

Using the Tea Wastages to Remove Methylene Blue as a Dye Pollutant from the Synthesis Waste Waters: Kinetic and Thermodynamic

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Abstract

Introduction: Many industrial processes use different synthetic chemical dyes for various purposes, including paper and pulp manufacturing, fabric and textile dyeing, leather treatment, printing, etc. Effluents from these industrial facilities are typically of high organic contents and color strength.⁽¹⁾

Aim: The main aim of this research was using tea wastes to remove methylene blue (MB), a cationic dye with $=N^+(CH_3)_2$ reactive group from aqueous solutions.

Materials and methods: Tea wastes as a non-living biomass was used to remove Methylene blue (MB) as a cationic dye according to Langmuir equation that is suitable for adsorption by dead biomass. Kinetic modeling and thermodynamic equation were used to evaluate the process.

Result: The maximum uptake capacity (Q_{max}) of methylene blue in a batch reactor was 0.328, 0.542 and 0.659 mmol/g at 15, 25 and 40°C, respectively. The enthalpy change (ΔH) and entropy change (ΔS) were 11.356 kJ/mol and 20.563 J/mol K respectively.

Conclusion: Thermodynamic studies showed that adsorption equilibrium constant (K_L) and Q_{max} increased by increasing temperature. The percent of MB removal with $C_0=0.01$ mM was shown about 85% at optimum conditions.

Key words: waste water, methylene blue, biosorption, tea wastages.

Introduction

The presence of deep color in wastewater can decrease the transparency of water and influence photosynthesis activity, hindering the microbial activities of submerged organisms. It is clear, however, that removal of dye causing the color from wastewater is a great challenge. The most common dyes are reactive, dispersed, acidic, and direct dyes. Most of the dyes are low in toxicity and easily when dissolved in water. Therefore, they can be applied for various industrial applications, e.g. in inks, cosmetics, soaps, and food products. At the present time, the major techniques for treatment of dye from wastewater are the use of adsorption principles and biological treatment.⁽²⁻⁹⁾

Activated carbon, due to its porous property with large specific surface area, can be an ideal adsorbent for dyes. Natural and synthetic zeolites are also used for water treatment due to their unique structure and cation-exchange properties. However, some disadvantages are

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also associated with each of these techniques. For example, activated carbon adsorption only transfers the dyes from the liquid phase to the solid phase.⁽¹⁰⁾

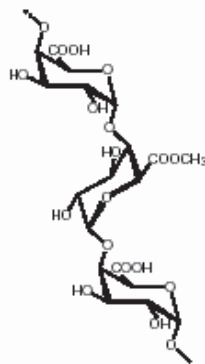
The major advantages of the heavy metals adsorption technology by biomass are its effectiveness in reducing the concentration of heavy metal ions to very low levels and the use of inexpensive biosorbent materials.^(11, 12) Furthermore, biosorption methods often provide better results than activated carbon and natural zeolites and are comparable to synthetic ion-exchange resins.⁽¹³⁾ Adsorbent materials (biosorbent) derived from suitable biomass both living and dead can be used for the effective removal and recovery of heavy metal ions from wastewater streams.⁽¹⁴⁾ The biomasses include bacteria⁽¹⁵⁾, fungi⁽¹⁶⁾, yeast⁽¹⁷⁾, marine algae⁽¹⁸⁾ and some other natural biomasses.

Biosorption using living aquatic plants (phytoremediation) is a relatively new technology to overcome the problem of heavy metals pollution. Pollutants are absorbed by plant roots and either decomposed or change to less harmful forms (for example CO₂ and H₂O) or accumulated in the plant tissues in phytoremediation.^(19, 20) Thus, phytoremediation is an environmentally friendly and inexpensive treatment method which can be performed in polluted places (remediation in situ) plus the products of decomposition do not require further utilization.^(19, 20)

On the other hand, because of the many problems inherent in maintaining active microbial populations under highly variable conditions of wastewaters, living systems are often unreliable. However, certain types of microbial biomass, even in non-living form, can serve as a basis for development of biosorbent materials for the efficient removal of the pollutants.^(14, 21) The non-living biosorbents can also be re-used after regenerating the exhausted biomass using a suitable eluant.⁽²²⁾

