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## RESEARCH ARTICLE

## Kinetic study of Malachite Green adsorption on used black tea leaves from aqueous solution

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### Abstract

This study presents a kinetic evaluation on the adsorptive removal of Malachite Green (MG), a common pollutant in the textile waste water, by Used Black Tea Leaves (UBTL) as a low cost adsorbent. The adsorption kinetic experiments were carried out in batch process. The effects of contact time, concentration, solution pH and temperature on this removal process were investigated. UV-visible spectrophotometer was used for analysis of MG at pH 4.0. Kinetic studies have shown that the adsorption data partially follow simple first order, second order, pseudo first order and Elovich equation for different initial concentrations at pH 2.0 but well expressed by pseudo second order rate equation. Pseudo second order rate equation was used to determine the equilibrium amount adsorbed and equilibrium concentration for different initial concentrations, temperatures and pH. The equilibrium amount adsorbed and pseudo second order rate constant were found to increase with increasing temperature indicating chemical nature of adsorption. The numerical values of apparent activation energy,  $E_a$  and thermodynamic parameters  $\Delta G^\circ$ ,  $\Delta H^\circ$ , and  $\Delta S^\circ$  of the process also supported the chemisorption of MG on UBTL at pH 2.0. The effect of solution pH on the adsorption kinetics showed that the amount adsorbed linearly increase with increasing solution pH suggesting deprotonation dominants the adsorption of MG on UBTL. The adsorption capacity of UBTL to MG was obtained 227.3 mg/g at pH 6.0 and 30° C.

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### Introduction

Most of dyes are harmful for human health and aquatic life. Various types of dyes are widely used in many industries such as textiles, tannery, pharmaceuticals etc. in different countries. The improper disposal of the wastewaters from these causes dye pollution in the environment. Malachite Green (MG) is one of the most useful dye in those industries, can cause injuries to humans and animals by direct contact of inhalation and ingestion (Culp and Beland, 1996). There are several methods to remove dyes from waste water such as coagulation (Malakootian and Fatehizadeh 2010), reverse osmosis (Mazloomi *et al.*, 2009), photodegradation (Lin and Valsaraj 2003; Maleki *et al.*, 2010), ion exchange (Kavitha and Namasivayam, 2007), ozonation (Malik and Saha, 2003; Koch *et al.*, 2002), oxidation (Gholami-Borujeni *et al.*, 2011), biodegradation (Gholami-Borujeni *et al.*, 2011), nano-technology (Mahvi *et al.*, 2009) and adsorption (Hossain *et al.*, 2011; Hossain and Hassan, 2013). From economic point of view, adsorption is the best process to remove pollutants such as colors, dyes and metal impurities from wastewaters (Hossain *et al.*, 2011; Hossain and Hassan, 2013; Hossain *et al.*, 2005a; Hossain *et al.*, 2005b; Hossain *et al.*, 2010; Mukhtat and Tahir, 2008). Some of the adsorbent materials such as rice husk (Malik, 2003), cornelian cherry, apricot stone, almond shell (Demirbas, 2004), cotton stalks (Attia *et al.*, 2004), charcoal (Khan 1994), Orange peel (Arami 2005), wood (Poots 1978) and sunflower stalks (Sun, 1997) were successfully performed for the removal of dyes from aqueous solutions by adsorption process. In present study, Used Black Tea Leaves (UBTL) was considered as a low cost adsorbent. Because very recently, high adsorption capacity of UBTL as a low cost

adsorbent to Cr (VI) was reported (Hossain *et al.*, 2005a; Hossain *et al.*, 2005b; Hossain *et al.*, 2010; Mukhtat and Tahir, 2008). Therefore, the present study was carried out to investigate the adsorptive removal of MG from aqueous system on UBTL. Kinetic of adsorption is very important physicochemical tool to evaluate the feasibility of the process. Therefore, the present study was carried out to investigate the kinetics of adsorption of MG on UBTL under various experimental conditions such as initial concentration of MG, solution pH and processing temperature. The factors affecting the rate constant and the adsorption capacity of the process was also investigated with different kinetic equations.

## Material and Methods

### Preparation of Adsorbent

The fresh tea leaves were collected from Dhaka city in Bangladesh. The tea leaves boiled with distilled water for eight hours to extract tea liquor from tea leaves and the separated tea leaves were dried at 105°C for ten hours after drying at room temperature. The dried tea leaves were sieved through the metallic sieves of mesh size 0.212 and 0.300 mm and stored in air tight bottles which were kept in a desiccator for use in experiments. The surface morphology of prepared UBTL was investigated by Scanning Electron Microscope (JSM-6490LA, JEOL, Japan) as shown in **Figure 1**.

### Adsorbate

Malachite Green (MG) is a basic dye which exists as cationic form in acidic to neutral media. Basic green 4 and Malachite green hydrochloride are synonyms of Malachite Green. Molecular formula of Malachite Green is  $C_{23}H_{26}N_2O \cdot HCl$  and structural formula is given in **Figure 2**. CAS number and molecular weight of Malachite Green are 123333-61-9 and 382.93 g, respectively.

