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Short communication

Adsorption of methylene blue from aqueous solution onto NaOH-modified rejected tea

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ABSTRACT

In this work, the removal of a basic dye, methylene blue (MB) from aqueous solution using NaOH-modified rejected tea (N-RT) was investigated. Equilibrium adsorption and kinetics were studied. The results confirmed that the adsorption isotherm data fitted well to Langmuir isotherm with monolayer adsorption capacity of 242.11 mg/g. The kinetics of MB adsorption process was found to follow pseudo-second-order rate expression. The results suggested that the N-RT would be an excellent alternative for the removal of MB by adsorption process.

1. Introduction

Many studies have been conducted to evaluate levels of aquatic toxicity, phototoxicity, and metal bioavailability for specific class of dyes from different water sources. Findings of these studies have led to the emergent of stringent environmental regulation laws [1]. This issue puts many in the textile dyeing industry and dyestuff manufacturing industry in somewhat awkward situation and now taking substantial measures to treat the dye containing wastewater. Besides, dyes are considered an objectionable type of pollutant because of they are toxic and cause allergy, dermatitis, skin irritation, cancer, and mutations in humans [2,3]. Not only this, they also interfere with the transmission of light and upset the biological metabolism processes which cause the destruction of aquatic communities present in ecosystem [4].

Adsorption by activated carbon is the most common process for dye removal from wastewater. Although, the process is highly effective, the running costs are high with the need for regeneration after each sorption cycle [5]. This has led to the search for other potentially suitable alternative, that is more economical and equally an effective materials for dye removal by adsorption [6]. A number of investigations have shown that agricultural by-products such as clay [7], durian shell [8], *Hevea brasiliensis* [9], banana stalk waste [10] and mango seed kernel powder [11] have the potential of being used as low cost adsorbent for the removal of dyes in textile wastewater. Some of the advantages of using agricultural waste for wastewater treatment include simple technique, requires little processing, good adsorption capacity, selective of adsorption effluent, low cost, free availability and easy regeneration [12]. Beside, the exhausted adsorbents can be disposed off by burning and the heat used for steam generation [13].

However, the application of untreated agricultural or plant waste as adsorbents can also bring several problems such as low adsorption capacity, high chemical oxygen demand (COD) and biological oxygen demand (BOD) as well as total organic carbon (TOC) due to release of soluble organic compounds contained in the plant wastes [14].

Therefore, the agricultural wastes need to be treated or modified before being used as adsorbent. In our previous work, we examined the use of rejected tea for methylene blue (MB) removal [15]. The objective of this work was to study the adsorption of MB onto sodium hydroxide modified rejected tea (N-RT).

2. Materials and methods

2.1. Adsorbate–methylene blue

Methylene blue (MB), $C_{16}H_{18}ClN_3S{\cdot}3H_2O$ supplied by Sigma Aldrich (M) Sdn Bhd, Malaysia was used as an adsorbate. Stock solution was prepared by dissolving 1.0 g of methylene blue (MB) in 1 L distilled water.

2.2. Adsorbent preparation and characterization

Raw rejected tea (R-RT) was prepared as described previously [15]. The dried rejected tea was treated in 0.05 M sodium hydroxide

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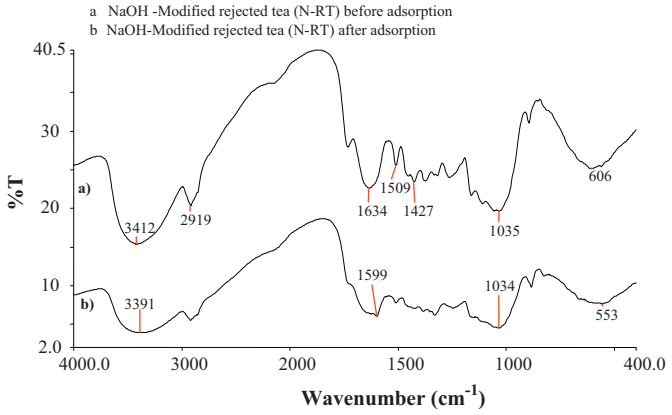

Fig. 1. FTIR spectrum of (a) NaOH-modified rejected tea (N-RT) before adsorption and (b) NaOH-modified rejected tea (N-RT) after adsorption.

(NaOH) solution for 4 h. The sample was then washed thoroughly with distilled water until the sample was neutralized and dried in the oven at 60 °C for 24 h. Finally, the resulting adsorbent (N-RT) was stored in air-tight container for further use to adsorption experiments.