It has been demonstrated that there are two general mechanisms associated with the separation of dissolved metals from water using aquatic plant biomass. The first is a fast metabolism (within minutes) independent of surface reaction that has been modeled as a diffusion process and ends when the soluble metal ions bind or adsorbed to the outer cell wall of the biomass. The second is a slow metabolism (within hours or days) dependent on cellular uptake that has been modeled as a mass transfer process from the outer cell wall to the cell or to the cell wall interior.^(12, 15) Taking these mechanisms into consideration, the advantages of using living cells over non-living biomass to remove heavy metals are i) that living cells work as well as dead when the metal concentration is low, and the living cells can generate new biomass through growth allowing the second removal mechanisms to occur, ii) the rapidly regenerating supply of biomass. The major disadvantage is the toxic effect the metals can have on the organism; therefore, using non-living biomass is preferred to remove the high concentrations of dye.⁽¹⁵⁾

The degree of pectin methylation (DM) in the cell wall of plants has been expressed as the relative content of methoxyl groups (-COOCH₃) in the chain, as well as the distribution of the carboxyl groups (-COOH) the chain.⁽¹⁹⁻²¹⁾ The structure of pectin has shown in Scheme 1:



Scheme 1. Structures of pectin.

Materials and methods

Pre-treatment of tea wastes

Each 2g of tea wastes was washed three times with deionized water (each time 100ml for 30 min) and was air-dried in sunlight. Tea wastages were then sieved to particles with two sizes of up to 2.0 mm before use as fine and coarse particles. The samples were then dried in oven at 60°C for 10h. The agitation rate in the activation and biosorption experiments was fixed at 125 rpm. In the pre-treatment process, the temperature was adjusted at $25 \pm 2^\circ\text{C}$.

Dye as pollutant

Methylene blue (CI: 52015), $\text{C}_{16}\text{H}_{18}\text{ClN}_3\text{S}$ with molecular weight of 319.86 and maximum wavelength at 660 nm was supplied by Merck.

Adsorption isotherms

The isotherms can be described by Langmuir equation that is suitable for adsorption by dead biomass: ^(14, 15)

$$q_e = Q_{\max} K_L C_e / (1 + b C_e) \quad (1)$$

Where q_e is the metals uptake (mmol adsorbed/g dry biomass or mg/g) and C_e is the metals equilibrium concentration or un-adsorbed (mM or mg/l). Q_{\max} (mmol/g or mg/g) and K_L (1/mM) or (1/mg), are the maximum adsorption capacity and a measure of adsorption energy (equilibrium adsorption constant), respectively. The Langmuir equation can be transformed to the linearized form as shown below:

$$C_e/q_e = C_e/Q_{\max} + 1/(Q_{\max} \cdot K_L) \quad (2)$$

Q_{\max} and K_L could be found from the slop and intercept of C_e/q_e vs. C_e linear plot such that $Q_{\max} = 1/\text{slope}$, and $K_L = (\text{slope}/\text{intercept})$. q_e is given by the following relationship:

$$q_e = (C_o - C_e)/(m/V) \quad (3)$$

Where: C_o is the initial concentration of the metal ions (mM or mg/l) and m is the biosorbent dry weight (g) and V is suspension volume (l).

Batch sorption experiments by tea wastes

To obtain adsorption isotherms, a series of flasks (100 ml, as batch sorption reactors) were prepared containing dye solutions with known concentrations (C_o) varying from 1×10^{-3} to 4×10^{-2} mM. The experimental conditions were as follows: addition of the tea wastages with dose of 2.0 g biomass /l (0.1 g in 50 ml), agitating mixtures (300 rpm) for 2h as the adsorption time at each temperature viz. $25 \pm 1^\circ\text{C}$ and adjusting adsorption pH at 7.0 ± 0.2 using 0.1M NaOH and 0.1M HCl during the equilibrium period. The biomass was removed at last by filtration through a 0.45 μm membrane filter (Millipore) and the filtrate was analyzed

for dye content (C_e) by spectrophotometer (JENWAY, Model 6405) in 660nm as λ_{\max} of methylene blue.

Results and discussion

Effect of adsorption medium pH on the dye uptake

Fig. 1 shows that the dye uptake ($C_0=0.01$ mM) increased continuously with increasing pH. The increase in sorption efficiency can be easily correlated to the effect of proton competition on chelation mechanism. Increasing the pH, cause a decrease in competition by proton which leads to an increase in the affinity of the sorbent for dye. At lower pH values (<7.0) carboxyl groups ($-\text{COOH}$) in the plants cell wall retain their protons reducing the possibility of binding to any positively charged species.⁽²³⁾ Whereas, at pH values above 7.0, the carboxylate ($-\text{COO}^-$) legends attract positively charged dye and binding occurs. This phenomenon indicates that the major process is an interaction between positively charged groups in cell walls and methylene blue as a cationic dye. Removal of dye is decreased at the strong alkali pHs due to competition by OH^- . The best result was obtained at $\text{pH } 8.0 \pm 0.2$, so the adsorption pH was adjusted to 8.0 ± 0.2 in the subsequent studies.

