finally, the adsorption capacity (q_t) of MB onto the AAST was calculated using the following equation:

$$q_t = \frac{V(C_0 - C_e)}{m} \quad (1)$$

Where C_0 and C_e are the initial and final concentrations of MB (mg/l) in the solution, V is the solution volume (L), and m is the weight of adsorbent (g).

Finally, the effect of the size of AAST particles was also studied in two different size ranges of 210-250 μm and 53-63 μm for varying dosages of AAST adsorbent (0.5 and 5.0 g/l).

The kinetic investigation of MB adsorption onto the AAST surfaces was performed via four widely used models, namely Lagergren's pseudo first-order, Ho's pseudo second-order, Elovich, and Weber and Morris's intraparticle diffusion. The non-linear forms of pseudo first-order, pseudo second-order, Elovich, and intraparticle diffusion kinetic models are expressed in equations 2, 3, 4, and 5, respectively, as follows:²⁵⁻²⁸

$$q_t = q_e(1 - \exp(-k_1 t)) \quad (2)$$

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad (3)$$

$$q_t = \left(\frac{1}{\beta}\right) \ln(1 + \alpha\beta t) \quad (4)$$

$$q_t = k_{id} \sqrt{t} + C_i \quad (5)$$

Where q_e and q_t (mg/g) are the adsorbed amount of MB at equilibrium state and at any time (t) (min). Furthermore, k_1 (1/min) and k_2 (mg/g.min) are the rate of sorption for pseudo first and pseudo second-order models, respectively. α (mg/g.min) and β (g/mg) are the constants of the Elovich kinetic model. Moreover, k_{id} (mg/g.min) and C_i are the intraparticle diffusion constant and constant depicting the boundary layer effect, respectively.

The complete linear forms of pseudo second-order kinetic model are demonstrated in table 1. Furthermore, to examine the reliability of all

applied models and their fitness to the experimental data of MB adsorption, r^2 as a valid and authenticated index was used as follows:²⁹

$$r^2 = \frac{\sum(q_m - q)^2}{\sum(q_m - q)^2 + \sum(q_m - q_t)^2} \quad (6)$$

Where q_m and q_t are the quantity of adsorbed pollutant onto the adsorbent at equilibrium contact time and any time (t) (mg/g), respectively. Moreover, q is the average of q_t .

Additionally, to obtain the kinetic parameters of MB adsorption onto the AAST using non-linear and linear approaches, MATLAB® version 7.11.0 (R2010b, The Mathworks Inc. Natick, MA, USA) and Microsoft Excel (Microsoft, Redmond, WA, USA) were used, respectively.

Results and Discussion

Characterization

Several selected physicochemical features of AAST are presented in table 2. Accordingly, pH_{zpc} of AAST was obtained (5.0 ± 0.2). Since, pH value of solution is lower than 5, surface charges of AAST will be positive. However, at pH values higher than 5, negative charges will occupy the surfaces of AAST and this plays a critical role in cationic dye adsorption. In this study, all experiments were performed at a pH value of 7.0, based on 2 degrees deviation from pH_{zpc} , and desirable conditions were provided for MB adsorption. Moreover, specific surface area of AAST was obtained to be 285.5 m^2/g that will be considered as an undeniable proof of the ability of AAST in MB adsorption.

Table 1. Linear forms of pseudo second-order kinetic model

Model type	Equation	Plot	Parameters
1	$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$	t/q vs. t	$q_e = 1/\text{slope}$, $k_2 = \text{slope}^2/\text{intercept}$
2	$\frac{1}{q} = \left(\frac{1}{k_2 q_e^2}\right) \frac{1}{t} + \frac{1}{q_e}$	1/q vs. 1/t	$q_e = 1/\text{intercept}$, $k_2 = \text{intercept}^2/\text{slope}$
3	$q = q_e - \left(\frac{1}{k_2 q_e}\right) \frac{q_t}{t}$	q vs. q/t	$q_e = \text{intercept}$, $k_2 = -1/(\text{intercept} \times \text{slope})$
4	$\frac{q}{t} = k_2 q_e^2 - k_2 q_e q$	q/t vs. q	$q_e = -\text{intercept}/\text{slope}$, $k_2 = \text{slope}^2/\text{intercept}$

q_e : 1/slope; k_2 : slope²/intercept; t: Time

Table 2. Several physicochemical characteristics of acid-activated spent tea (AAST)

Parameters	Values
Moisture content (%)	3.72 ± 0.4
Water soluble compounds (%)	1.20 ± 0.3
Insoluble compounds (%)	95.10 ± 0.4
Volatile fraction (%)	64.30 ± 2.9
Ash content (%)	30.90 ± 2.7
Elemental analysis (%)	
C	57.50 ± 1.1
H	7.30 ± 0.5
N	0.4
O	30.30 ± 0.9
S	4.50 ± 0.3
pH _{pzc}	5.00 ± 0.2
Bulk density (kg/m ³)	258
Particle size (µm)	100-250
BET surface area (m ² /g)	285.5