A stock solution of 1000 mg/L was prepared by dissolving MG (Analytical grade) in distilled water from which different concentrated solutions were prepared. The pH of different concentrated solutions was adjusted at 4.0 adding either 0.05 mol/L  $HNO_3$  or 0.05 mol/L NaOH solution. The absorbance of each solution was measured at pre-determined  $\lambda_{max} = 617$  nm and optimum pH 4.0 by using a computerized UV-visible spectrophotometer (UV-1650A, Shimadzu, Japan). A calibration curve was constructed using measured absorbance as a function of respective concentration. According to Beer-Lambert law, the calibration limit of MG was determined which 0.1 to 15.0 mg/L at optimum pH 4.0 and the molar absorption coefficient was  $4.5 \times 10^4$  L/mol.cm. All the chemicals were used of analytical grade.

### Kinetic Experiments

Adsorption kinetic experiments were carried out in batch process. 0.0025 g dry UBTL was taken in each of 5 bottles containing 25 mL of a fixed concentration of MG solution at pH 2.0 as an optimum pH for UBTL (Hossain *et al.*, 2011; Hossain *et al.*, 2005; Hossain and Alam, 2012) and was shaken in a thermostatic mechanical shaker (HAAKE SWB20, Fissions Ltd., Germany) at  $30.0 \pm 0.2^\circ C$ . After shaking of different time of intervals, the mixtures were separated by centrifuge. After proper dilution of supernatant, pH was adjusted at 4.0 and measured the absorbance using UV-visible spectrophotometer at  $\lambda_{max}$  617 nm. Before adsorption, the absorbance of the initial solution with proper dilution and pH adjusted at 4.0 was also measured by UV-visible spectrophotometer at  $\lambda_{max}$  617 nm to determine the initial concentration of the solution.

### Effect of Concentration

The effect of concentration of MG on the adsorption kinetics on UTBL was investigated by performing adsorption kinetic experiments with different initial concentrations. The amounts adsorbed of MG,  $q_t$  on UBTL for different contact times were calculated from the analytical data using the following Eq. (1)

$$q_t = (C_o - C_t) \times \frac{V}{W} \quad (1)$$

where,  $q_t$  is the amount of adsorbed (mg/g),  $W$  is the amount of UBTL (g),  $C_o$  is the initial concentration of MG (mg/L),  $C_e$  is the equilibrium concentration of MG (mg/L) and  $V$  is the volume (L) of solution in each bottle.

### Effect of Temperature

To investigate the effect of temperature on the adsorption kinetics, adsorption kinetic experiments were carried out at 30, 40 and 50°C using same initial concentration of 100 mg/L of MG remaining other parameters fixed. The variation of amount adsorbed of MG with time for different temperatures was determined.

### Effect of pH

For determination the effect of pH, adsorption kinetic experiments were carried out at different initial pH using same initial concentration of 100 mg/L of MG at 30.0 ± 0.2°C, remaining other parameters fixed. The variation of amount adsorbed of MG with time for different pH was determined.

## Result

### Effect of Concentration

The progress of adsorption is closely related with the initial concentration of adsorbate. **Figure 3** shows the adsorption kinetics of MG on UBTL surface for different initial concentrations. The amount adsorbed increased rapidly at the initial stage with time for different initial concentrations and adsorption became very slow at later. Different kinetic equations were applied to the dynamic experimental data to evaluate the feasibility of the adsorption of MG on UBTL.

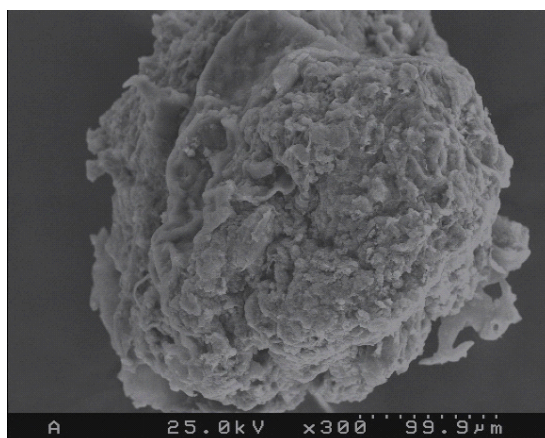


Figure 1. SEM micrograph of prepared used black tea leaves (UBTL) ×300

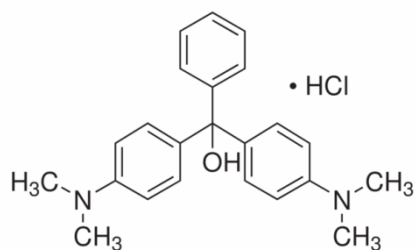
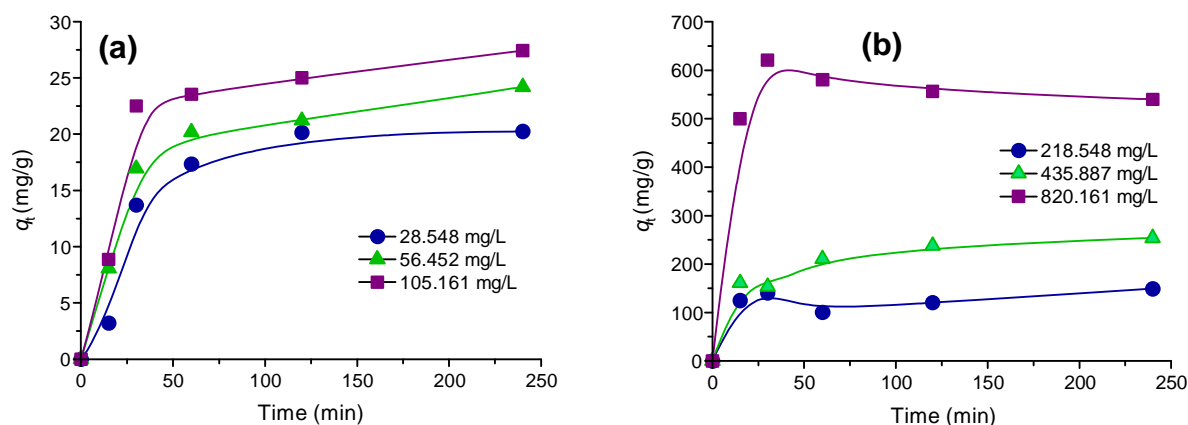