Fourier transform infrared (FTIR) analysis was applied to determine the surface functional groups, using FTIR spectroscope (FTIR-2000, PerkinElmer), where the spectra were recorded from 4000 to 400 cm^{-1}. Surface morphology was studied using Scanning Electron Microscopy (JEOL JSM 6301-F) analysis. Finally, the BET surface area, total pore volume and average pore size of the N-RT were measured using ASAP 2020 Micrometrics instrument by Brunauer–Emmett–Teller (BET) method.

2.3. Equilibrium and kinetic studies

Equilibrium studies were carried out by contacting fixed amount of N-RT (0.50 g) with 200 mL of MB solution with different initial concentrations (50,100, 200, 300, 400 and 500 mg/L) in 250 mL stopper Erlenmeyer flasks at a temperature of 30 ± 2 °C and pH of 7. The procedure was repeated for temperatures 40 and 50 ± 2 °C. MB concentrations were determined by spectrometry at the wavelength of maximum absorbance, 668 nm using a double beam UV–Vis spectrophotometer (Shimadzu, Model UV 1601, Japan). In kinetics studies, the samples were taken at preset time intervals, and the concentrations of MB were measured.

3. Results and discussion

3.1. Characterization of N-RT

FTIR spectra of N-RT before and after adsorption are shown in Fig. 1. In N-RT before adsorption spectrum, the broad and intense absorption peaks at around 3412 cm^{-1} correspond to the O–H stretching vibrations due to inter- and intra-molecular hydrogen bonding of polymeric compounds (macromolecular associations), such as alcohols, phenols and carboxylic acids, as in pectin, cellulose and lignin, thus, showing the presence of "free" hydroxyl groups on the adsorbent surface [16]. The peak at 2919 cm^{-1} is attributed to the symmetric and asymmetric C–H stretching vibration of aliphatic acids [16]. The peak at 1634 cm^{-1} is due to asymmetric stretching vibrations of C=O and the peak observed at 1509 cm^{-1} can be assigned to aromatic compound group. The other prominent peaks are due to NH_2, C=O and –C–C– (1427, 1035 and 606 cm^{-1}, respectively) groups. Some distinct changes are noted in the spectrum between R-RT (unmodified [15]) and N-RT (Fig. 1(a)). It can be seen that two new peaks were formed at 2919 and 1427 corresponding to aliphatic C–H and NH_2 deformations. However, in the case of N-RT (Fig. 1(b)) after adsorption, there is remarkable shift in positions of –OH, C=O and –C–C– group peaks which indicates MB binding mostly at –OH and C=O groups. Moreover, it can be seen that most of the absolute values of N-RT were larger than those of R-RT [15], which indicates that N-RT has higher physical stability and surface activity. The changes in FTIR spectra confirm the complexation of MB with functional groups present in the adsorbents.

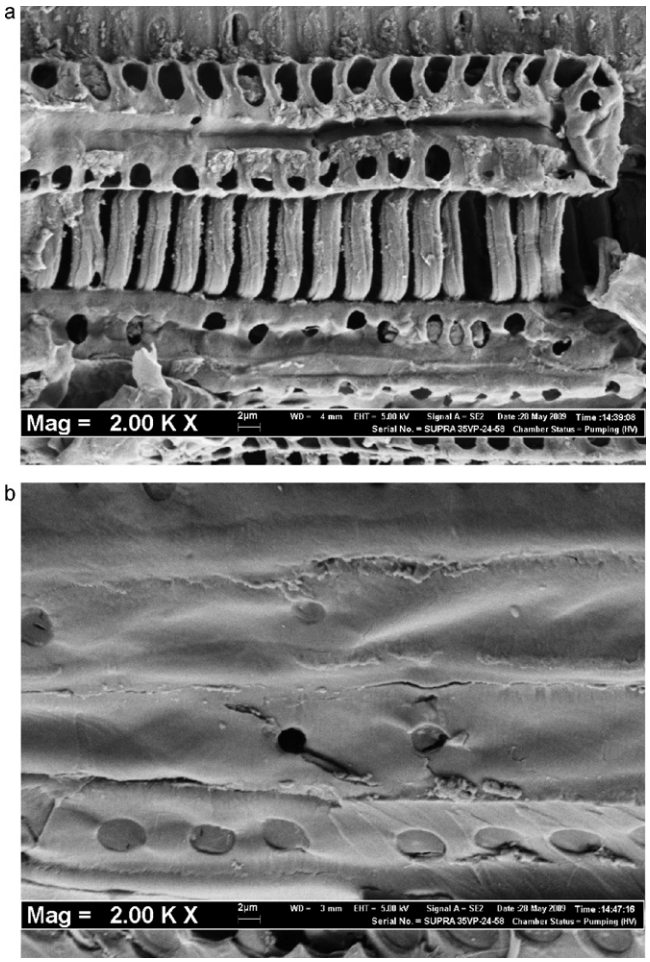

Fig. 2. Scanning electron microscope of (a) NaOH-modified rejected tea (N-RT) before dye adsorption and (b) NaOH-modified rejected tea (N-RT) after dye adsorption.