BET: Brunauer–Emmett–Teller

Figure 2 illustrates the SEM image of AAST. Based on figure 2, the porous and rough structure of AAST is evident which is attributed to the effect of treatment with strong sulfuric acid. The created porosity on the AAST surfaces is a great tool to increase the capacity of the adsorbent in adsorbing the adsorbate. The FTIR spectra of AAST before and after adsorption of MB are presented in figure 3. As shown in figure 3 and table 3, the spectra display a number of

absorption peaks, indicating the complex nature of the AAST. As it is clear from figure 3, the presence of OH-phenolic functional group is proved by a broad band peak at 3396 cm⁻¹.³⁰ The aliphatic C-H stretch in cellulose and hemicelluloses are assigned at wave numbers of 2924 cm⁻¹, 2853 cm⁻¹, and 1457 cm⁻¹.³¹⁻³³ In addition, the carbonyl stretch of carboxyl and C=O stretching mode conjugated with the NH₂ are illustrated in 1719 cm⁻¹ and in the range of 1640–1660 cm⁻¹, respectively.³¹ The two peaks at wave numbers of 1519 cm⁻¹ and 1319 cm⁻¹ are attributed to the secondary amine group and symmetric bending of CH₃, respectively.³³ Table 3 illustrates the absorption peak of all functional groups of AAST surfaces before and after adsorption of MB. It can be seen that among all mentioned functional groups, bonded -OH groups, secondary amine group, C=O stretching of ether group, aliphatic C-H group, C-N stretch of aliphatic amines, and symmetric bending of CH₃ have important roles in the process of adsorption of MB from aqueous solution.³⁴ Several adsorption bands participating in the biosorbent indicated that AAST is an excellent sorbent for the removal of MB.

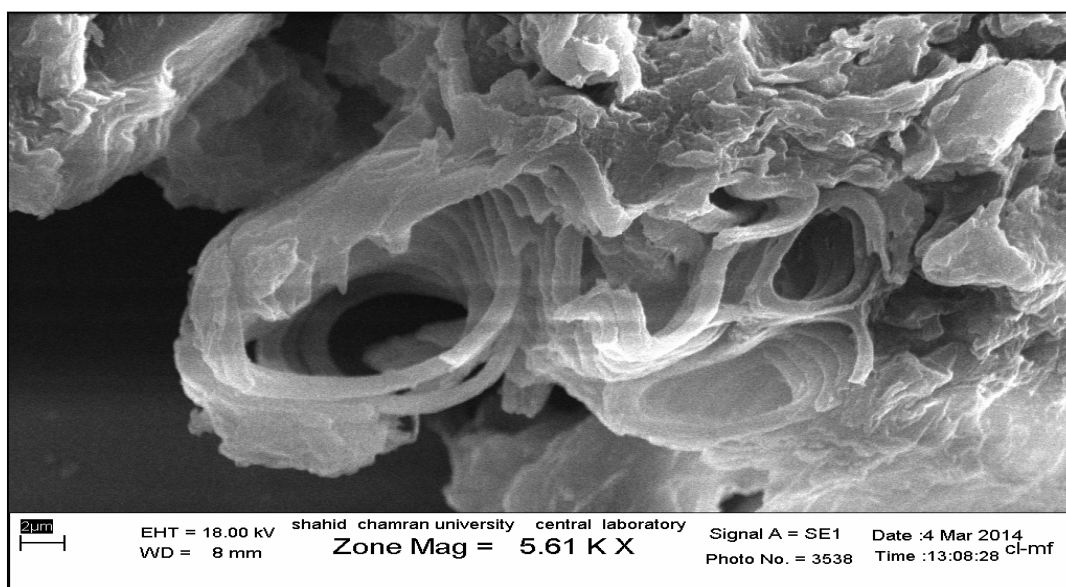


Figure 2. Scanning electron microscope (SEM) image of acid-activated spent tea (AAST)