Figure 2. Structural formula of malachite green



**Figure 3(a & b). Variation of amount adsorbed of MG on UBTL with time for different initial concentrations at pH 2.0 and  $30 \pm 0.2^\circ\text{C}$**

### First order kinetics

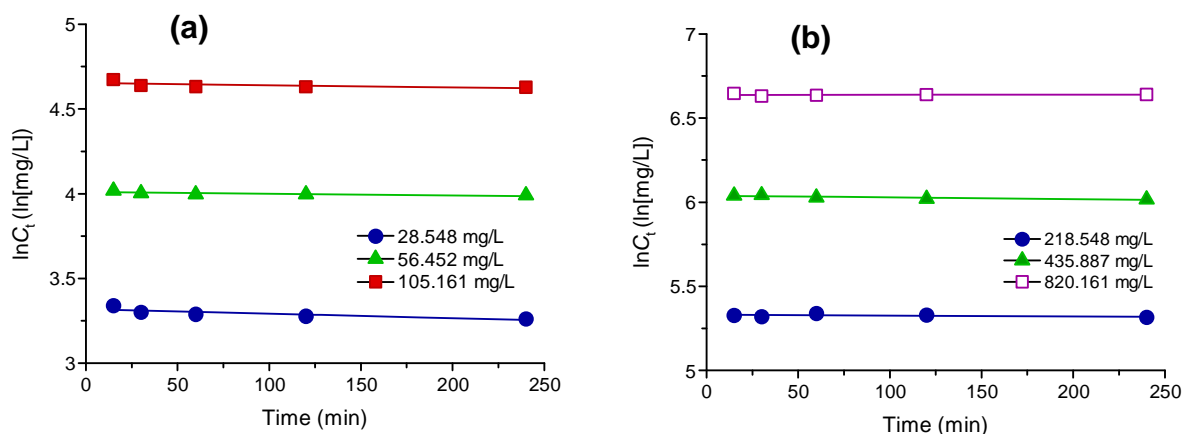
First order kinetic Eq. (2) (Hossain *et al.*, 2011; Hossain and Hassan, 2013; Hossain *et al.*, 2005a; Hossain and Alam 2012; Gupta *et al.*, 2001; Cimino *et al.*, 2000) was applied to the adsorption of MG on UBTL.

$$\ln C_t = k_1 t + \ln C_o \quad (2)$$

where,  $C_o$  is the initial concentration of reactant (mg/L),  $C_t$  is the concentration of reactant after time  $t$  (mg/L) and  $k_1$  is the first order rate constant. Applicability of the first order kinetics (Eq. 2) was verified by plotting  $\ln C_t$  versus  $t$  as shown in **Figure 4 (a and b)**. The figure shows that the adsorption of MG on UBTL does not follow (regression factor,  $R^2$  values given in **Table 1**) the simple first order kinetic equation for different initial concentrations of MG at pH 2.0 and  $30.0 \pm 0.2^\circ\text{C}$ .

### Second order kinetics

The adsorption of MG on UBTL for different initial concentrations was verified by using second order kinetic Eq. (3) (Hossain *et al.*, 2011; Hossain and Hassan, 2013; Hossain and Alam 2012; Gupta *et al.*, 2001), and the

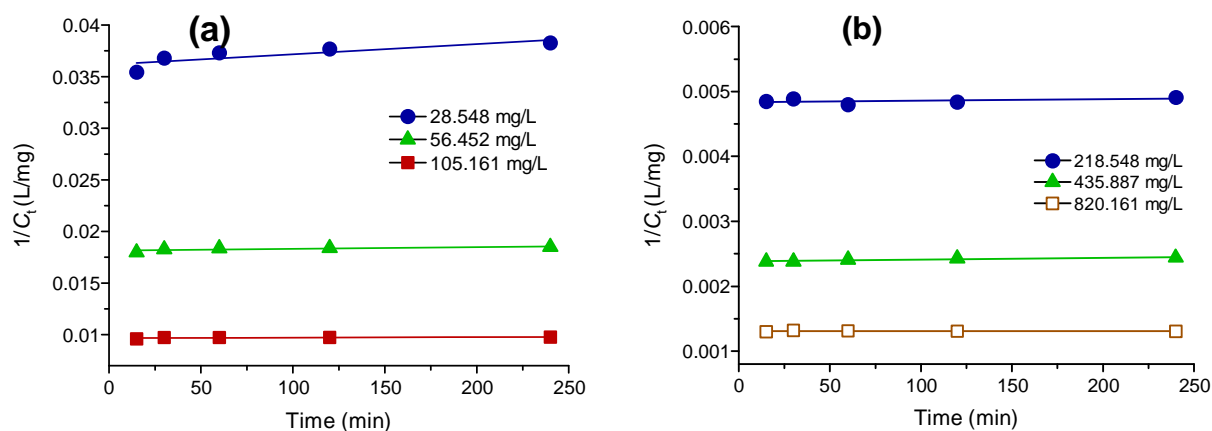


**Figure 4 (a & b). Application of the first order kinetic equation for the adsorption of MG on UBTL at pH 2.0 and  $30 \pm 0.2^\circ\text{C}$**

plot of  $1/C_t$  versus  $t$ .

