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KINETICS AND THERMODYNAMICS OF ADSORPTION FOR THE REMOVAL OF FAST GREEN ON USED BLACK TEA LEAVES FROM ACQUATIC ENVIRONMENT

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ABSTRACT: *This study involves the kinetics and thermodynamics of adsorption for the remediation of Fast Green (FG) from aqueous solution by used black tea leaves (UBTL) as a low cost adsorbent. The effects of initial dye concentration, contact time, solution pH and processing temperature on the adsorption kinetics were investigated in batch process. Kinetic parameters and related correlation coefficients for pseudo-first order, pseudo-second order kinetic and Elovich models were calculated and discussed. The results revealed that the adsorption kinetics is in good agreement with the pseudo- second order equation. The equilibrium amount adsorbed obtained at 30^{o}C is 114.4 mg/g which was found to increase with the increase of adsorption temperature, suggested endothermic nature of the adsorption. Thermodynamic parameters such as enthalpy change (ΔH^o), free energy change (ΔG^o) and entropy change (ΔS^o) were calculated from the equilibrium adsorption constant, and the adsorption of FG on UBTL at pH 6.0 was found to be spontaneous, endothermic and physisorption in nature. Again, the equilibrium amount adsorbed calculated from pseudo-second order kinetic plots for different initial pH of solution and was found to decrease with decrease of solution pH from 6.0 to 2.0 indicating the electrostatic repulsion between cationic FG$^+$ with protonated UBTL surface at low pH and a probable mechanism was proposed.*

KEYWORDS: Fast Green, Used black tea leaves, Adsorption kinetics, Thermodynamics

INTRODUCTION

Environmental pollution by industrial effluents is an important issue in recent years. Many industries like plastics, papers, textile and cosmetics use dyes to color their products. These dyes are common pollutants and they may be frequently found in industrial wastewaters of developing countries (Hajira and Mohammed, 2008). Over 10,000 dyes with an annual production over 7 Mt are commercially available worldwide and 5-10% of the dye stuff is lost in the industrial effluents (Priyadharshini *et al*, 2014). Most of dyes are toxic and carcinogenic compounds posing a serious threat to human and animal health which is not only limited to themselves but may be passed onto further generations (Crini, 2007). Fast Green (FG) is widely used for coloring foodstuffs and as a staining agent for histones at alkaline pH after acid extraction of DNA. Toxicological data reveal that FG is highly toxic (Aksu and Cagatay, 2006). It is an allergen to humans and causes eyes and skin irritation and affects the upper respiratory tract (Van Hooft, 2002). The proven toxicity of the dye attracted our attention to develop an economic method for the removal of Fast Green from the wastewaters. A large number of methods have been developed to treat FG pollution. The most common methods are chemical bleaching (Bhasikuttan *et al*, 1995), photodegradation (Senthilkumar and Porkodi, 2000), photolytic degradation (Sohrabi and Ghavami, 2008; Sleiman *et al*, 2007; Sahoo *et al*, 2005), cation exchange membrane (Wu *et al*, 2008), micellar enhanced ultrafiltration (Zaghbani *et al*, 2008), feston–biological treatment (Lodha and Chaudhari, 2007) and adsorption (Zaghbani *et al*, 2007). Among the removal methods of dye from wastewater, adsorption technique is considered to be easy and economic. Recently, used black tea leaves (UBTL) has been studied as a low cost adsorbent, due to their high adsorption capacity and easy to recover the adsorbate from adsorbed UBTL (Hossain, 2006). In the present study, Fast Green was selected as a common acidic dye available in textile effluent and its removal process was searching using UBTL as an adsorbent. The study was carried out to investigate the kinetics and thermodynamics of Fast Green adsorption on UBTL under various operational conditions to evaluate the efficiency of the method.

MATERIAL AND METHODS

Adsorbent

Used black tea leaves (UBTL) were prepared from fresh black tea leaves collected from local market in Dhaka City of Bangladesh. Coloured materials were removed from fresh black tea leaved by boiling with distilled water. After dried at 105^{o}C for 12 hours, prepared leaves were sieved through the metallic sieves of mesh size 212 and 300 μm and stored in air tight bottles in a desiccator. The surface morphology of the prepared UBTL was investigated under Scanning Electron Microscopy (SEM) (JSM-6490LA, JEOL, Japan) and presented in Figure 1.