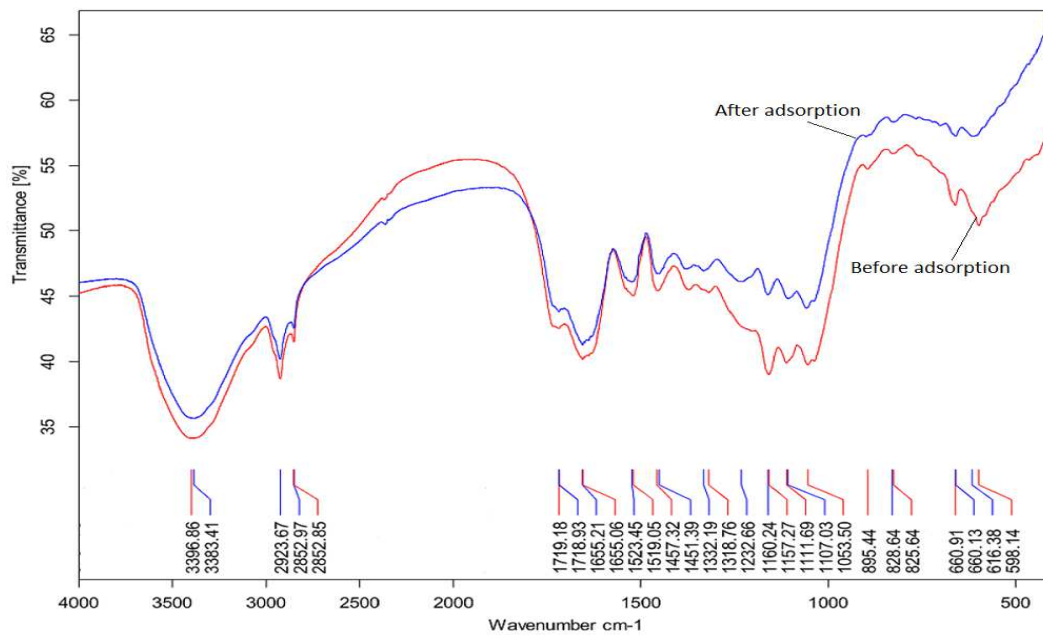


Figure 3. Fourier transform infrared spectroscopy (FTIR) spectra of acid-activated spent tea (AAST) before and after adsorption of methylene blue (MB)

Table 3. Fourier transform infrared spectroscopy (FTIR) spectra of acid-activated spent tea (AAST) before and after adsorption of methylene blue (MB)

FTIR peaks	Frequencies (cm ⁻¹)			Assignment
	Before adsorption	After adsorption	Differences	
1	3397	3383	+14	Bonded-OH groups
2	2924	2924	0	aliphatic C-H stretch
3	2853	2853	0	aliphatic C-H stretch
6	1719	1719	0	carbonyl stretch of carboxyl
7	1655	1655	0	C=O stretching
8	1519	1523	-4	secondary amine group
9	1457	1451	+6	aliphatic C-H stretch
10	1319	1332	-13	symmetric bending of CH ₃
11	1157	1160	-3	C=O stretching of ether groups
12	1112	1107	+5	C-N stretch of aliphatic amines
13	1054	Disappeared	Unknown	C=O stretching
14	895	Disappeared	Unknown	aromatic C-H stretching
15	826	829	-3	aromatic C-H stretching
16	661	660	+1	C-Br stretch of alkyl halides
17	598	616	-18	C-Br stretch of alkyl halides

FTIR: Fourier transform infrared spectroscopy

Kinetic studies

Kinetic studies of MB adsorption onto AAST surfaces were accurately carried out using four widely used non-linear kinetic models together with four linear types of the pseudo second-order model. The non-linear graphs of pseudo first-order, pseudo second-order, Elovich, and

intraparticle diffusion models were depicted based on the adsorption time (t) against the adsorption capacity of MB (q_t) (Figure 4). As is clear from figure 4, the kinetic of reaction between adsorbent and adsorbate was apparently high in the first 30 minutes of the experiments; over 90% of the initial MB concentration was adsorbed onto the AAST

surfaces. However, with the passing of time, reaction decreases and reaches equilibrium state. The most probable reason for this observation is rooted mainly in the vacancy of surface area of adsorbents and their extreme tendency toward adsorbate sorption which will drop significantly with the passing of reaction time and filling of the surface area. The results of non-linear kinetic studies have been reported in table 4. Accordingly, the obtained q_t of pseudo first-order and pseudo second-order models has a significant correlation with the experimental q_t . Furthermore, the pseudo second-order model, in

comparison with other models, has the highest r^2 with the experimental data in all initial MB concentrations (except 10 mg/l). The findings of the study by Yao et al. showed that the data on MB adsorption onto the carbon nanotube had the most significant correlation with the pseudo second-order kinetic model.³⁵

Moreover, the linear graphs of the pseudo second-order model are illustrated in figure 5. In order to obtain kinetic parameters using linear approach, the graphs 5 (a-d) were drawn based on t vs. t/q , $1/t$ vs. $1/q$, q vs. q/t , and q/t vs. q , respectively.