The SEM micrographs of N-RT before and after MB adsorption are shown in Fig. 2(a) and (b). It is clear that there are good enhancements in pores at N-RT surface which exhibits pores like honeycomb shape gaps after modification with NaOH solution. The modification process involves changing original surface texture of rejected tea. The rejected tea after modification process was found to have a macroreticular with enhanced physical characteristic which shown in Fig. 2 (a). The BET surface area, total pore volume and average pore diameter were measured to be 6.5 m^2/g, 0.0064 cm^3/g and 61 Å, respectively.

3.2. Adsorption isotherm studies

Langmuir [17] and Freundlich [18] isotherm models were commonly used to analyze the isotherm data. The Langmuir and Freundlich isotherms are given by Eqs. (1) and (2), respectively.

$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e} \quad (1)$$

Table 1
Adsorption isotherm parameters for adsorption of MB by N-RT at temperature 30 °C.

Isotherm	Isotherm constants
Langmuir isotherm	
q_{max} (mg/g)	242.11
K_L (L/mg)	0.13
R^2	0.993
Freundlich isotherm	
K_F	40.87
$1/n$	0.474
R^2	0.934

Table 2
Comparison of adsorption capacity of various modified adsorbents for methylene blue.

Adsorbent	Adsorbent capacity (mg/g)	References
NaOH-modified rejected tea	242.11	This work
Peanut hull treated with sulfuric acid	123.5	[19]
NaOH-treated raw koalin	16.34	[20]
NaOH-treated pure koalin	20.49	[20]
Phosphoric acid treated Parthenium hysterophorus	88.49	[21]
Sulfuric acid treated Parthenium hysterophorus	39.68	[21]
Modified wheat straw	432.8	[22]
Modified rice straw	208.33	[23]
Beech sawdust pretreated with $CaCl_2$	13.02	[24]
Activated carbon from oil palm shell	243.90	[25]
Tea waste	85.5	[26]

$$q_e = K_F C_e^{1/n} \quad (2)$$

where q_{max} is the maximum amount of adsorption (mg/g), K_L the adsorption constant (L/mg), K_F the constant representing the adsorption capacity, and n is the constant depicting the adsorption intensity.

The isotherm data were analyzed using non-linear regression and the determined isotherm constants are listed in Table 1. It was observed that Langmuir adsorption isotherm can accurately describe the adsorption of MB onto N-RT (R^2 = 0.993) with adsorption capacity of 242.11 mg/g at 30 °C. It was found that the chemical modification of rejected tea N-RT resulted in enhancing its adsorption capacity from 147 mg/g [15] to 242.11 mg/g. The enhancement of adsorption capacity can be explained on the basis of NaOH treatment which improved the N-RT surface with negatively charge. As the adsorbent surface is negatively charged, the increasing electrostatic attraction between positive adsorbate species and adsorbent particles would lead to increase adsorption of MB. The adsorption capacity of N-RT is compared with some agricultural by-product and activated carbons as shown in Table 2.

The essential characteristic of Langmuir isotherm can be expressed in terms of a dimensionless separation factor, R_L [27]:

$$R_L = \frac{1}{1 + K_L C_0} \quad (3)$$

where K_L is the Langmuir constant and C_0 is the highest initial dye concentration (mg/L). The value of R_L for adsorption of MB onto N-RT was 0.015, 0.011 and 0.010 at temperature 30, 40 and 50 °C, respectively. This value indicated that the adsorption behavior of N-RT was favorable for the MB (R_L < 1).