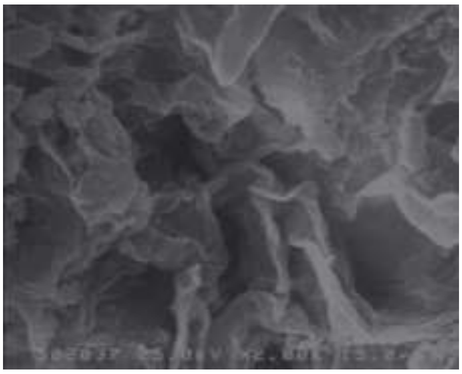

Figure 1. SEM micrograph of prepared used black tea leaves (UBTL) × 2000.

Adsorbate

The chemical formula of Fast Green is $C_{37}H_{37}N_2O_{10}S_3$ and IUPAC name is ethyl-[4-[[4-[ethyl-[(3-sulfophenyl)methyl]amino]phenyl]-(4-hydroxy-2-sulfophenyl)methylide -ne]-1cyclohexa-2,5-dienylidene]-[(3-sulfophenyl)methyl]azanium. Fast green is highly soluble in water. The molar mass of Fast Green is 765.89 g/mole. The structural formula of Fast Green is shown in Figure 2.

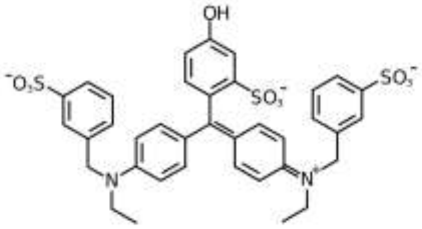

Figure 2. Structural formula of Fast green.

Experiments for Adsorption Kinetics

Effect of concentration

The effect of concentration on adsorption kinetics was investigated by using 0.01 g of UBTL, which was taken in each of 6 bottles containing 25 mL of fixed concentrated FG solution at pH 6.0 as an optimum pH, determined by preliminary experiment and was shaken in a thermostatic mechanical shaker at 30±0.2°C (EYELA NTS 400, Rikakikai, Japan). After shaking of different time of intervals, the mixtures were separated by centrifuged. The supernatant of each bottles were adjusted at pH 6.0, as an optimum pH for analysis of FG, with proper dilution and addition of HNO_3 or NaOH solutions. Then the absorbance of solutions was measured using UV-vis spectrophoto-meter (UV-1650PC, Shimadzu, Japan) at λ_{max} 617 nm. To determine the initial concentration of FG in solution, the absorbance of the solution, before adsorption, was also measured with proper dilution by UV-vis spectrophotometer at λ_{max} 617 nm at pH 6.0. Similar kinetic experiments were performed using five different initial concentrations of FG solutions. The amount adsorbed was calculated for different initial concentration at different contact times using the following equation (1)

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

where, C_o is the initial concentration of FG (mg/L), C_t is the concentration of FG at time t (mg/L), q_t is the amount adsorbed at time t (mg/g), V is the volume of solution (L) and W is the mass of adsorbent (g).

Effect of temperature

The effect of temperature on the adsorption kinetics was performed by using 0.01 g UBTL in each of the 6 bottles containing 25 mL of a fixed concentrated FG solution at pH 6.0 and all bottles were separately shaken in a thermostatic mechanical shaker (EYELA NTS 400, Rikakikai, Japan) at four different temperatures. After shaking of different time intervals, the mixtures were separated and the pH of supernatant of each bottle were adjusted at 6.0 with proper dilution and measured the absorbance using UV-vis spectrophotometer at λ_{max} 617 nm. To determine the initial concentration of solution, before adsorption, the absorbance of the solution was also measured with proper dilution by UV-vis spectrophotometer at λ_{max} 617 nm at pH 6.0.

