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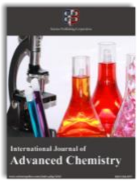

Comparison studies for the removal of a basic dye from aqueous solution using coffee residues and waste tea

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Abstract

Dyes are one of the most important industrial pollutants, especially in textile industries. The coffee residues and wastes tea are food industrial solid wastes, were used as low-cost adsorbents for the removal of methylene blue (MB) dye from aqueous solution. Many methods have been proposed in order to remove color from wastewater among which, adsorption is more acceptable due to the ability for its use in the large scale. The influence of various experimental factors such as contact time, adsorbent dosage, temperature and pH of dye solution was investigated. Two simplified kinetic models including pseudo-first-order and pseudo-second-order equation were selected to follow the adsorption processes. It was observed that chemisorptions pseudo-second order kinetic model described the sorption process with high coefficients of determination (R2) better than pseudo-first order kinetic model. Thermodynamic parameters such as $\Delta G°$, $\Delta H°$, and $\Delta S°$ were calculated the results of this parameteres indicated that the adsorption of methylene blue onto residues coffee and waste tea were spontaneous process.

Keywords: *Adsorption; Methylene Blue; Coffee Residues; Waste Tea; Kinetics.*

1. Introduction

Wastewater effluents from many industries, including paper, leather, textiles, rubber, plastics, printing, cosmetics, pharmaceuticals and food, contain several kinds of synthetic dyestuffs (Chatterjee 2009). These industries have shown a significant increase in the use of synthetic dyes as a coloring material. Since dyes have a synthetic origin and complex aromatic molecular structures, they are inert and difficult to biodegrade when discharged into waste streams (Kumar et al. 2011). The toxicity of most dye is the tendency for some of them to undergo chemical reactions within the exposed environment and formed products that are more toxic than the primary dye. Methylene blue (MB) is a cationic dye having various applications in chemistry, biology, medical science and dyeing industries. Its long term exposure can cause vomiting, nausea, anemia and hypertension (Hameed 2009). Various methods have been developed for dyes removal including biological treatment (Kapdan et al. 2002), biochemical methods (Tocchi et al.2012), membrane separation (Zhang et al. 2006), ion-echange (Dabrowski 2004), ultrafiltration (Ennigrou 2009), coagulation-flocculation (Kristianto 2019), chemical oxidation and photocatalytic processes (Hu 2007), chemical precipitation (Ku and Jung 2001), electrochemical process (Panizza et al. 2007) and adsorption techniques (Cui et al. 2015). Of the removal methods, adsorption is one that is gaining increasing attention due to its potential efficiency, low energy consumption, high selectivity at molecular level, easy operation, and ability to separate various chemical compounds (Yagub et al. 2014; Akpomie et al. 2015). Adsorption is by nature a surface phenomenon, its performance being strongly related to the unique properties of specifically designed sorbent material (Benhachem et al. 2019). Adsorption is a very effective separation technique and it's considered to be superior to other techniques for water treatment in terms of initial cost, simplicity of design, ease of operation and resilience to toxic substances (Mohammad et al.2010; Sun et al. 2012). Adsorption process can be a physisorption which involve only relatively weak intermolecular forces, and chemisorptions which involve the formation of a chemical bond between the sorbate molecule and the surface of the adsorbent (Sintayehu and Lencha 2016). In the present study, we used two biomaterials as an adsorbent to remove this dye by adsorption technique. The coffee residues and wastes tea, than are food industrial solid wastes, were used as low-cost adsorbents for the removal of methylene blue (MB) dye from aqueous solution. Various parameters affecting adsorption process, such as contact time, initial dye concentration, adsorbent concentration, temperature and PH were investigated. In addition, kinetic parameters were also calculated to determine adsorption mechanism was fitted into adsorption isotherms in order to give the best fit correlation.