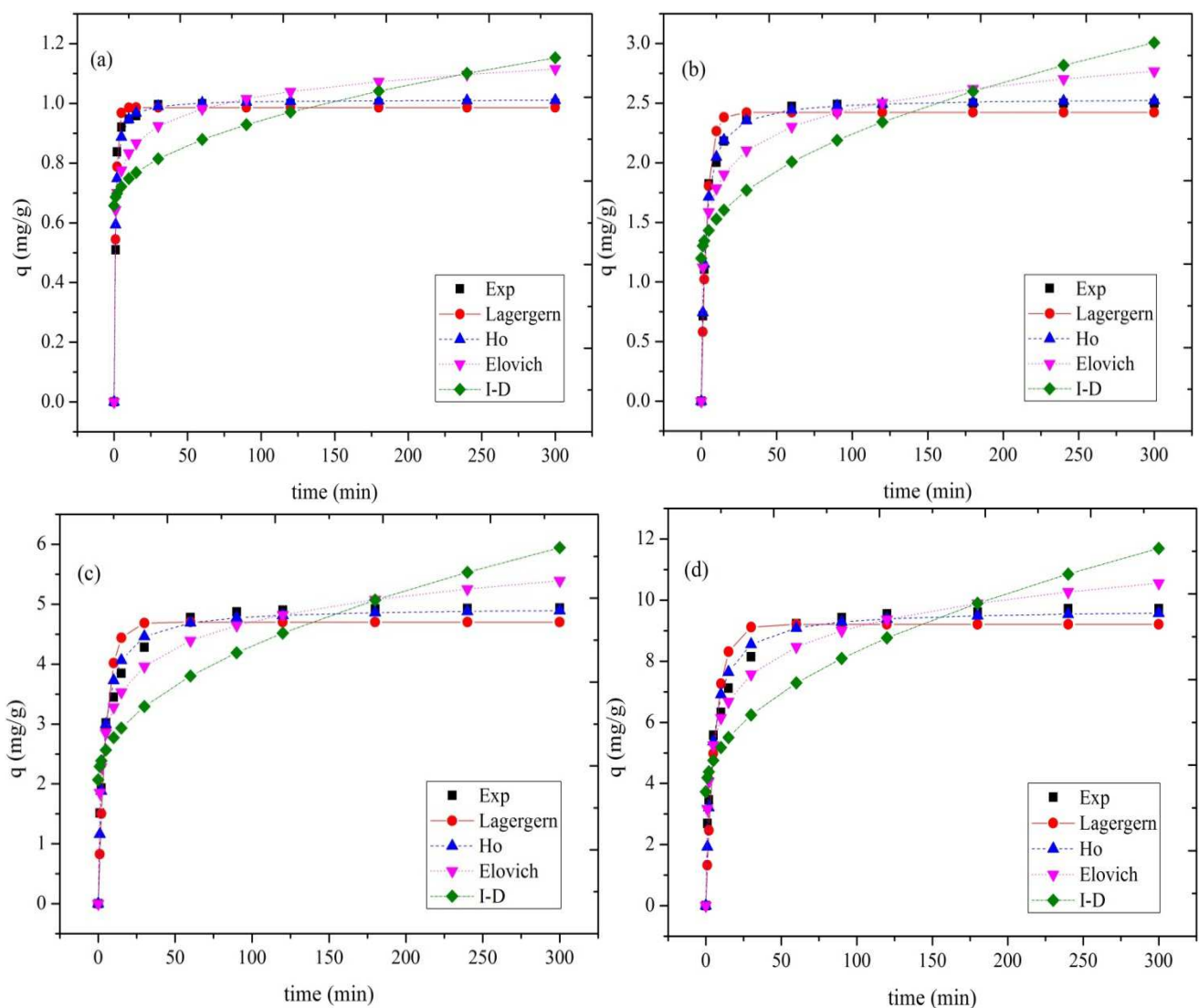


Figure 4. Non-linear kinetic plot of MB adsorption onto AAST surfaces at different initial MB concentrations (a: 10, b: 25, c: 50, and d: 100 mg/l⁻¹)

Table 4. Kinetic parameters of methylene blue (MB) adsorption onto acid-activated spent tea (AAST) surfaces using non-linear regression approach

Model	Parameter	Initial MB concentrations (mg/l)			
		10	25	50	100
Pseudo first-order	q_e (mg/g)	0.986	2.422	4.700	9.207
	k_1 (1/min)	0.803	0.274	0.193	0.156
	r^2	0.991	0.979	0.944	0.940
Pseudo second-order	q_e (mg/g)	1.013	2.543	4.946	9.702
	k_2 (g/mg.min)	1.398	0.163	0.062	0.026
	r^2	0.984	0.998	0.990	0.987
Elovich	α (mg/g.min)	197.10	14.15	12.26	14.93
	β (g/mg)	12.09	3.47	1.61	0.77
	r^2	0.889	0.922	0.966	0.973
Intraparticle diffusion	k_{id} (mg/g.min)	0.029	0.104	0.224	0.460
	C_i	0.658	1.199	2.068	3.727
	r^2	0.326	0.552	0.660	0.702

qe: 1/slope; k₂: slope²/intercept; k_{id}: intraparticle diffusion constant; C_i: constant depicting the boundary layer effect