Effect of pH

The effect of pH on the adsorption kinetics was carried out by using 0.01g UBTL which was taken in 6 bottles containing 25 mL of a fixed concentrated FG solution at different pH values. Before the mixing of UBTL, the pH of each solution was adjusted at three different values by carefully addition of minimum volume of nitric acid or sodium hydroxide solution. The mixtures were shaken in a thermostatic mechanical shaker at 30±0.2°C (EYELA NTS 400, Rikakikai, Japan). After shaking of different time of intervals, the mixtures were separated and the pH of supernatant of each bottles were adjusted at 6.0 with proper dilution and addition of HNO_3 or NaOH, and measured the absorbance using UV-vis spectrophotometer at λ_{max} 617 nm. Before the mixing of UBTL with each solution, the absorbance of each solution was also measured at pH 6.0 with proper dilution by UV-vis spectrophotometer at λ_{max} 617 nm to determine the initial concentration of each solution.

RESULTS AND DISCUSSION

Characteristics of Adsorbent

Used black tea leaves (UBTL) were selected as low cost adsorbent for the adsorption of First Green (FG). Polyphones, flavones, polysaccharides, cellulose and hemicelluloses, protein, lipids, lignin, caffeine etc. are the main constituents of black tea leaves. The continuous treatment of black tea leaves by boiling water brings a considerable change in composition while preparing UBTL from black tea leaves. Cellulose and lignin are main composition of UBTL (Hossain, 2006). Figure 1 shows the SEM (Scanning Electron Microscopy) SEM micrograph of prepared UBTL which like as a heterogeneous surface to adsorb on.

Adsorption Kinetics

Effect of concentration

The efficiency of an adsorbent can be well defined with the help of kinetics of adsorption. The effect of FG concentration on adsorption kinetics was investigated by performing a series of kinetic experiments, change of concentration with contact time at constant temperature, solution pH, adsorbent dose and agitation rate. The FG adsorbed on the UBTL surface resultant the decreased of FG concentration in solution as the time passes. Figure 3(a & b) shows the variation of amount adsorbed of FG with contact time for a fixed amount of adsorbent. Figure 3(a & b) also shows that the amount of FG adsorbed per unit mass of UBTL increased with increase in FG concentration which indicated that the extent of adsorption is highly dependent on the concentration of FG.

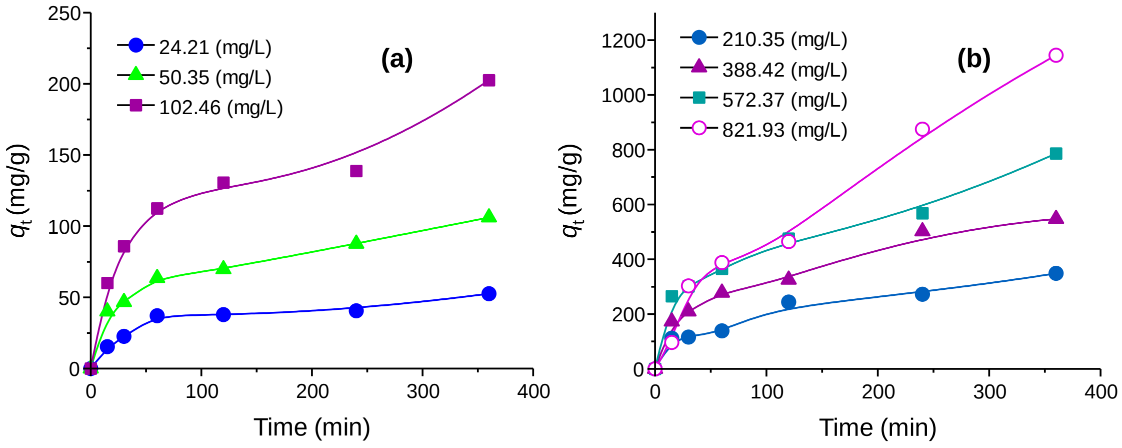

Figure 3. Variation of the amount adsorbed of FG on UBTL with time for different initial concentration of FG where solution pH 6.0, particle size: 250 - 300 μm and temperature: 30±0.2°C.

Kinetic modeling

Adsorption is a physiochemical process that involves mass transfer of a solute from liquid phase to the adsorbent surface. With the maximum agitation speed of 150 rpm, it was assumed to offer no mass transfer (both external and internal) resistance to the overall adsorption process. Therefore the adsorption kinetics can be studied through the residual adsorbate concentration in the solution (Hossain and Hassan 2013). Three of the most widely used kinetic models, i.e. Lagergren-first order, pseudo-second order and Elovich equation were used to analyze the adsorption kinetic behavior of FG on UBTL. The best fit model was selected based on the linear regression correlation coefficient values (R^2) (Tong *et al*, 2012).