$$\frac{1}{C_t} = k_2 t + \frac{1}{C_0} \quad (3)$$

where,  $C_t$  is the final concentration after time  $t$  (mg/L),  $C_0$  is the initial concentration (mg/L) and  $k_2$  is the second order rate constant (g/mg·min). **Figure 5 (a and b)** shows that the adsorption of MG on UBTL does not follow ( $R^2$  values given in **Table 1**) the simple second order kinetic equation for different initial concentrations of MG at pH 2.0 and at  $30.0 \pm 0.2^\circ\text{C}$ .



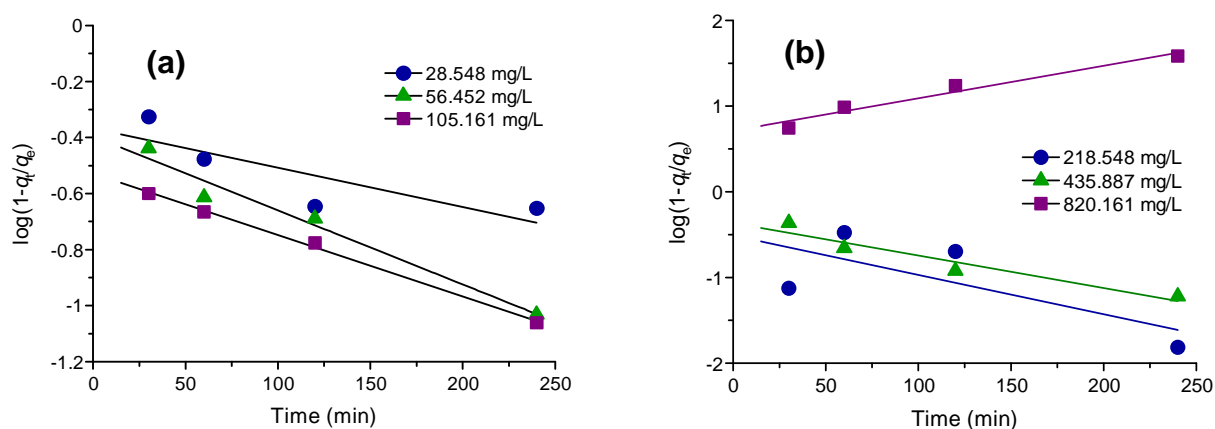
**Figure 5 (a & b).** Application of the second order kinetic equation for the adsorption of MG on UBTL at pH 2.0 and  $30 \pm 0.2^\circ\text{C}$

### Pseudo first order kinetics

Lagergren pseudo-first order rate equation is commonly used to the adsorption of liquid/solid system based on adsorbent capacity (Hossain and Hassan, 2013; Hossain *et al.*, 2005a; Hossain and Alam 2012; Lagergren 1898). According to this model, one adsorbate species reacts with one active site on surface. The linearized form of the pseudo-first order kinetic equation is expressed as follows by Lagergren (Hossain and Hassan, 2013; Hossain *et al.*, 2005a; Hossain and Alam, 2012):

$$\log(q_e - q_t) = \log q_e - \frac{k_{1p}}{2.303} t \quad (4)$$

where,  $q_e$  and  $q_t$  are the adsorption capacity at equilibrium and at time  $t$ , respectively (mg/g),  $k_{1p}$  is the rate constant of pseudo first order equation (L/min). In order to obtain the rate constants,  $k_{1p}$ , the values of  $\log(q_e - q_t)$  were linearly correlated with  $t$  by plot of  $\log(q_e - q_t)$  versus  $t$  to give a linear relationship from which  $k_{1p}$  and predicted  $q_e$  can be determined from the slope and intercept of the plot, respectively (Demirbas *et al.*, 2004; Hossain and Alam, 2012). The applicability of the pseudo-first order equation to experimental data generally, differs in two ways; the parameter 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 (Hossain and Alam, 2012; Ho and McKay 1998). **Figure 6** shows the weak fitness of pseudo-first order plots at different initial concentrations. Values of correlation coefficients for different initial concentrations of MG are given in **Table 1**. The results showed that the pseudo first order rate constant,  $k_{1p}$  is irregularly changes with concentration i.e.  $k_{1p}$  independent of initial concentration. Similar result has been presented in literatures (Hameed *et al.*, 2007; Abechi *et al.*, 2011).