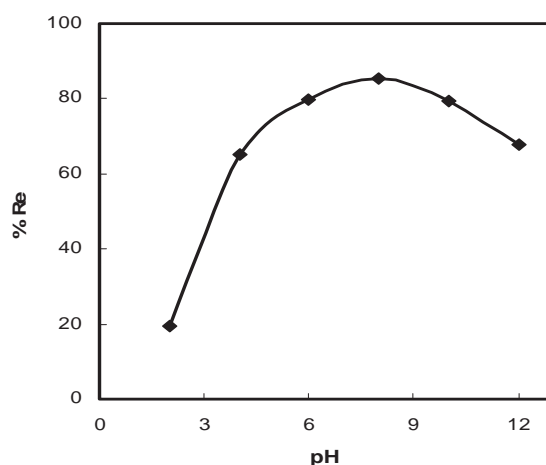


Fig.1- Effect of adsorption pH on the dye uptake.

Kinetic studies (effect of contact time)

As can be seen from Fig. 2, the rate of dye uptake (C_0 0.01 mM) was rather fast so that 85% of the total uptake was occurred in the first two hours. The adsorption of dye was completed after about 48 hours. In other words, the rate of dye uptake both in the initial contact and at the last parts sorption can be increased with increasing time. The adsorption time was adjusted to 2h in the subsequent experiments.

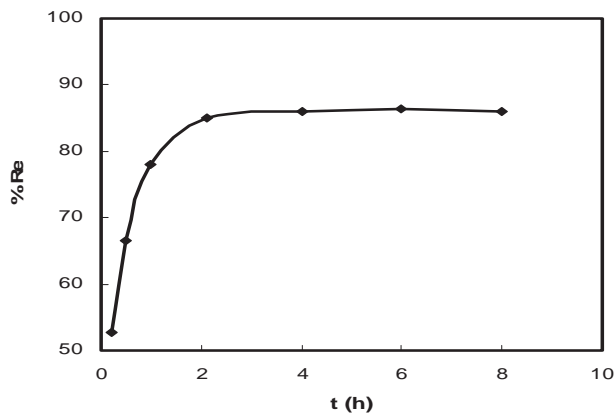


Fig.2- Effect of contact time on removal of MB by tea wastage.

Adsorbtion isotherms

Fig. 3 shows the adsorbtion isotherms by samples of tea waste at different temperatures.

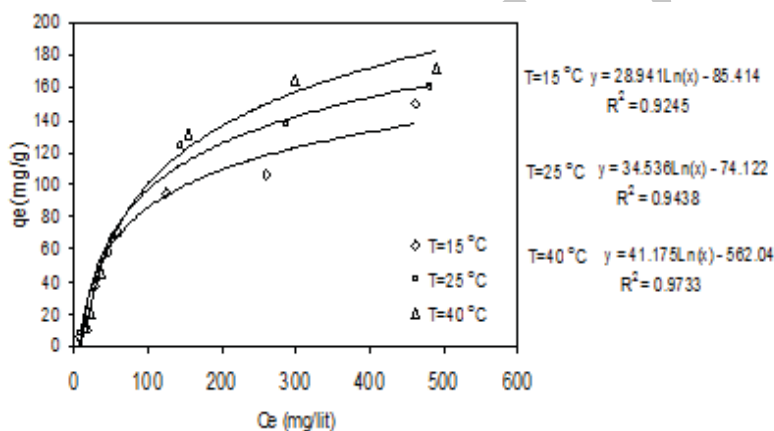


Fig.3 - Adsorbtion isotherms for removal of MB by tea waste.

According to Table 1, Q_{max} and K_L values were increased with increasing temperature for biomass. It also can be seen that the change of biosorption temperature has an effect on the shift and slop of adsorbtion isotherms by biomass. The parameters of adsorbtion isotherms are also presented in Table 1.