Pseudo-first order kinetics

The pseudo–first order kinetic equation given by Lagergren 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 following equation (2):

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \qquad (2)$$

where, q_e and q_t are the amount adsorbed at equilibrium and at time t, respectively (mg/g), k_1 is the rate constant of pseudo-first order adsorption (L/min). Applicability of the pseudo-first order kinetic equation (2) was examined by plotting log(q_e-q_t) vs t as shown in Fig. 4(a & b) which indicated that the adsorption of FG on UBTL partially follow the pseudo-first order kinetic equation for different initial concentrations of FG and regression values are given in Table- 1.

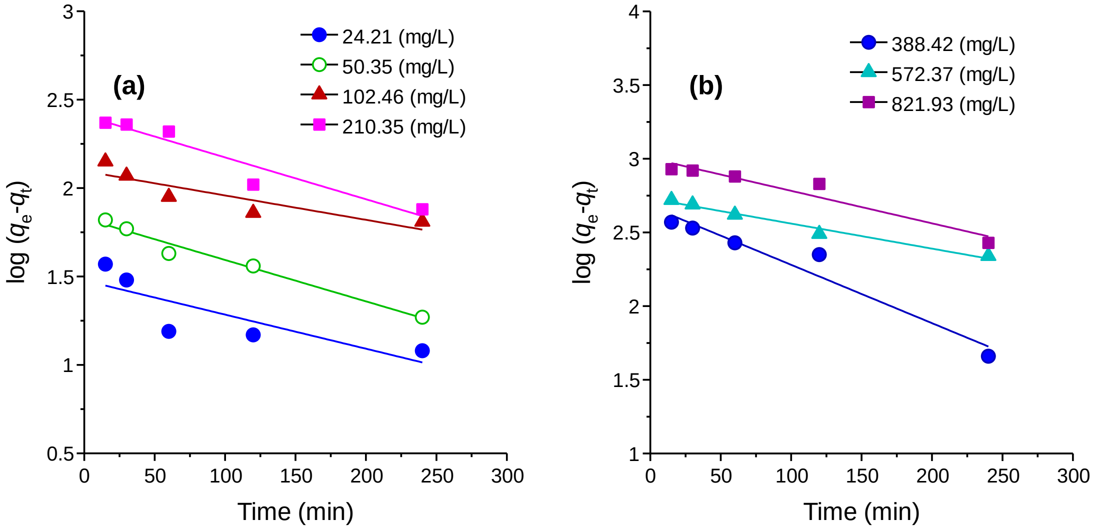

Figure 4(a & b). Pseudo-first order kinetics of FG on UBTL at various initial concentration at pH 6.0 and temperature 30± 0.2°C.

Pseudo-second order kinetics

Ho and McKay's pseudo second order rate equation (Ho and McKay, 2000) is applied to the adsorption kinetics of the present system. The linear form of the Ho and McKay's pseudo second order rate equation is given by Eq. (4).

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{t}{q_e} \qquad (4)$$

where, q_t is the amount adsorbed at time t (mg/g), q_e is the equilibrium amount adsorbed (mg/g) and k is the pseudo-second order rate constant (g/mg·min). To investigate the feasibility of adsorption FG on UBTL equation (4) was verified by plotting t/q_t vs. t as shown in Figure 5(a & b). From the figure it can be concluded that each plot does not give straight line with the whole range of concentration but the regression value is better than other two models. A comparison of the regression factor for the fitness of pseudo-first order, pseudo-second order and Elovich model to the adsorption of FG on UBTL at pH 6.0 is given in Table 1.

Elovich Model

The Elovich equation is commonly used to describe the adsorption kinetics of several adsorption processes (Renugadevi and Sangeethga, 2011; Theivarasu and Mylsamy, 2010; Alzaydien and Manasreh, 2009). The integrated form of Elovich equation is shown in Eq. (5).