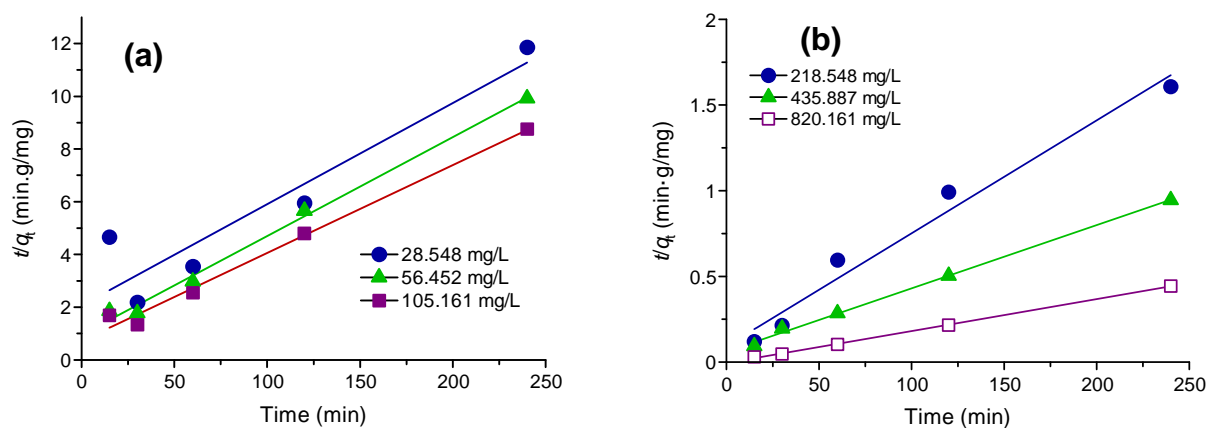
**Figure 6 (a & b).** Application of the pseudo first order kinetic equation for the adsorption of MG on UBTL at pH 2.0 and  $30 \pm 0.2^\circ\text{C}$

### Pseudo second order kinetics

Ho and McKay's (Hossain and Alam, 2012; Ho and McKay, 2000) pseudo second order rate equation was applied for the adsorption of MG on UBTL at different initial concentrations. The linearized form of Ho and McKay's pseudo second order rate equation is shown in Eq. (5),

$$\frac{t}{q_t} = \frac{1}{k_{2p}q_e^2} + \frac{t}{q_e} \quad (5)$$

where,  $q_t$  is the amount adsorbed at time,  $t$  (mg/g),  $q_e$  is equilibrium amount adsorbed (mg/g) and  $k_{2p}$  is pseudo second order rate constant (g/mg·min). The plot of  $t/q_t$  vs.  $t$  as shown in **Figure 7** gives a straight line with a slope  $1/q_e$ . This figure shows the satisfactory fitness of data to the straight line. Hence from the slope and intercept of the plots for different initial concentrations, equilibrium amount adsorbed and equilibrium concentration can be calculated and then pseudo second order rate constant,  $k_{2p}$  can also be calculated from Eq.5.



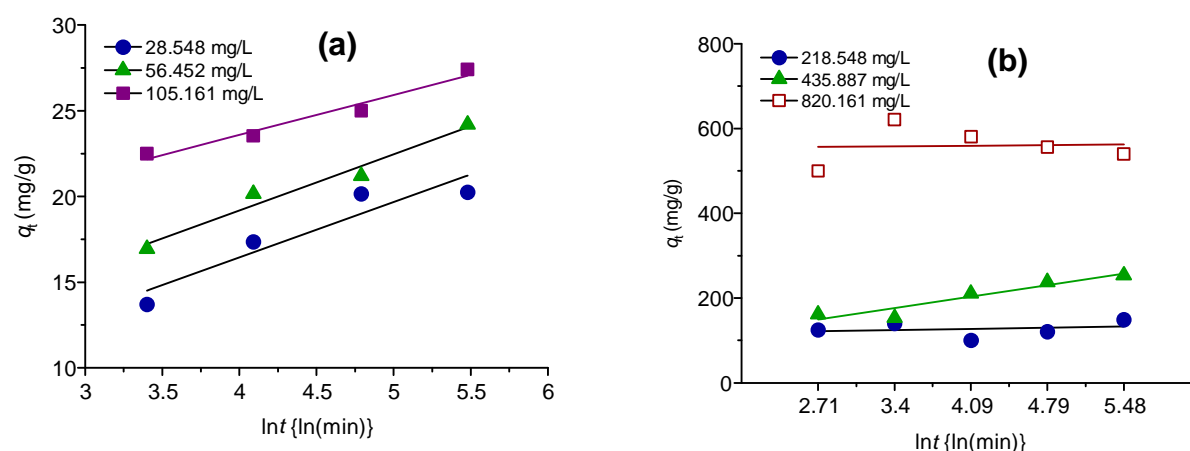
**Figure 7 (a & b).** Application of the pseudo second order kinetic equation for the adsorption of MG on UBTL at pH 2.0 and  $30 \pm 0.2^\circ\text{C}$

### Elovich equation

The integrated form of Elovich equation was applied for several studies (Theivarasu and Mysamy, 2010; Alzaydien and Manasreh, 2009) which is shown in Eq. (6).

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \quad (6)$$

where,  $\alpha$  is the initial adsorption rate (mg/g.min) and  $\beta$  is related to the extent of surface coverage and the activation energy for chemisorption (g/mg). The adsorption of MG on UBTL for different initial concentrations were verified by using Eq. (6) and the plot of  $q_t$  versus  $\ln t$  in **Figure 8 (a and b)** which show that the adsorption of MG on UBTL does not follow the Elovich equation for different initial concentrations of MG at pH 2.0 and at  $30 \pm 0.2^\circ\text{C}$ . A comparison of the regression factor for the fitness of simple first order, second order, pseudo first order, pseudo second order kinetic and Elovich equations to the adsorption kinetics of MG on UBTL is given in **Table 1**.