2. Materials and methods

2.1. Adsorbate

Coffee residues and waste tea, a low-cost materials acquired from different cafeterias were used as adsorbent. The dye used herein in experiments was methylene blue. It has the molecular formula $C_{16}H_{18}ClN_3S$ and the molecular weight of 319.85 $g.mol^{-1}$ supplied by Sigma-Aldrich. Double distilled water was employed for preparing all the solutions and reagents. Stock solution was prepared by dissolving the required amount of MB in double distilled water. The test solutions were prepared by diluting stock solution to the desired concentrations.

2.2. Experimental protocol

The batch adsorption experiments were conducted in a set of 250 mL of Erlenmeyer flask containing adsorbent and 100 mL of MB solution with various initial concentrations. Methylene blue concentrations were determined by measuring the absorbent values in each experiment with UV/Visible spectrophotometer (OPTIZEN 1412V) at $\lambda = 665$ nm. The pH of solution was adjusted with 1N HCl and 1N NaOH solutions.

The amount of dye adsorbed and percentage removal of MB were calculated using the following expressions respectively:

$$q_e = \frac{(C_0 - C_e)V}{m}$$

And

$$R\,(\%) = \frac{(C_0 - C_e)}{C_0} * 100$$

Where q_e is the equilibrium adsorption capacity of Methylene Blue adsorbed on unit mass of the biomaterials ($mg.g^{-1}$); C_0 and C_e are the initial Methylene Blue concentration ($mg.L^{-1}$) and Methylene Blue concentration ($mg.L^{-1}$) at equilibrium, respectively; V is the volume of the Methylene Blue solution (L); and m is the weight of the biomaterials (g).

3. Result and discussion

3.1. Effect of pH

The pH of a dye solution is an important influencing factor for the adsorption of MB onto coffee residues and waste tea. The effect of initial pH on adsorption of MB was studied from pH 2 to 12 at initial MB concentration of 15 $mg.L^{-1}$, adsorbent dosage of 0.1 g of residues coffee and 0.05 g of waste tea. Ability of adsorbent to adsorb adsorbate also was affected by acidity condition of adsorbent surface. Long contact of adsorption was conducted at optimum contact time yielded before i.e. at 60 minutes. Acid condition at pH 2 until 6, waste tea and coffee residues could remove methylene blue 32.17% and 42.81% till 93.14% and 92.14% respectively. After pH 6 till pH 12, capability of waste tea and residues coffee to adsorb methylene blue stayed on better in 92%. pH effect on the adsorption of methylene blue was showed at Fig. 1.

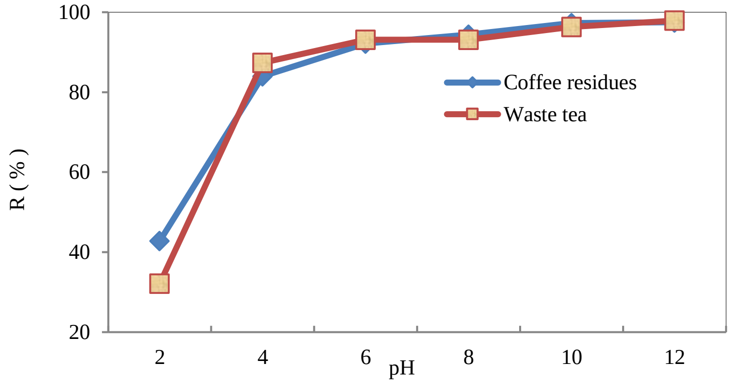

Fig. 1: Effect of PH in Methylene Blue Removal.

The efficiency of adsorption is dependent on the solution pH because variation in pH leads to the variation in the degree of ionization of the adsorptive molecule and the surface properties of adsorbent (Sen et al 2011).

3.2. Effect of contact time

The impact of contact time on the adsorption of dye from an aqueous phase onto waste tea and residues coffee were investigated at different time intervals in the range of 10 to 150 min. The extent of removal of MB by these biomaterials was found to increase, reach a maximum value with increase in contact time. The relative increase in the extent of removal of dye after 60 min of contact time is not significant for the both biomaterials and hence it is fixed as the optimum contact time. The effect of different contact time on the adsorption capacity of MB is illustrated in figure 2.

