Kinetics and Thermodynamics of Adsorption for Removal of Basic Violet14 by Used Black Tea Leaves from Aqueous Solution

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Abstract— Most of dyes are synthetic chemical compounds having complex aromatic structures, which make them more stable and difficult to biodegradable. Dyes are extensively used to color the products in the textile, cosmetic, plastic, food, and pharmaceutical industries. The major problem in the recent years concerning in the dyes and textile industries wastewaters contains colored effluent. Basic violet 14 (BV-14) is one of the common pollutants in industrial wastewaters. This study involves the evaluation of kinetics and mechanism of adsorption for the remediation of BV-14 from aqueous solution by used black tea leaves (UBTL) as a low cost adsorbent. The concentration of BV-14 in aqueous solution was analyzed using UV-visible spectrophotometer. The effect of initial dye concentration, contact time, solution pH and temperature on the adsorption kinetics was investigated in batch process. Kinetic parameters and related correlation coefficients for simple first order, second order and pseudo second-order kinetic models were calculated and discussed. The results revealed that the adsorption kinetics was in good agreement with the pseudo second-order equation. The rate constant, equilibrium amount adsorbed and equilibrium concentration were calculated from pseudo second order kinetic plots for different initial concentrations. The equilibrium amount adsorbed obtained from pseudo second order kinetic plots for different temperatures were found to decrease with increase in temperature i.e. the process is exothermic. Thermodynamic parameters such as the change of enthalpy (ΔH_{ads}), free energy (ΔG_{ads}) and entropy (ΔS_{ads}) were calculated from the equilibrium adsorption constant, and the adsorption of BV-14 on UBTL at pH 6.0 was found to be spontaneous and exothermic in nature. Again the calculated values of equilibrium amount adsorbed from pseudo second order kinetic plots were found to be increased with increase of solution pH from 4.0 to 6.0 and then decreases with the increase of solution pH 6.0 to 8.0. This observation might be due to the amphoteric nature of Basic violet 14 and zero point charge pH of UBTL (pH_{zpc}=4.2).

Keywords — Basic violet 14, Used Black Tea Leaves, Adsorption Kinetics, Thermodynamics.

1 INTRODUCTION

Synthetic color dyes are playing an important role in making our life as fine looking as rainbow. Many industries such as textiles, tanneries, Printing, cosmetics & Plastics etc., are using dyes in their way of journey in the production. Due to the increase of dyes and dye based products usage in the market and their discharge cause the damage to the environment. Dyes are the main source of color in effluents. Some industries that discharge highly some of the adsorbent materials such as cornelian cherry, apricot stone, almond shell [1] (Demirbas *et al.*, 2004), charcoal colored effluents are paper and pulp mills, textiles and dye-making industries, alcohol distilleries and leather industries. Moreover, these dyes may cause suspected carcinogenic and genotoxic effects. Especially, basic violet 14 dye have high brilliance and intensity of colors and are highly visible even in a very low concentration. Thus, different techniques like coagulation [2] (Malakootian *et al.*, 2010), precipitation, biodegradation, oxidation, membrane separation, ion exchange [3] (Kavitha and Namasivayam, 2007) and photo degradation [4] (Lin *et al.*, 2003), have been employed to remove dyes from textile wastewater. These chemical or physical-chemical methods are less efficient, costly, of limited applicability and produce wastes, which are difficult to dispose of. Among the available treatment technologies, adsorption is superior and reliable in simplicity of design, convenience, initial cost, ease of operation and insensitivity to the toxic substance. [5] Khan (1994) and [6] Poots *et al.*, (1978) were successfully performed for the removal of dyes from aqueous solutions by adsorption process. Daily, a large amount of UBTL is being thrown away from restaurants, hotels and kitchens. So, UBTL are available as low cost bio-sorbent. Another important fact is that after adsorption, UBTL can be easily destroyed and the adsorbed adsorbate can be recovered from solution [7] (Hossain *et. al.* 2005). In

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the current investigation, used black tea leaves (UBTL) were selected as a low cost adsorbent to remove the Basic Violet 14 (BV-14) by adsorption from aqueous solution. The influence of some parameters such as solution pH, contact time, initial dye concentration, and temperature on the adsorption kinetics and equilibrium adsorption, were studied. Kinetics and isotherm modeling were carried out to evaluate the adsorption mechanism and its feasibility to use in practically.