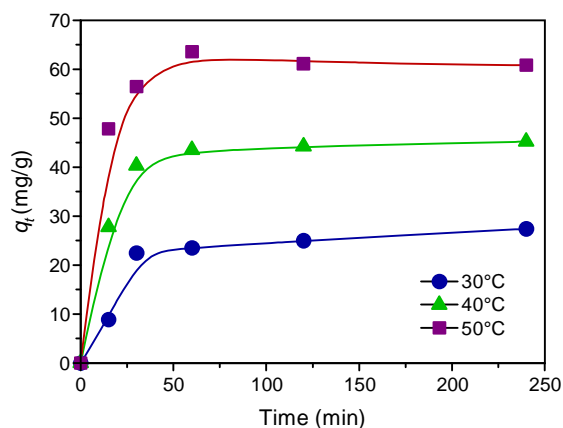
**Figure 8 (a and b).** Application of the Elovich equation for the adsorption of MG on UBTL at pH 2.0 and  $30 \pm 0.2^\circ\text{C}$

**Table 1** A comparison of the experimental data fitness to the simple first order, second order, pseudo first order, pseudo second order and Elovich kinetic equations

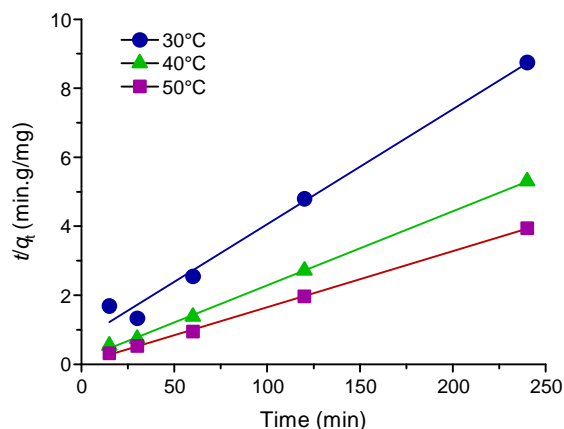
Initial conc. $C_0$ (mg/L)	First order $R^2$	Second order $R^2$	Pseudo First order $R^2$	Pseudo second order $R^2$	Elovich equation $R^2$
28.548	0.509	0.511	0.636	0.881	0.819
56.452	0.602	0.609	0.872	0.994	0.870
105.161	0.379	0.430	0.761	0.989	0.738
218.548	0.256	0.236	0.530	0.974	0.061
435.887	0.789	0.817	0.941	0.998	0.902
820.161	0.016	0.048	0.483	0.999	0.003

### Effect of Temperature

The adsorption kinetic data of MG on UBTL at pH 2.0 for different temperatures are shown in **Figure 9a**. Pseudo second order kinetic equation is applicable for the adsorption of MG on UBTL at different temperatures as shown in **Figure 9b**. The equilibrium amount adsorbed and equilibrium concentration were calculated from the slope and intercept of pseudo second order kinetic plots. Variation of equilibrium amount adsorbed with different temperatures was shown in the **Figure 10** which indicates the increase of equilibrium amount adsorbed with increase of temperature i.e. the process is endothermic.



**Figure 9a.** Variation of amount adsorbed of MG on UBTL with time at different temperatures for a fixed concentration of MG at pH 2.0



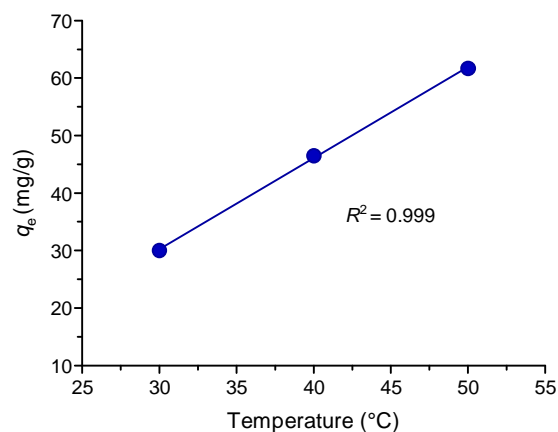
**Figure 9b.** Application of the pseudo second order kinetic equation to the adsorption of MG on UBTL for different temperatures at pH 2.0

### Adsorption Thermodynamics

#### The apparent activation energy

The apparent activation energy,  $E_a$  was calculated from the slope of the plot of the natural logarithm of pseudo second order rate constant,  $k_{2p}$  values at different temperatures against the reciprocal of absolute temperature as





**Figure 10. Variation of equilibrium amount adsorbed with temperature for adsorption of MG on UBTL at pH 2.0**

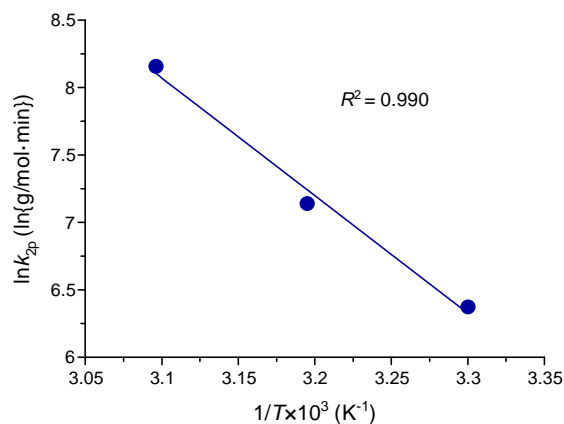
shown in **Figure 11**, according to the Arrhenius type relationship, Eq. (7) (Bayramoglu *et al.*, 2009),

$$\ln k_{2p} = -\frac{E_a}{RT} + \ln A \quad (7)$$

where,  $A$  is Arrhenius temperature independent factor,  $R$  is the gas constant (8.314 J/K.mol) and  $T$  is the absolute temperature (in K). The estimated apparent activation energy,  $E_a = + 72.58$  kJ/mol suggested that the process is chemical in nature ( $E_a = 65 - 250$  kJ/mol) (Yu *et al.*, 2001).