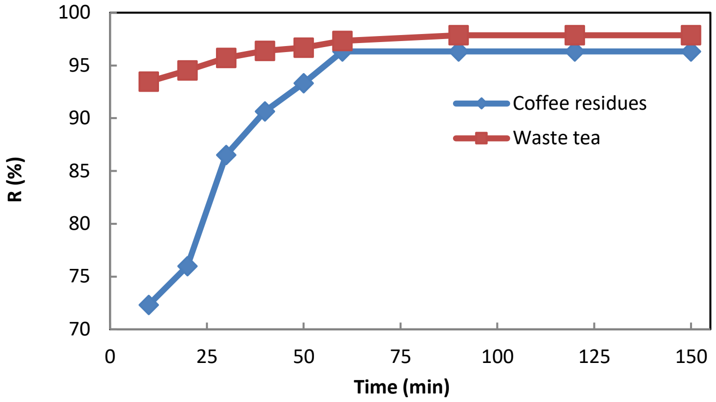

Fig. 2: Effect of Contact Time on Adsorption of MB with Coffee Residues and Waste Tea.

3.3. Effect of adsorbent mass

The effect of adsorbent dose on dye adsorption, varies from 10-175 mg by using 15 mg.L^{-1} methylene blue dye solution. It was observed that the removal efficiency of coffee residues was 96.33% and 97.43% for waste tea at 60 min, by the addition of 100 mg of adsorbent dose while removal efficiency of coffee residues was found to be 62.25% at 10 mg and 91.17% for waste tea adsorbent dose howsoever at higher adsorbent dose removal efficiency was higher. The removal of MB dye is also graphically shown in fig.3.

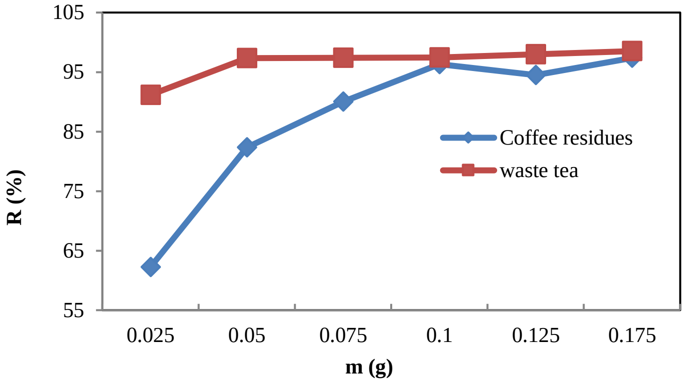

Fig. 3: Effect of Adsorbent Dose on Adsorption of MB with Coffee Residues and Waste Tea.

3.4. Effect of temperature

It is important to investigate the effect of temperature on adsorption in a view of practical application. The effect of temperature on the adsorption of methylene blue at 0.1 g of coffee residues and 0.05g of waste tea in 100 mL adsorbent concentration, 60 min of contact time and BM concentration 15 mg.L^{-1} seen in figure 5 was investigated. The adsorption isotherms at different temperatures (25, 35, 45, 55 and 65°C) are studied in this effect. The results obtained indicate that the change in temperature in the specified range has almost no effect on the adsorption capacity of Methylene Blue (Zaker 2013), the removal efficiency varies between 96.33 to 93.73% for coffee residues and 97.33 to 98.60 % for waste tea (figure 4). For this reason, a room temperature of 25 °C was used throughout this work.