Table 1- Adsorbtion isotherms parameters to remove MB by tea wastage.

t (°C)	Q_{max} (mmol/g)	K_L (1/mM)	ΔG (KJ/mol)	ΔH (KJ/mol)	ΔS (J/mol.K)
15	0.328	0.456	-0.653		
25	0.542	0.836	-0.886	11.356	20.563
40	0.659	1.054	-0.963		

Kinetic modeling

With respect to the kinetic modeling, the first- and second-order kinetic models were used. The first-order rate expression of Lagergren considers that the rate of occupation of adsorbtion sites is proportional to the number of unoccupied sites, i.e.:

$$dq/dt = k_{1,ads}(q_e - q) \tag{4}$$

Where q_e and q (mg/g) are the amount of adsorbed heavy metals on the adsorbent at equilibrium and at time t (min) and $k_{1,ads}$ (1/min) is the rate constant of first-order sorption. Integrating (4) between the limits, $t = 0$ to $t = t$ and $q = 0$ to $q = q_e$, Eq.(5) will result in:

$$\log(q_e - q) = \log q_e - (k_{1,ads}/2.303) t \quad (5)$$

Linear plots of $\log(q_e - q)$ versus t indicate the applicability of this kinetic model.^(24, 25) However, to adjust Eq.(5) to the experimental data, the value of q_e (equilibrium sorption capacity) must be pre-estimated by extrapolating the experimental data to $t = \infty$.

Only the data corresponding to the first 25 min are adjusted, approximately. Since after this period, the experimental data considerably deviated from those of theoretical.

The Lagergren first-order rate constant ($k_{1,ads}$) and the equilibrium amount of metal removed (q_e) determined from the model are presented in Table 2 along with the corresponding correlation coefficients. However, the most important feature of this model is that it fails to estimate q_e .

Table 2- Kinetic parameters for removal of MB by tea wastes.

First-order kinetic model			Second-order kinetic model			$q_{e,exp}$ (mg/g)
$k_{1,ads}$ (1/min)	q_e (mg/g)	R^2	$k_{2,ads}$ (g/mg min)	q_e (mg/g)	R^2	
11.53×10^{-3}	23.42	0.756	4.75×10^{-3}	74.96	0.999	74.20

The dye sorption is considered to be a pseudo-second-order reaction. The observed kinetics can be modeled assuming that the rate of occupation of adsorption sites is proportional to the square of the number of unoccupied sites, i.e.:

$$dq/dt = k_{2,ads}(q_e - q)^2 \quad (6)$$

Where $k_{2,ads}$ (g /mg.min) is the rate constant of second-order biosorption. Integrating (6) for the boundary conditions $t = 0$ to $t = t$ and $q = 0$ to $q = q_e$, Eq.(7), which corresponds to the integrated rate law for a second-order reaction, will result in:

$$1/(q_e - q) = 1/q_e + k_{2,ads} \cdot t \quad (7)$$

Eq. (7) can be rearranged and linearized to obtain:

$$t/q = 1/(k_{2,ads} \cdot q_e^2) + (1/q_e) t \quad (8)$$

The plot of t/q versus t should give a straight line if second-order kinetics is applicable and q_e and $k_{2,ads}$ can be determined from the slope and intercept of the plot, respectively. It is important to notice that for the application of this model to the experimental estimation of q_e is not necessary.

Both parameters and the correspondent coefficients of correlation are also presented in Table 2. The correlation coefficients for the second-order kinetic model are equal to 0.999 for MB uptake by biomass and the theoretical values of q_e also agree very well with the experimental ones. Both facts suggest that the sorption of MB follow the second-order kinetic model, which relies on the assumption that biosorption may be rate-limiting step.

Thermodynamic study

The free energy change of the sorption reaction is given by:

$$\Delta G^\circ = -RT \ln K_L \quad (9)$$

Since K_L is the equilibrium constant, its dependence on temperature can be used to estimate both enthalpy change (ΔH°) and entropy change (ΔS°) associated with the sorption process.

According to the following equation:

$$\ln K_L = -\Delta G^\circ / RT = -\Delta H^\circ / RT + \Delta S^\circ / R \quad (10)$$

Where ΔH and ΔS are found from the slope and intercept of the plot of $\ln K_L$ as a function of $1/T$ yields, respectively. R is the universal gas constant (1.987 cal/mol K) and T is the absolute temperature. As seen in Table 1, the positive value of ΔH confirms the endothermic character of biosorption, whereas the low values of ΔS indicates that no remarkable change on entropy is associated with the biosorption process. The negative values of ΔG validate the feasibility of the sorption process, and the spontaneity of sorption (Table1).