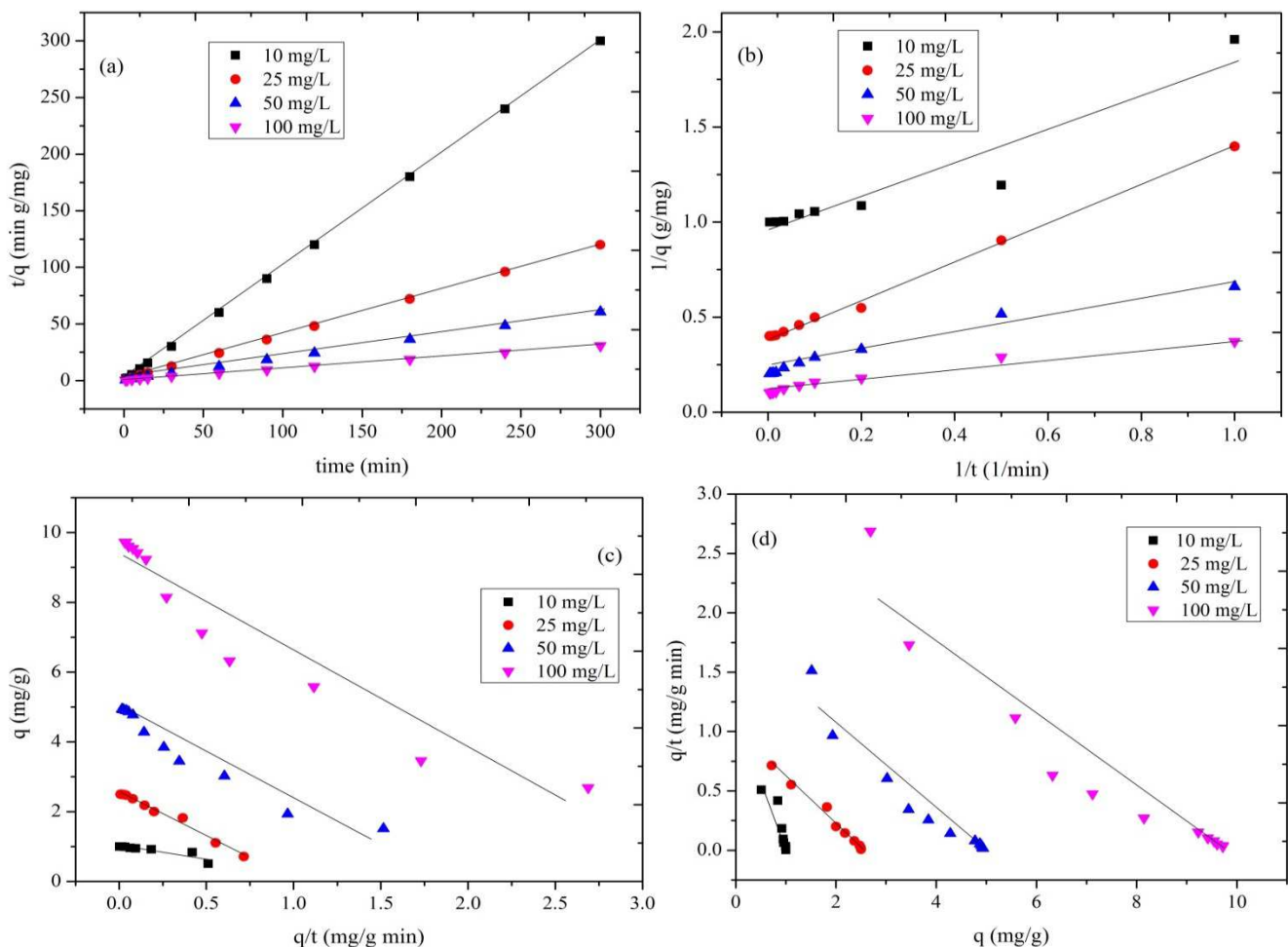
**Figure 5. Linear plot of pseudo second-order kinetic model of methylene blue (MB) onto acid-activated spent tea (AAST) surfaces (a: form 1, b: form 2, c: form 3, and d: form 4)**