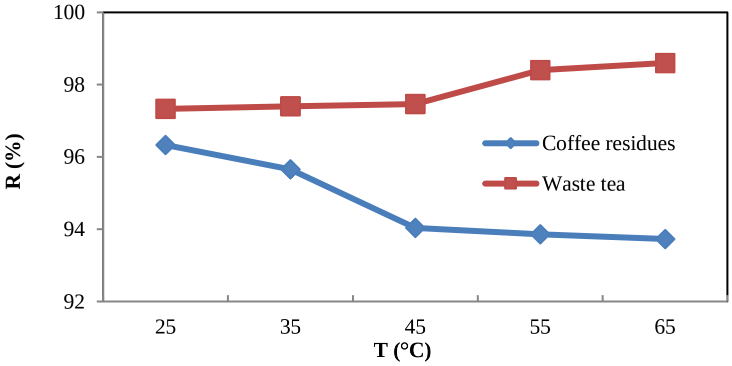

Fig. 4: The Effect of Temperature on the Adsorption of MB onto Coffee Residues and Waste Tea.

3.5. Kinetics studies

3.5.1. Pseudo first order

The Largergren model, proposed in 1898, assumes a first order adsorption kinetics and can be represented by the equation (Zhang et al. 2015):

$$\frac{dq_t}{dt} = k_1(q_e - q_t)$$

Where: q_e and q_t are adsorption capacity at equilibrium and at time t, respectively (mg.g^{-1}), k_1 is the rate constant of pseudo first order adsorption (min^{-1}). After integration and applying boundary conditions t=0 to t=t and q_t=0 to q_t=q_e, the integrated form becomes:

$$\mathrm{Log}\ (q_e - q_t) = \log(q_e) - \left(\frac{k_1}{2{,}03}\right) t$$

The values of log (q_e–q_t) were linearly correlated with t (figure. 5). The plot of log (q_e–q_t) versus t should give a linear relationship from which k_1 and q_e can be determined from the slop and intercept of the plot, respectively (Demirbas 2004). The applicability of the pseudo-first order equation to experimental data generally, differs in two ways; the parameter k_1(q_e–q_t) does not represent the number of available sites and the parameter log(q_e) is an adjustable parameter and often found not equal to the intercept of the plot log (q_e–q_t) versus t, whereas in true first order, log(q_e) should be equal to the intercept (Ho and McKay 1998).

3.5.2. The pseudo second- order

The pseudo second-order adsorption kinetic rate equation is expressed as (Andrew and Hsieh 2015):

$$\frac{dq_t}{dt} = k_1(q_e - q_t)^2$$

Where k_2 is the rate constant of the pseudo second order adsorption (g.mg^{-1}.min^{-1}). For the boundary conditions t=0 to t=t and q_t=0 to q_t=q_e, the integrated form of the equation becomes (the integrated rate law for the pseudo second-order reaction):

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

A plot of t/q_t versus t gives a linear relationship, from which q_e and k_2 can be determined from the slope and intercept (figure. 6). The results for the adsorption of MB on coffee residues and waste tea were applied to pseudo first and second order kinetic models and the results are presented in Table 1.

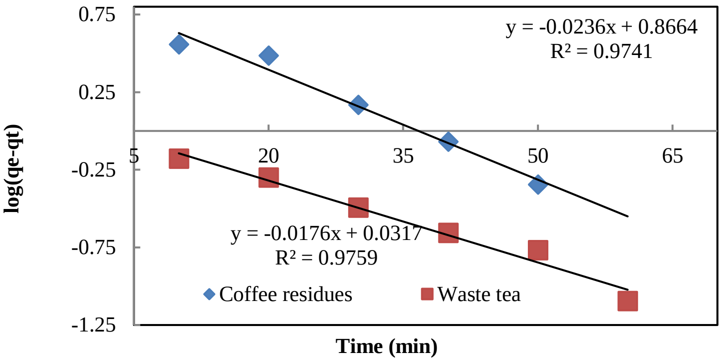

Fig. 5: Application of Pseudo-First Order Model of Adsorption of Methylene Blue on Biomaterials.