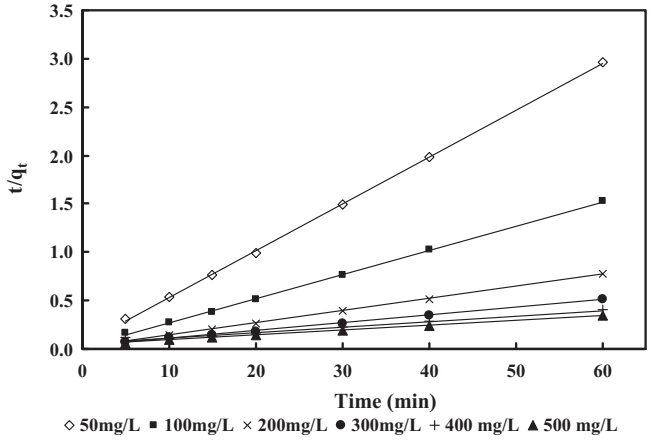

Fig. 3. Pseudo-second-order kinetics for adsorption of MB dye onto N-RT (temperature = 30 °C, W = 0.50 g/0.20 L solution, stirring rate = 130 rpm).

3.3. Adsorption kinetics studies

The linearized form of the pseudo-second order kinetic expression [28] is represented by Eq. (4).

$$\frac{t}{q_t} = \frac{1}{k_2 q_{eq}^2} + \frac{1}{q_e} t \quad (4)$$

where the equilibrium adsorption capacity (q_e), and k_2 (g/g min) is the rate constant of the pseudo-second-order equation. Value of k_2 can be calculated from the plot t/q_t against t (Fig. 3). The kinetic data for the adsorption of N-RT were calculated and are listed in Table 3. The coefficients of determination (R^2) for the pseudo-second-order kinetic model were ≥0.969 indicating the applicability of this kinetic equation. Besides the value of R^2, the applicability of both kinetic models is verified through the normalized standard deviation, Δq. The adsorption kinetics of MB on N-RT was tested at different initial concentrations. The validity of each model was determined by standard deviation (Δq, %) given by:

$$\Delta q(\%) = 100 \times \sqrt{\frac{\sum \left[(q_{t,exp} - q_{t,cal})/q_{t,exp}\right]^2}{n-1}} \times 100 \quad (5)$$

where the $q_{t,exp}$ and $q_{t,cal}$ refer to the experimental and calculated values, respectively, and n is the number of data points. The higher the value of R^2, and the lower the value of Δq, the better will be the goodness of fit. Table 3 lists the calculated results. It was found that the adsorption of MB on N-RT can be best described by the pseudo-second-order kinetic model.

Table 3
Pseudo-second order kinetics parameters for the adsorption of MB by N-RT.

C_o (mg/L)	$q_{e,exp}$ (mg/g)	q_e (mg/g)	q_e (mg/g)	k_2 (g/mg.min)	R^2	Δq (%)
50	20.61	2.44	20.66	0.049	1.000	0.098
100	39.57	3.99	40.00	0.026	1.000	0.446
200	77.34	19.8	80.00	0.008	1.000	1.405
300	116.84	71.42	125.00	0.002	0.998	2.851
400	155.04	103.21	166.67	0.001	0.969	3.061
500	187.69	122.07	200.00	0.001	0.999	2.678

3.4. Thermodynamic parameters

Thermodynamic parameters such as change in enthalpy ΔH°, entropy (ΔS°) and free energy (ΔG°) were calculated using the following equations:

$$InK_D = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{R}\frac{1}{T} \quad (6)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (7)$$

where K_D is the distribution coefficient, ΔS° is standard entropy (J/mol K), ΔH° is standard enthalpy, T the absolute temperature and R is the gas constant. The values of ΔH° and ΔS° were determined from slope and intercept, respectively, of van' Hoff plot (InK_D versus $1/T$). The positive value of ΔH° (7.169 kJ/mol) suggests the endothermic nature of adsorption. The positive value of ΔS° (56.082) confirmed the increased randomness at the solid–solute interface during adsorption processes, which suggest that MB ions replace some water molecules from the solution previously adsorbed on the surface of adsorbent. These displaced molecules gain more translation entropy than is lost by the adsorbent ions, thus allowing the prevalence of randomness in the system [29].

The negative values of ΔG°, −9.823, −11.049 and −11.941 kJ/mol at 30, 40 and 50 °C respectively, indicates the adsorption of MB onto N-RT is spontaneous process which confirming the affinity of N-RT for the MB.

4. Conclusion

It was confirmed that modification of rejected tea is capable of improving its adsorption capacity for MB and can serve as cheap non-conventional adsorbent in wastewater treatment. Experimental equilibrium data were fitted to Langmuir and Freundlich isotherms. It was found that the equilibrium data follow Langmuir isotherm with a monolayer adsorption capacity of 242.11 mg/g. The rate of adsorption was found to conform to pseudo-second-order kinetic model with good correlation, $R^2 \geq 0.969$. The results demonstrate the N-RT could be economically feasible for removal of MB from aqueous solution.

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