Table 5 shows the kinetic parameters of four linear forms of the pseudo second-order model at various initial MB concentrations. Increasing initial MB concentrations from 10 to 100 mg/l caused considerable enhancement in the adsorption capacity of MB. Kumar and Tamilarasan, in a similar study, stated that an increasing trend was observed in MB adsorption capacities onto the *Acacia fumosa* seed shell activated carbon as a result of increasing the initial MB concentrations.³⁶ According to table 5, the linear form 1 of pseudo second-order had the maximum r^2 value that confirm its correlation with experimental data of MB adsorption, while forms 3 and 4 showed lower correlation. The differences between obtained parameters of linear models were mainly derived from the complexity in calculating the kinetic parameters. Such contradiction revealed that changing the non-linear to linear methods triggered significant transformation in obtained results and reduction of their validity. The various outcome parameters, in addition, of varying linear types of pseudo second-order are principally due to the changing error function that is differentiated by the linearization process of non-linear models. Of course, such error function, depending on the linearization method, may lead to either better or worse outcome parameters. The linear regression

concept is based on the belief that the distribution of points in adjacency of the line follows the Gaussian distribution in which the standard deviation is relatively similar at each X value. Such assumptions are not correct after the alteration of the experimental data that will entirely change the relationship between X and Y. In this regard, form 1 of the pseudo second-order model, compared to forms 3 and 4, can better fit the experimental data of MB adsorption with relatively high r^2 . Consequently, it can be said that changing the non-linear to linear approach led to improvement of the efficiency of form 1, while in the case of forms 3 and 4, lower performance efficiency was observed. Additionally, different outputs of the four linear types of pseudo second-order can be ascribed to the various axial conditions that change the findings of linear regression method and impact the determination procedure.³⁷ linear method only indicates the slope and intercept that are useful for predicting Y for corresponding X values. Therefore, the appropriateness of fitting experimental data to various linear forms which originate from different axial settings would be adjustable. In the linear regression approach, it is not considered whether the kinetic reaction trend is linear or not, but it is supposed that the experimental data are intrinsically linear.

Table 5. kinetic parameters of methylene blue (MB) adsorption onto acid-activated spent tea (AAS) surfaces using linear regression approach

Pseudo second-order kinetic model	Parameter	Initial MB concentrations (mg/l)			
		10	25	50	100
Form 1	q_e (mg/g)	1.002	2.522	5.005	9.881
	k_2 (g/mg.min)	2.166	0.196	0.058	0.022
	r^2	1.000	1.000	1.000	1.000
Form 2	q_e (mg/g)	1.044	2.568	4.710	9.093
	k_2 (g/mg.min)	0.965	0.150	0.090	0.041
	r^2	0.920	0.998	0.968	0.965
Form 3	q_e (mg/g)	1.031	2.566	4.653	8.961
	k_2 (g/mg.min)	1.076	0.151	0.096	0.044
	r^2	0.920	0.998	0.968	0.965
Form 4	q_e (mg/g)	1.031	2.490	4.774	9.278
	k_2 (g/mg.min)	1.089	0.115	0.029	0.007
	r^2	0.836	0.989	0.927	0.774

q_e : 1/slope; k_2 : slope²/intercept; MB: Methylene blue

In addition, different outputs of the linearization process apparently proved that in the case of linear method, X value is absolutely clear while Y is uncertain. Moreover, according to tables 4 and 5, the reaction rate coefficient (k_2), an important parameter in the adsorption process design, estimated by linear models differs from that estimated by non-linear models. Therefore, the use of a linear model is a questionable and controversial approach to determining kinetic parameters. This evidence supports the likelihood of abnormality assumption for linear regression approach. Therefore, since in non-linear regression method, error structure does not change and all the kinetic parameter are fixed in a similar axis, it would be advantageous to predict the parameters related to kinetic study of experimental data of MB adsorption.

Effect of particles size

In the adsorption process, particle size and surface area of the adsorbent are the most important factors affecting the adsorption capacity. Therefore, the effect of particle size on the removal of MB was studied with two different size ranges of 210-250 μm and 53-63 μm . As shown in figure 6, decreasing the particle size of AAST adsorbent from the range of 210-250 μm to 53-63 μm has increased the removal efficiency of the initial concentration of 50 mg/l MB dye from 31.8 to 42.5% and from 87.0 to 97.5% using 0.5 g/L and 5.0 g/l AAST adsorbents, respectively. The extent of the adsorption process increases with increased specific surface areas. The specific surface available for adsorption will be greater for smaller particles, and hence, the adsorption efficiency of MB increases as particle size decreases. For larger particles, the diffusion resistance to mass transport is higher, and most of the internal surface of the particle may not be utilized for adsorption. Consequently, lower amounts of MB are adsorbed. These results demonstrate that smaller particles provide more surface area, and thus, increase the adsorption capacity.