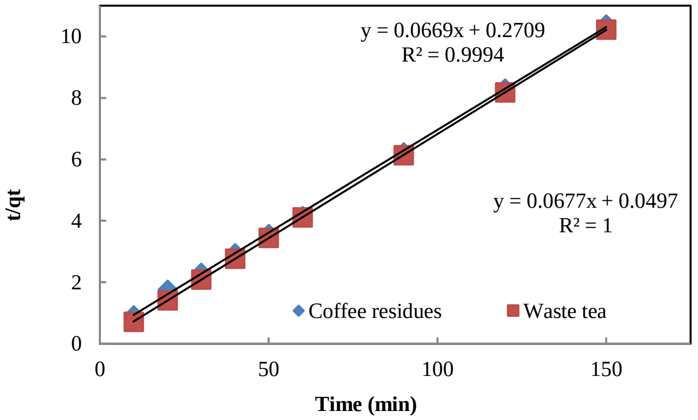

Fig. 6: Application of the Pseudo-Second Order Model of Methylene Blue Adsorption on Biomaterials.

The correlation coefficient of second order kinetic model (0.999) is greater than for first order kinetic model (0.97). This confirmed that the rate limiting step is chemisorptions.

Table 1: Kinetic Parameters for the Adsorption of MB onto Biomaterials

	Pseudo first order model			Pseudo second order model		
	K_1 (min-^{1})	q_e (mg.g^{-1})	R^2	K_2 (g/mg.min)	q_e (mg.g^{-1})	R^2
Coffee residues	0.046	7.34	0.974	0.016	15.15	0.999

Waste tea	0.034	1.07	0.975	0.08	14.92	1

3.6. Adsorption isotherms

3.6.1. Langmuir adsorption isotherm

The Langmuir adsorption isotherm is based on monolayer, uniform, and finite adsorption site assumptions, therefore a saturation value is reached beyond which no further adsorption takes place.

The Langmuir equation which is valid for monolayer adsorption onto a surface with a finite number of identical sites is given by (Langmuir 1916):

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \left(\frac{1}{K_L q_m}\right)$$

Where C_e is the concentration of the dye solution at equilibrium (mg.L^{-1}), q_e is the amount of dye adsorbed per unit mass of adsorbent (mg.g^{-1}), and K_L is the constant related to the free energy of adsorption (L.mg^{-1}). q_m is the maximum adsorption capacity.

The results of Langmuir were calculated from this isotherm and their values are given in Table 2.

Numerous studies incorporate another important parameter, R_L, namely the separation factor. The value of R_L indicates the type of the isotherm to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$) and is expressed by (Hall 1966):

$$R_L = \frac{1}{1 + K_L C_0}$$

Where K_L is the Langmuir constant (L.mg^{-1}) and C_0 is the highest initial dye concentration (mg.L^{-1}).

The R_L values were found to be 0.0056-0.069, i.e. $0 < R_L < 1$ for all MB mg.L^{-1} concentrations C_0 in the range of 10-175 mg. According to the values of R_L, all the systems show favorable adsorption of MB, i.e., $0 < R_L < 1$. The low values of R_L indicate high and favorable adsorption of MB onto the both biomaterials.

3.6.2. Freundlich adsorption isotherm

Freundlich model attempts to account for surface heterogeneity (Foo 2012), Freundlich isotherm model:

$$\log(q_e) = \log(K_F) + \left(\frac{1}{n}\right)\log(C_e)$$

Where log K_F is roughly a measure of the adsorption capacity and 1/n is an indicator of adsorption effectiveness; q_e is the amount of dye adsorbed per unit mass of adsorbent (in mg.g^{-1}) and C_e is the equilibrium concentration of dye (in mg.L^{-1}).

Freundlich constants (K_F) and n are determined from the plot of log(q_e) versus log(C_e). The parameters K_F and 1/n are related to sorption capacity and the sorption intensity of the system. The magnitude of the term (1/n) gives an indication of the favorability of the sorbent/adsorbate systems (Malik 2003).

The results obtained by the application of the two-parameter model, Langmuir and Freundlich equations are presented in Table 2. From this table, the correlation coefficients for Freundlich isotherm are significantly high than that of Langmuir isotherm. The results show that the value of 1/n is less than unity indicating that the dye is favorably adsorbed.