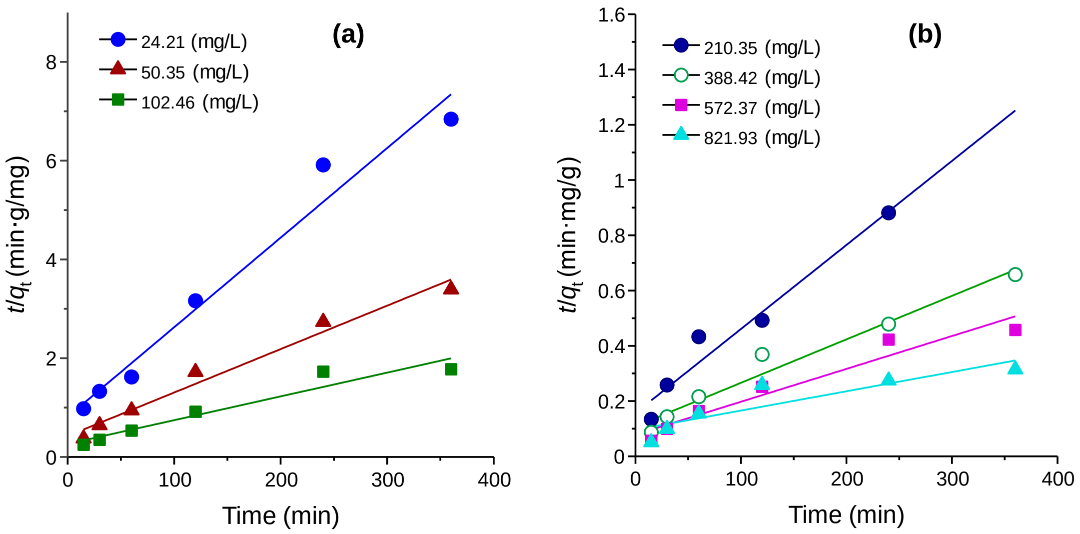

Figure 5(a & b). Pseudo-first order kinetics of FG on UBTL at various initial concentration at pH 6.0 and temperature 30.0 ± 0.2°C.

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln t \qquad (5)$$

where, α is the initial adsorption rate (mg/g·min) and β is related to the extent of surface coverage and the activation energy for chemisorption (g/mg). The adsorption of FG on UBTL for different initial concentrations were verified by using Eq. (5) and the plot of q_t versus ln$t$ in Figure 5(a & b) which shows that the adsorption of FG on UBTL does not follow the Elovich equation for different initial concentrations of FG at pH 6.0 and at 30±0.2°C. A comparison of the correlation of co-efficient for the fitness of pseudo- first order, pseudo-second order kinetic and Elovich equations to the adsorption kinetics of FG on UBTL is given in Table 1.

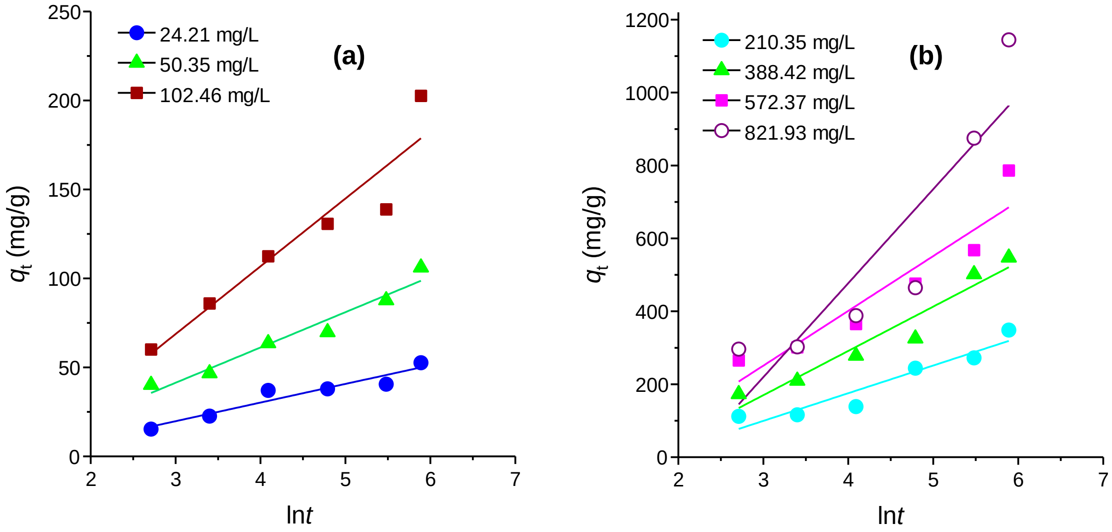

Figure 6(a & b). Elovich kinetic model of FG on UBTL at various initial concentration at pH 6.0 and temperature 30±0.2°C.