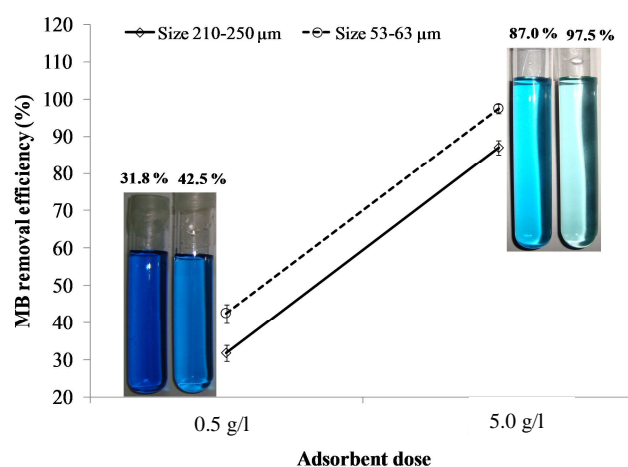


Figure 6. Particle size effect of acid-activated spent tea (AAST) on methylene blue (MB) adsorption efficiency (pH = 7.0 ± 0.1 ; time = 120 min, $C_0 = 50 \text{ mg/l}$)

Conclusion

In the present study, a kinetic survey of MB adsorption was performed using the four most common kinetic models. Furthermore, the linear and non-linear forms of pseudo second-order kinetic model were fitted to the experimental data of MB adsorption onto AAST surfaces. The findings of batch experiments revealed that MB adsorption is a merely concentration-dependent process and entirely depends on the initial MB concentration. Among all kinetic models, the pseudo second-order model, due, principally, to its high r^2 , best fit the obtained data. Moreover, investigation of the linear forms of pseudo second-order model demonstrated that, in all initial MB concentrations, form 1 best fit the MB adsorption data. Additionally, comparison of linear and non-linear kinetic methods revealed that non-linear approach, due to the lack of disorder on error construction, is the best method to undertake a kinetic study. Therefore, based on the findings of this research, the use of the non-linear approach of kinetic models is confidently advised in the study of contaminant removal. Furthermore, results of particle size experiments indicated that higher MB adsorption was apparently achieved in lower size adsorbents. This study shows that AAST is

a promising biosorbent for the removal of dye from colored aqueous solutions.

Conflict of Interests

Authors have no conflict of interests.

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References

- Ravikumar K, Deebika B, Balu K. Decolourization of aqueous dye solutions by a novel adsorbent: application of statistical designs and surface plots for the optimization and regression analysis. *J Hazard Mater* 2005; 122(1-2): 75-83.
- Bulut Y, Aydin H. A kinetics and thermodynamics study of methylene blue adsorption on wheat shells. *Desalination* 2006; 194(1-3): 259-67.
- Malik PK, Saha SK. Oxidation of direct dyes with hydrogen peroxide using ferrous ion as catalyst. *Separation and Purification Technology* 2003; 31(3): 241-50.
- Koch M, Yediler A, Lienert D, Insel G, Kettrup A. Ozonation of hydrolyzed azo dye reactive yellow 84 (CI). *Chemosphere* 2002; 46(1): 109-13.
- Panswad T, Wongchaisuwan S. Mechanisms of Dye Wastewater Colour Removal by Magnesium Carbonate-Hydrated Basic. *Water Science & Technology* 1986; 18(3): 139-44.
- Arabi S, Sohrabi MR. Removal of methylene blue, a basic dye, from aqueous solutions using nano-zerovalent iron. *Water Sci Technol* 2014; 70(1): 24-31.
- Al-Bastaki N, Banat F. Combining ultrafiltration and adsorption on bentonite in a one-step process for the treatment of colored waters. *Resources, Conservation and Recycling* 2004; 41: 103-13.
- Gupta VK, Jain R, Varshney S. Removal of Reactofix golden yellow 3 RFN from aqueous solution using wheat husk-an agricultural waste. *J Hazard Mater* 2007; 142(2): 443-8.
- Gupta VK, Jain R, Varshney S, Saini VK. Removal of Reactofix Navy Blue 2 GFN from aqueous solutions using adsorption techniques. *J Colloid Interface Sci* 2007; 307(2): 326-32.
- Han R, Wang Y, Yu W, Zou W, Shi J, Liu H. Biosorption of methylene blue from aqueous solution by rice husk in a fixed-bed column. *J Hazard Mater* 2007; 141(3): 713-8.
- Vadivelan V, Kumar KV. Equilibrium, kinetics, mechanism, and process design for the sorption of methylene blue onto rice husk. *J Colloid Interface Sci* 2005; 286(1): 90-100.
- Hameed BH, Mahmoud DK, Ahmad AL. Sorption of basic dye from aqueous solution by pomelo (*Citrus grandis*) peel in a batch system. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 2008; 316(1-3): 78-84.
- Ncibi MC, Mahjoub B, Seffen M. Kinetic and equilibrium studies of methylene blue biosorption by *Posidonia oceanica* (L.) fibres. *J Hazard Mater* 2007; 139(2): 280-5.
- Garg VK, Amita M, Kumar R, Gupta R. Basic dye (methylene blue) removal from simulated wastewater by adsorption using Indian Rosewood sawdust: a timber industry waste. *Dyes and Pigments* 2004; 63(3): 243-50.
- Gurses A, Dogar C, Yalcin M, Acikyildiz M, Bayrak R, Karaca S. The adsorption kinetics of the cationic dye, methylene blue, onto clay. *J Hazard Mater* 2006; 131(1-3): 217-28.
- Dogan M, Alkan M, Turkyilmaz A, Ozdemir Y. Kinetics and mechanism of removal of methylene blue by adsorption onto perlite. *J Hazard Mater* 2004; 109(1-3): 141-8.
- Kumar KV, Ramamurthi V, Sivanesan S. Modeling the mechanism involved during the sorption of methylene blue onto fly ash. *J Colloid Interface Sci* 2005; 284(1): 14-21.
- Han R, Wang Y, Zou W, Wang Y, Shi J. Comparison of linear and nonlinear analysis in estimating the Thomas model parameters for methylene blue adsorption onto natural zeolite in fixed-bed column. *J Hazard Mater* 2007; 145(1-2): 331-5.
- Amarasinghe BMWP, Williams RA. Tea waste as a low cost adsorbent for the removal of Cu and Pb from wastewater. *Chemical Engineering Journal* 2007; 132(1-3): 299-309.
- Wasewar KL, Atif M, Prasad B, Mishra IM. Batch adsorption of zinc on tea factory waste. *Desalination* 2009; 244(1-3): 66-71.
- Ho YS, McKay G. Pseudo-second order model for sorption processes. *Process Biochemistry* 1999; 34(5): 451-65.
- Allen SJ, Gan Q, Matthews R, Johnson PA. Kinetic modeling of the adsorption of basic dyes by kudzu. *J Colloid Interface Sci* 2005; 286(1): 101-9.
- Blanchard G, Maunaye M, Martin G. Removal of heavy metals from waters by means for natural zeolites. *Water Res* 1984; 18(2): 1501-7.
- Yargic A, Yarbay Sahin RZ, Ozbay N, Onal E. Assessment of toxic copper(II) biosorption from