2 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. Colored materials were removed from fresh black tea leaves by boiling with distilled water. After dried at 105°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 desiccators. The surface morphology of the prepared UBTL was investigated under Scanning Electron Microscopy (SEM) (JSM-6490LA, JEOL, Japan) and presented in Fig.1.

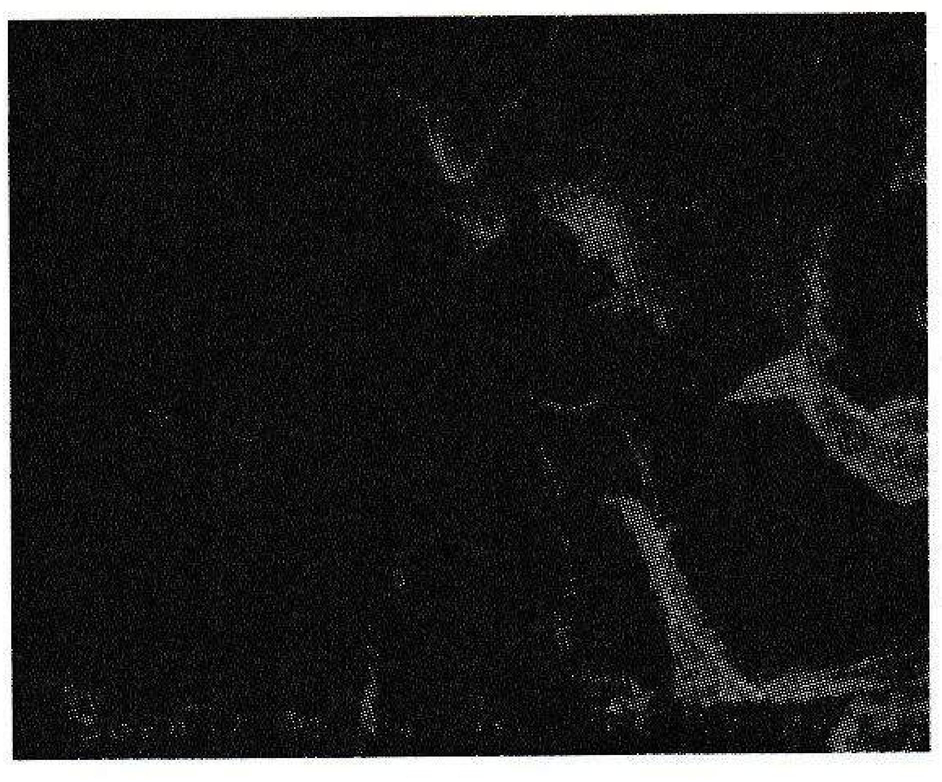


Fig. 1. SEM micrograph of prepared used black tea leaves (UBTL) × 2000.

Adsorbate

The chemical formula of Basic violet 14 is $C_{20}H_{20}ClN_3$ and IUPAC name is 4-[(4-aminophenyl)-(4-imino-3-methylcyclohexa-2,5dien1ylidene) methyl]aniline;hydrochloride. Basic violet 14 (BV-4) is highly soluble in water. The molar mass of Basic violet 14 is 337.851 g/mol. The structural formula of Basic violet 14 is shown in Fig. 2.