Table 1. A comparison of the data fitness to the pseudo-first order, pseudo-second order and Elovich kinetic models.

Initial concentration C₀ (mg/L)	Pseudo-first order model, R^2 (-)	Pseudo-second order model, R^2 (-)	Elovich model R^2 (-)
24.21	0.683	0.970	0.919
50.35	0.977	0.976	0.956
102.46	0.791	0.930	0.899
210.35	0.922	0.954	0.906
388.42	0.947	0.967	0.936
572.37	0.979	0.937	0.889
821.93	0.930	0.965	0.812

Effect of Temperature

The effect of temperature plays a vital role on the adsorption kinetics. To observe the effect of temperature on the adsorption kinetics, several adsorption kinetic experiments were performed at different temperatures using constant concentration at pH 6.0. Figure 7(a) reveals that adsorption increases slightly with the increase in temperature. Pseudo-second order kinetic equation was also applied for the system at different temperatures (which is not shown). The equilibrium amount adsorbed was calculated from the slope of each straight line. The plot of equilibrium amount adsorbed *vs* temperature shown in Figure 7(b), indicates that the equilibrium amount adsorbed increases with increase of temperature i.e the process is endothermic (Hossain and Hassan 2013).

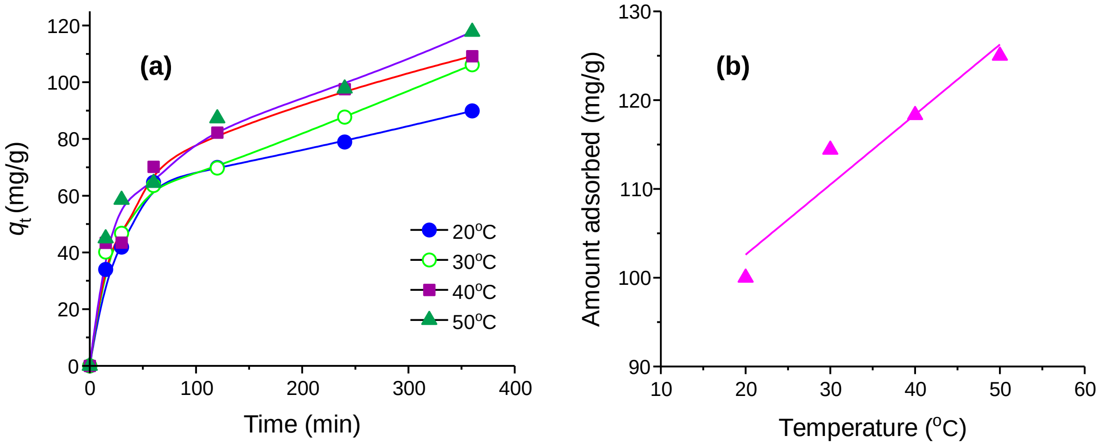

Figure 7(a). Change of the amount adsorbed with time during the adsorption of FG on UBTL at pH 6.0 for different temperatures, (b) Variation of equilibrium amount adsorbed with temperature for adsorption of FG on UBTL at pH 6.0.