Effect of using NaCl and CaCl₂ to remove MB

It can be seen from Figs. 4a and 4b that using NaCl and CaCl₂ in adsorption solutions decreased the ability of tea waste to remove Mb ($C_0=0.01$ mM). It can be due to competition between Na⁺ and Ca²⁺ with =N⁺(CH₃)₂ of Mb as cationic dye to connect by -COO⁻ of cell wall polysaccharides in tea wastage such as pectin.

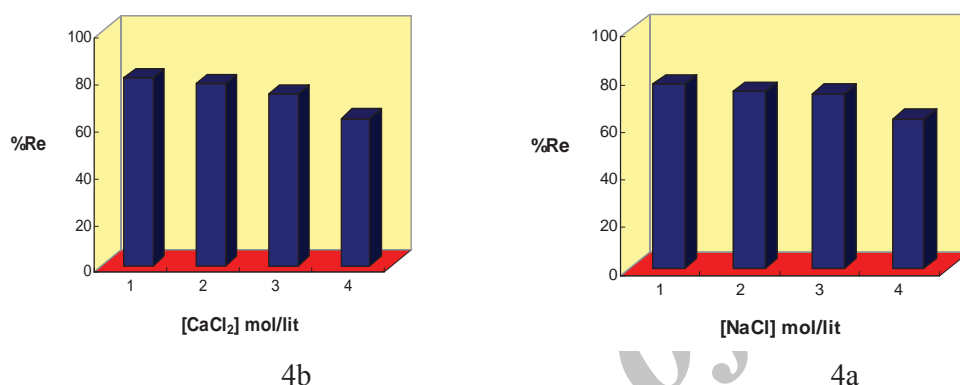


Fig. 4- 4a Effect of using NaCl and 4bCaCl₂ to remove MB

Effect of tea wastage dose on MB removal

As seen in Fig. 5, increasing the dose of tea wastage up to 2gr/lit increases the removal of MB. It can be due to increasing the number of effective contact between dye and the uptake sites of biomass. The desorption from adsorbed sites due to crowding and contact excessively can be the reason of decreasing uptake in the higher doses.

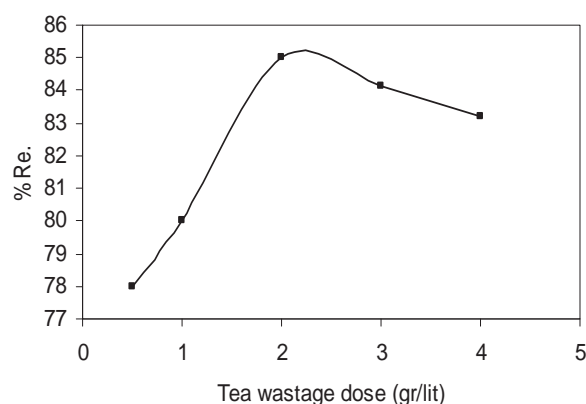


Fig. 5- The effect of increasing tea waste dose on removal of Mb

Conclusions

The results suggested that the tea wastage is able to remove MB corresponding to the Langmuir isotherm and second-order kinetic model.

The kinetic modeling of MB uptake by tea wastage showed that only the data corresponding to the first 30 min are adjusted approximately with pseudo-first-order model, since after this period the experimental data deviated considerably from those of theoretical. These data were fitted well with pseudo-second-order kinetic model.

The thermodynamic studies showed that the biosorption process of MB by tea wastage was spontaneity and endothermic.

Abbreviations and symbols

C_o	initial dye concentration (mg/l)
C_e	equilibrium dye concentration (mg/l)
C_f	final dye concentration (mg/l)
q	adsorbed dye on the adsorbent at time t (mg/g dry biomass)
q_e	adsorbed dye on the adsorbent at equilibrium (mg/g dry biomass)
Q_{max}	Langmuir parameter, maximum adsorption capacity (mg/g dry biomass)
K_L	Langmuir constant, sorption binding constant (l/mg)
V	suspension volume (l)
m	biosorbent dry weight (g)
$k_{1,ads}$	rate constant of first-order sorption (1/min)
$k_{2,ads}$	rate constant of second-order biosorption (g /mg.min)
ΔG	free energy change (kcal /mol)
ΔH	enthalpy change (kcal /mol)
ΔS	entropy change (cal /mol K)
R	universal gas constant (1.987 cal/mol K)
T	absolute temperature (K)

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