#### The equilibrium adsorption constant

The equilibrium adsorption constant values,  $K_C$  for MG dye on UBTL were calculated at different temperatures by the following Eq. (8) (Hossain and Hassan, 2013; Singha and Das, 2012),



**Figure 11. A plot of  $\ln k_{2p}$  versus  $1/T$  for determination of apparent activation energy**

$$K_C = \frac{C_{ad}}{C_e} \quad (8)$$

where,  $C_{ad}$  is the equilibrium concentration of the adsorbate on adsorbent (mg/L),  $C_e$  is the equilibrium concentration of the adsorbate in solution (mg/L) and  $K_C$  is the equilibrium adsorption constant (-). The equilibrium adsorption constant values increase with increasing the initial concentration of MG solution as shown in **Table 2**.

### Thermodynamic parameters

The values of equilibrium adsorption constant,  $K_C$  were used to calculate the thermodynamic parameters,  $\Delta G^\circ$  and  $\Delta H^\circ$  by using Eq. (9 and 10) (Hossain and Hassan, 2013; Ada *et al.*, 2009; Nandi *et al.*, 2008),

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

$$\ln K_C = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (10)$$

where,  $\Delta G^\circ$  is the standard free energy (kJ/mol) and  $\Delta H^\circ$  is the standard enthalpy (kJ/mol),  $R$  is the gas constant (8.314 J/K.mol) and  $T$  is the absolute temperature (K).

**Table 2** Derived data for pseudo second order rate constant and equilibrium adsorption constant and the thermodynamic parameters for MG adsorption on UBTL at different temperatures.

$T$ (K)	$k_{2p} \times 10^3$ (g/mg·m in)	$k_{2p} \times 10^3$ (g/mol· min)	$\ln k_{2p}$	$\Delta E^\circ$ (kJ/mol)	$K_C \times 10^3$ (mL/g)	$\ln K_C$	$\Delta G^\circ$ (kJ/mol)	$\Delta H^\circ$ (kJ/mol)	$\Delta S^\circ$ (kJ/K· mol)
303	1.531	5.86	6.374		2.677	-5.923	14.920		0.061
313	3.297	12.63	7.141	+ 72.58	4.389	-5.429	14.128	+ 33.47	0.062
323	9.113	34.90	8.158		6.079	-5.103	13.704		0.061

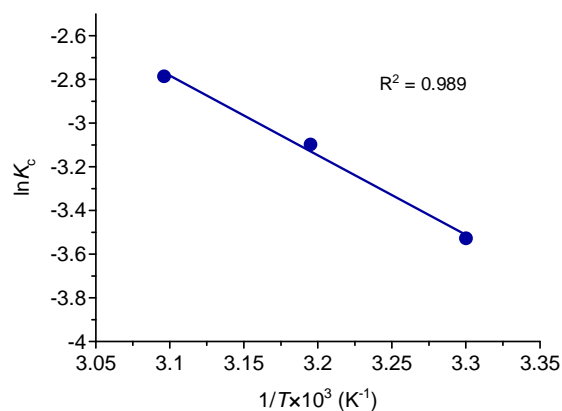
The standard enthalpy,  $\Delta H^\circ$  (+ 33.47 kJ/mol) was calculated from the slope of  $\ln K_C$  versus  $1/T$  as shown in **Figure 12**. The standard entropy values (kJ/K.mol),  $\Delta S^\circ$  were calculated by using Eq. (11),

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} \quad (11)$$

The  $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$  values of MG on UBTL at different temperatures are presented in **Table-2**. The positive values of  $\Delta G^\circ$  and  $\Delta H^\circ$  indicate the adsorption of MG was non-spontaneous and endothermic. The positive value of  $\Delta S^\circ$  means fragmentation of adsorbed molecule might be occurred on UBTL.

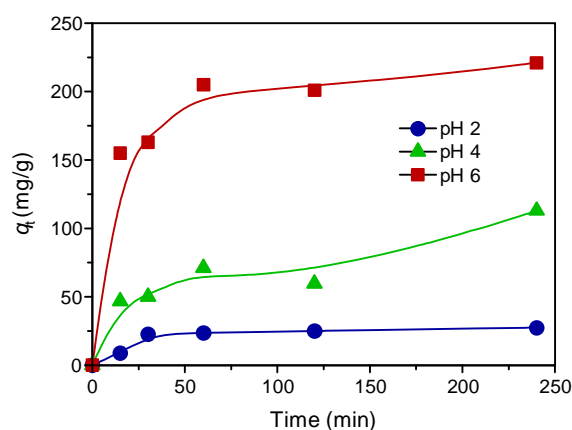
### Effect of pH

The variation of amount adsorbed with time at different pH values is shown in **Figure 13**. The adsorption kinetics of MG on UBTL at different pH values are also follows the pseudo second order rate equation (Figure not shown). The equilibrium amount adsorbed obtained from the pseudo second order kinetic plots shows that amount adsorbed