Thermodynamic parameters

Thermodynamic studies play an important role to understand the actual nature of adsorption. Thermodynamic parameters such as free energy change (ΔG^o), enthalpy change (ΔH^o) and entropy change (ΔS^o), related to the adsorption of FG on UBTL, were also determined form the thermodynamic equilibrium constant (K_C). The value of the equilibrium constant at various temperatures was calculated according to the following equation (6) (Hossain and Hassan, 2013; Singha and Das, 2012; Hossain and Rahman, 2012).

$$K_C = \frac{C_{ad}}{C_e} \quad (6)$$

where, C_{ad} is the equilibrium concentration of FG on UBTL surface (mg/L), C_e is the equilibrium concentration of the FG in solution (mg/L) and K_C is the equilibrium adsorption constant (-). The values of equilibrium adsorption constant, K_C at different temperatures were used to calculate the thermodynamic parameters by using Eq. (7 and 8) (Hossain and Hassan, 2013; Ada *et al.*, 2009).

$$\Delta G^o = -RT \ln K_C \quad (7)$$

$$\ln K_C = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \quad (8)$$

where, ΔG^o is the standard free energy change (kJ/mol) and ΔH^o is the standard enthalpy change (kJ/mol), R is the molar gas constant (8.314 J/K.mol) and T is the absolute temperature (K). The value of ΔG^o was calculated from equation (7). The values of ΔH^o and ΔS^o were obtained from the slope and intercept of the linear plot of $\ln K_c$ versus $1/T$ which is shown in Figure 8. The ΔG^o values of FG on UBTL under different temperatures as well as ΔH^o and ΔS^o values are presented in Table 2. The negative value of ΔG^o indicates the adsorption is favorable and spontaneous (Fathi *et al.*, 2014). The positive value of enthalpy change (ΔH^o) confirms an endothermic nature of the adsorption. The positive value of entropy change means fragmentation of adsorbed FG molecule might be occurred on UBTL (Hossain *et al*, 2011; Hossain and Hasan 2013).

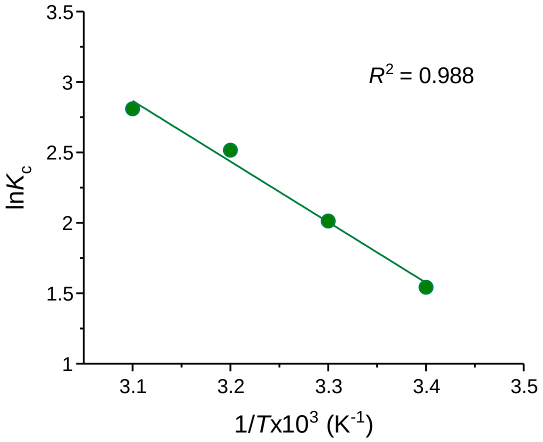

Figure 8. A plot of $\ln K_c$ vs $1/T$ for the determination of thermodynamic parameter during the adsorption of FG on UBTL.

Effect of pH

The effect of solution pH on the adsorption of FG on UBTL was performed by using a series of adsorption kinetic experiments at different pH. The change of amount adsorbed with time at different initial pH is presented in Figure 9(a). Pseudo-second order rate equation was verified for different pH by plotting t/q_t vs t as [which is not shown]. From the slope and the intercept of the straight lines, equilibrium amount adsorbed and rate constant were calculated for different pH values of the solutions. The variation of equilibrium amount adsorbed with pH is shown in Figure 9(b) which indicated the increase of equilibrium amount adsorbed with increase of solution pH from 2 to 6. The observation can be explained by the $\mathrm{pH_{zpc}}$ of UBTL, 4.2 (Hossain and Islam, 1998; Hossain *et al.*, 2013). The cationic species of FG^+ are expected to be adsorbed more at higher pH values of solution than the $\mathrm{pH_{zpc}}$ of UBTL surface which leads to neutral to electron rich surface due to the presence of OH groups of cellulose molecules in UBTL which are protonated ($-OH_2^+$) at low pH of solution (Hossain *et al.*, 2005b; Islam *et al.*, 2013). The result of experiment agreed with the expectation of electrostatic interaction between the positively charged cationic FG^+ molecules and neutral to electron rich UBTL surface. Again, at low pH of solution UBTL surface became positively charge due to the protonation of OH groups of cellulose molecules in UBTL and repulse the positively charged FG^+ molecules resultant the less adsorption of FG^+ on UBTL. The above mechanism can be diagrammatically shown in Figure 10.

Table 2. Adsorption equilibrium constant and thermodynamic parameters for FG adsorption on UBTL at different temperatures.