- aqueous solution by chemically-treated tomato waste. *Journal of Cleaner Production* 2015; 88(0): 152-9.
25. Lagergren S. About the theory of so-called adsorption of soluble substances, *Kungliga Sven. Vetensk Handl* 1898; 24: 1-39.
 26. Ho YS, McKay G. The kinetics of sorption of basic dyes from aqueous solution by sphagnum moss peat. *The Canadian Journal of Chemical Engineering* 1998; 76(4): 822-7.
 27. Ho YS, McKay G. Application of Kinetic Models to the Sorption of Copper(II) on to Peat. *Adsorption Science & Technology* 2002; 20(8): 797-815.
 28. Weber WJ, Morris JC. Kinetics of Adsorption on Carbon from Solution. *Journal of the Sanitary Engineering Division* 1963; 89(2): 31-60.
 29. Ng JCY, Cheung WH, McKay G. Equilibrium Studies of the Sorption of Cu(II) Ions onto Chitosan. *Journal of Colloid and Interface Science* 2002; 255(1): 64-74.
 30. Lin-Vien D, Colthup NB, Fateley WG, Grasselli JG. *The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules*. Philadelphia, PA: Elsevier; 1991.
 31. Kapoor A, Viraraghavan T. Heavy metal biosorption sites in aspergillus niger. *Bioresource Technology* 1997; 61(3): 221-7.
 32. Yun YS, Park D, Park JM, Volesky B. Biosorption of trivalent chromium on the brown seaweed biomass. *Environ Sci Technol* 2001; 35(21): 4353-8.
 33. Malkoc E, Nuhoglu Y. Removal of Ni(II) ions from aqueous solutions using waste of tea factory: adsorption on a fixed-bed column. *J Hazard Mater* 2006; 135(1-3): 328-36.
 34. Baran A, Bicak E, Baysal SH, Onal S. Comparative studies on the adsorption of Cr(VI) ions on to various sorbents. *Bioresour Technol* 2007; 98(3): 661-5.
 35. Yao Y, Xu F, Chen M, Xu Z, Zhu Z. Adsorption behavior of methylene blue on carbon nanotubes. *Bioresour Technol* 2010; 101(9): 3040-6.
 36. Kumar M, Tamilarasan R. Modeling studies for the removal of methylene blue from aqueous solution using *Acacia fumosa* seed shell activated carbon. *Journal of Environmental Chemical Engineering* 2013; 1(4): 1108-16.
 37. Ho YS. Selection of optimum sorption isotherm. *Carbon* 2004; 42: 2113-30.