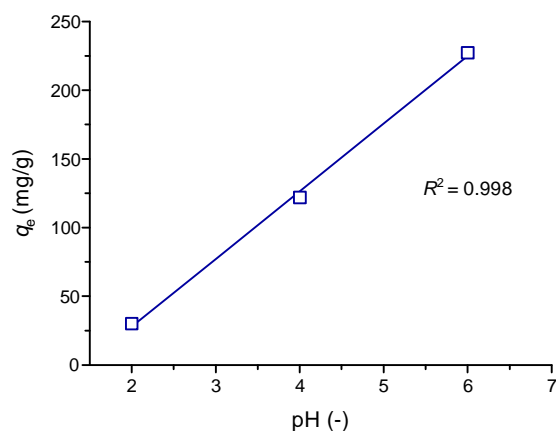


**Figure 12.** A plot of  $\ln K_c$  versus  $1/T$  for determination of standard enthalpy

linearly increased with increase of solution pH from 2.0 to 6.0 as shown in **Figure 14**. This effect might be due to the positive surface of UBTL at lower pH and also the positive nature of MG species ( Hossain and Rahman, 2012; Hossain *et al.*, 2013).



**Figure 13.** Variation of amount adsorbed of MG on UBTL with time at different pH of solution at  $30 \pm 0.2^\circ\text{C}$



**Figure 14.** Variation of equilibrium amount adsorbed with pH for adsorption of MG on UBTL at  $30 \pm 0.2^\circ\text{C}$

## Discussion

Kinetics of adsorption governs the rate, which determines the residence time, and it is one of the important characteristics defining the efficiency of an adsorbent (Krishnan and Anirudhan, 2003). The adsorption kinetic of MG on UBTL surface was studied in batch process for different initial concentrations. **Figure 3** shows the variation in MG adsorption with contact time. From the figure, it can be determined that the adsorption of MG quite rapid initially, however the adsorption rate becomes slower with passage of time. The initial faster rate of MG adsorption may be due to the availability of the uncovered surface area of the adsorbents, since adsorption kinetics depends on the surface area of the adsorbent (Qadeer and Akhtar, 2005). The adsorption kinetic also concerned with the effect of the observable parameters such as concentration of adsorbate, processing temperature, solution pH, etc. Different kinetic equations such as simple first order (Gupta *et al.*, 2001; Cimino *et al.*, 2000), second order (Gupta *et al.*, 2001), pseudo-first order (Lagergren, 1898), pseudo-second order (Ho and McKay, 1998) and Elovich equation (Chien and Clayton, 1980) were applied to the experimental kinetic data to evaluate the feasibility of the adsorption of MG on UBTL. The conformity between experimental data and the model-predicted values was expressed by the correlation coefficients ( $R^2$ , values close or equal to 1). The relatively higher value is the more applicable model to the kinetics of MG adsorption on UBTL surface.

In this study, a comparison of the fitness of different kinetic model equations was presented in **Table 1**. Based on the values of coefficient of determination ( $R^2$ ), experimental data adsorption is well expressed by pseudo-second order kinetic equation. Several studies have been reported (Hossain *et al.*, 2005a; Mekhemer, 2008; Suyamboo and Perumal, 2012; Awala and Jamal, 2011; Suteu and Bilba, 2005) that the adsorption of divalent ions follows pseudo second order kinetics. Again, the Lagergren's pseudo-first order kinetic equation is for one adsorbate species reacts with one active site on surface (Hossain *et al.*, 2005a; Lagergren, 1898). Therefore, it can be suggested that two active sites of MG are interacted with the UBTL surface. The transport mechanism of the process was investigated using different transport model equations towards the kinetic data (Hossain and Hossain, 2013).

Thermodynamic parameters such as  $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$  of MG adsorption on UBTL were determined to evaluate the nature of adsorption. The calculated values presented in **Table 2** indicated (positive values of  $\Delta G^\circ$  and  $\Delta H^\circ$ ) that the adsorption of MG is non-spontaneous and endothermic. Again, the positive value of  $\Delta S^\circ$  suggested that the adsorbed molecules might be fragmented into several species resultant the increase of entropy.

The effect of pH on the adsorption kinetics was investigated to evaluate the nature of interaction of between MG and the UBTL surface. Heterogeneous surface (**Figure 1**) of prepared used black tea leaves (UBTL) contained several active sites to adsorbed cationic or anionic dyes depending on the solution pH (Hossain and Mori, 2013). Since the MG is a basic dye which exists as cationic form in acidic to neutral media, favorable adsorption could be possible at basic media. Such observation was obtained from the experimental result (**Figure 14**), the amount adsorbed linearly increased with increase of solution pH. This observation could be explain by the point of zero charge pH of UBTL ( $pH_{zpc} = 4.2$ ) (Hossain and Hassan, 2013; Hossain 2006; Islam *et al.*, 2013). The UBTL surface became negative at solution pH higher than its point of zero charge pH, but the MG exist still in positive species, resultant the high amount adsorbed of MG on negative surface of UBTL at higher pH.

## Conclusion

Adsorption kinetics of Malachite Green (MG) on UBTL follows pseudo second order kinetic equation. The values of thermodynamic parameters suggested that the adsorption of MG on UBTL is non-spontaneous and endothermic. The UBTL (used black tea leaves) is a good adsorbent for removal of Malachite Green (MG) from neutral to basic solution.

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