T (K)	C_a (mg/L)	C_e (mg/L)	K_C (-)	lnK_c	Δ*G*º (kJ/mol)	Δ*H*º (kJ/mol)	Δ*S*º (kJ/K.mol)
293	40.00	8.55	4.68	1.543	-3.76	35.79	0.0135
303	45.76	6.11	7.49	2.013	-5.08		0.0135
313	47.33	3.82	12.39	2.516	-6.55		0.0135
323	50.33	3.01	16.61	2.810	-7.55		0.0135

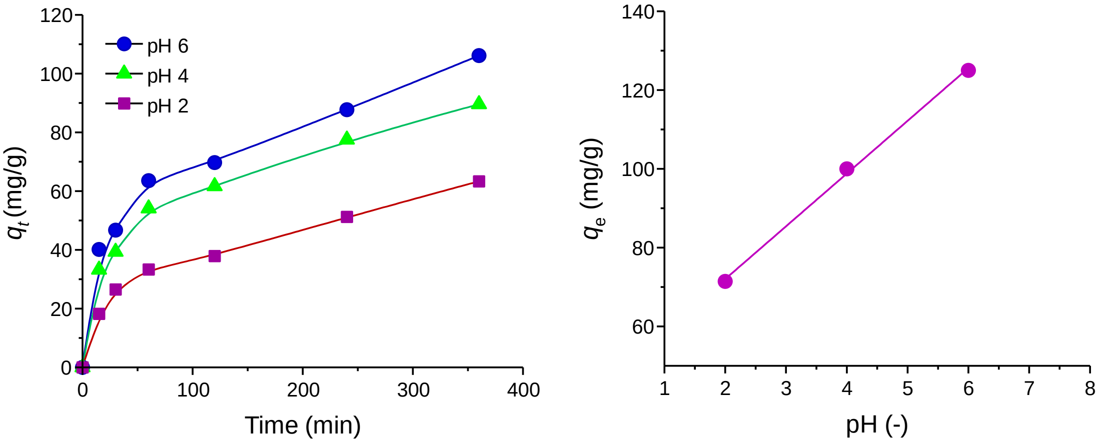

Figure 9(a). Change of the amount adsorbed of FG with time for different pH with initial concentration of 50 mg/L at 30±0.2°C, (b) Variation of equilibrium amount adsorbed with pH for adsorption of FG on UBTL at 30±0.2°C.

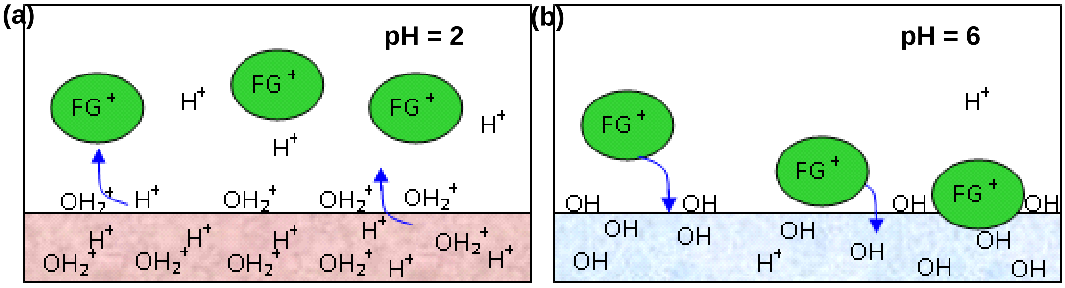

Figure 10. Adsorption mechanism of FG on UBTL from acidic (pH 2) and neutral (pH 6) media.

CONCLUSIONS

The adsorption of Fast Green on UBTL partially follows pseudo-first order kinetics and Elovich model equation but it follows pseudo-second order kinetic equation for different initial concentrations at pH 6. The equilibrium amount adsorbed obtained from pseudo-second order kinetic plots for different temperatures were found to be increased with increase in temperature i.e. the process is endothermic. The calculated standard enthalpy change of the adsorption is 35.79 kJ/mol. The negative value of standard free energy change indicated that the adsorption process is spontaneous. The positive value of standard entropy change means the fragmentation of adsorbed molecules might be occurred on the UBTL surface. The equilibrium amount adsorbed was found to be increased with increase of solution pH from 2 to 6 indicating electrostatic interaction between cationic FG with anionic surface of UBTL dominated at higher pH.

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