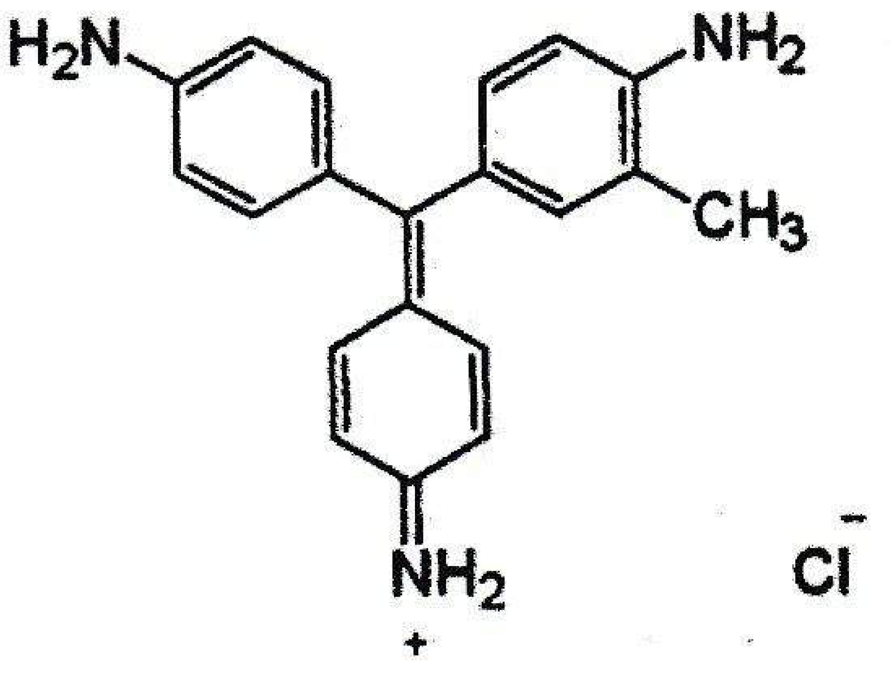


Fig. 2: Structural formula of Basic violet 14.

3 Experiments For Adsorption Kinetics

Effect of concentration

To investigate the effect of concentration on the adsorption kinetics, 0.1 g of UBTL was taken in each of 6 bottles containing 25 mL of fixed concentrated Basic Violet 14 solution at pH 6.0 as an optimum pH for UBTL [8] (Alam, 2010) and was shaken in a thermostatic mechanical shaker (NTS-4000 Eyela, Japan) at 30 ± 0.2°C. After shaking of different time of intervals, the mixtures were separated. The pH of supernatant of each bottles were adjusted at 6.0 with proper dilution and measured the absorbance using UV-vis spectrophotometer (UV-1650PC, Shimadzu, Japan) at λ_{max}= 543 nm. Before adsorption, the absorbance of the solution at pH 6.0 with proper dilution was also measured by UV-vis spectro-photometer at λ_{max}= 543 nm to determine the initial concentration of the solution. The amount adsorbed was calculated for different initial concentration at different contact times using the following equation (1).

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

where, C_o = initial concentration of BV-14 mg·L^{-1}, C_t is the concentration of BV-14 at time t (mg·L^{-1}), q_t is the amount adsorbed at time t (mg·g^{-1}), V is the volume of solution in Liter and W is the mass of adsorbent in g.

Effect of temperature

The effect of temperature on the adsorption kinetics was executed by using 0.1 g UBTL in each of the 6 bottles containing 25 mL of a fixed concentrated BV solution at pH 6.0 and all bottles were separately shaken in a thermostatic mechanical shaker (EYELA NTS 400, Rikakikai, Japan) at three 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} 543 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} 543 nm at pH 6.0.

Effect of pH

To investigate the effect of pH on adsorption of BV-14 on UBTL, 25 mL BV-14 solution of about 100 mg·L^{-1} concentrations was taken into each of three reagent bottles. The pH of each solution bottles was adjusted at 4.0, 6.0, and 8.0. Then 0.1 g of UBTL was added in each of three bottles and started shaking in a thermostatic shaker at 30 °C. After 6 hours shaking, each mixture was separated from UBTL and necessarily diluted for analysis. The diluted solution was analyzed at pH 6.0 using UV-visible spectrophotometer.

4 RESULTS AND DISCUSSION

Characteristics of Adsorbent

Used black tea leaves (UBTL) were selected as low cost adsorbent for the adsorption of Basic Violet14. 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 used black tea leaves (UBTL) from black tea leaves. Cellulose and lignin are main composition of UBTL [9] (Hossain, 2006). Fig. 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 competence of an adsorbent can be well defined with the help of kinetics of adsorption. The effect of BV-14 concentration on adsorption kinetics was evaluated by performing a series of kinetic experiments, change of concentration with contact time at constant temperature, solution pH, adsorbent dose and agitation rate. The BV-14 adsorbed on the UBTL surface resultant the decreased of BV-14 concentration in solution as the time passes. Fig. 3(a & b) shows the variation of amount adsorbed of BV-14 with contact time for a fixed amount of adsorbent.

Fig. 3(a & b) also shows that the amount of BV-14 adsorbed per unit mass of UBTL increased with increase in BV-14 concentration which indicated that the extent of adsorption is highly dependent on the concentration of BV-14.