Table 2: Langmuir and Freundlich Isotherm Constants for MB

	Langmuir model			Freundlich model		
	Q_{max} (mg.g^{-1})	K_L (L.mg^{-1})	R^2	1/n	K_F (mg$^{1-1/n}$.L$^{1/n}$.g^{-1})	R^2
Coffee residues	45.45	1.69	0.957	0.475	23.24	0.977
Waste tea	50	1.33	0.951	0.452	22.04	0.994

3.7. Thermodynamics studies

Thermodynamic considerations of an adsorption process are necessary to conclude whether the process is spontaneous or not. Gibb's free energy change, ΔG°, is the fundamental criterion of spontaneity.

To evaluate the effect of temperature on adsorption process of MB onto coffee residues and waste tea, the thermodynamic parameters such as Gibbs free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) are calculated using the following equations.

$$\ln K_d = \left(\frac{\Delta S^0}{R}\right) - \left(\frac{\Delta H^0}{RT}\right)$$

$$\Delta G^0 = -RT \ln K_d$$

Where R is the universal gas constant (8.314 J.mol^{-1} .K^{-1}), k_d is the Langmuir constant (L.g^{-1}) and T is the absolute temperature (K). ΔS° and ΔH° were calculated from the intercept and slope of the plot of ln(k_d) versus 1/T (figure 7). The thermodynamic parameters were listed in Table 3.

Table 3: Thermodynamic Parameter of MB Adsorption onto Coffee Residues and Waste Tea

	ΔH° (KJ.mol^{-1})	ΔS° (J.K^{-1}.mol^{-1})	ΔG° (KJ.mol^{-1})			
T (K)	298	298	298	308	328	338
Coffee residues	-11.75	-12.44	-8.05	-7.92	-7.67	-7.54
Waste tea	15.12	80.06	-8.73	-9.53	-11.14	-11.94

The positive value of ΔH° (15.12 KJ.mol^{-1}) indicates that the adsorption of MB onto waste tea is an endothermic reaction but exothermic (-11.75 KJ.mol^{-1}) onto coffee residues.

The negative value of ΔG° suggests the feasibility and the spontaneous nature of the adsorption.

In general, the values of ΔG° between 0 and −20 KJ.mol^{-1} indicate that the adsorption process is physisorption, while the values in between −80 and −400 KJ.mol^{-1} correspond to chemisorption (Nasuha and Hameed 2011). The values of ΔG° suggest the adsorption onto the waste tea and residues coffee are physisorption process.

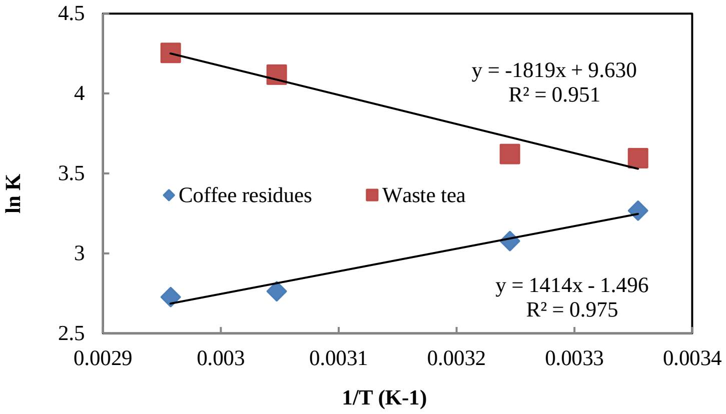

Fig. 7: Enthalpy and Entropy Determination for MB Removal.

4. Conclusion

The Methylene Blue in aqueous solutions can be adsorbed by coffee residues and waste tea. By comparing coefficient of regression, the Freundlich isotherm has higher coefficient of determination than that of Langmuir. By using the adsorption equilibrium constant obtained from Langmuir isotherm, thermodynamic parameter ΔG° was calculated to describe the spontaneity of the adsorption reaction. The values of ΔH° and ΔS° were also obtained from a slope and intercept of the relationship between ΔG° and reaction temperature.

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