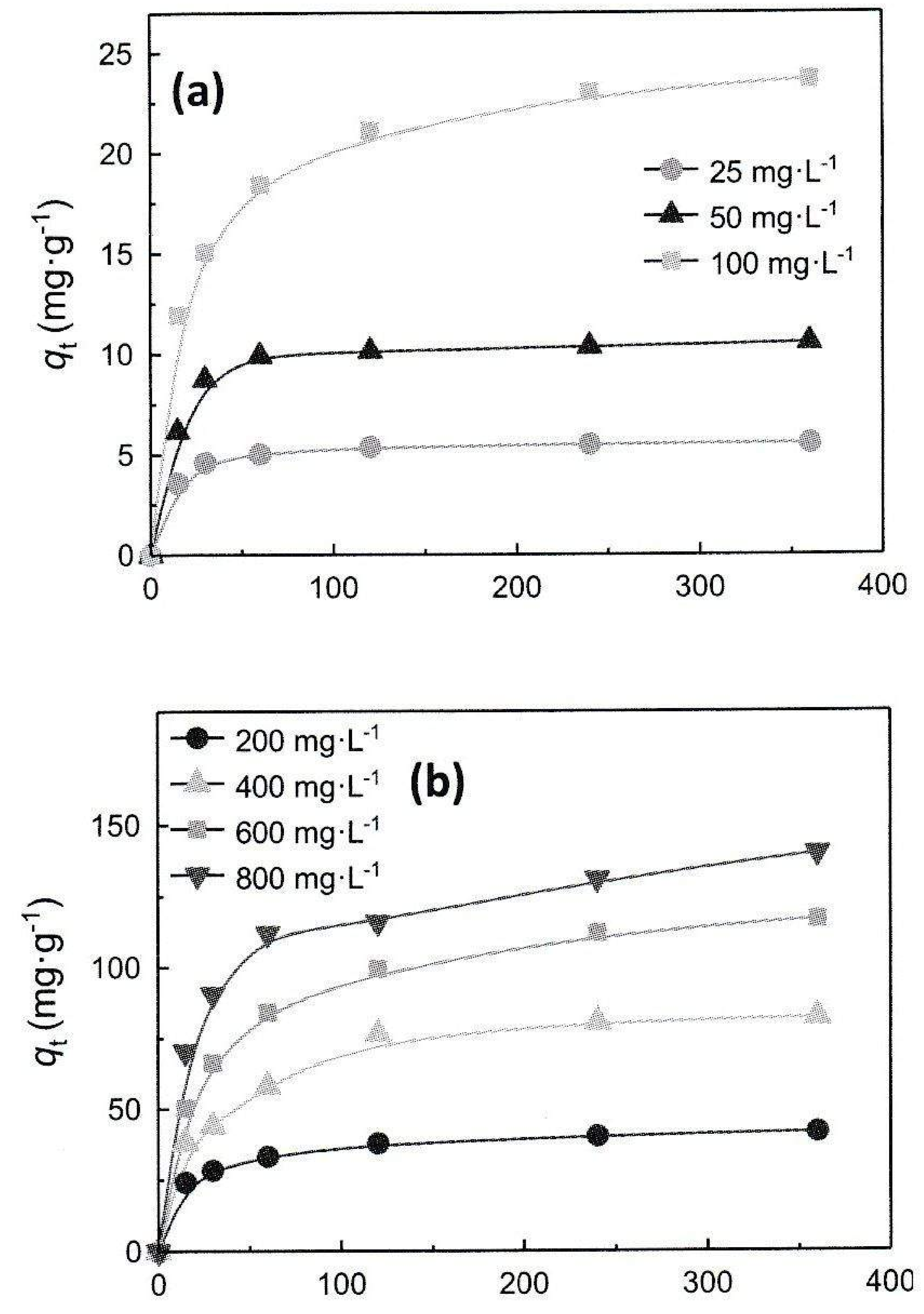


Fig. 3 (a & b) Variation of the amount adsorbed of BV-14 on UBTL with time for different initial concentration of BV-14 where solution pH 6.0, particle size: 212 - 300 µm and temperature: 30±0.2°C.

Kinetic modeling

Three of the most widely used kinetic models, i.e. first order, second order and pseudo-second order 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) [10] (Tong *et al*, 2012).

First order kinetics

A first-order reaction depends on the concentration of only one reactant (a uni-molecular reaction). Other reactants can be present, but each will be zero-order. The integrated from of first order rate equation is given by

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

where, C_t = Final concentration of reactant after time t (mg·L^{-1}), C_o = Initial concentration of reactant (mg·L^{-1}), k_t = First order rate constant, which has units of time. Simple first order kinetic equation (Eq.-2) was verified by plotting lnC_t versus t. as shown in Figure 4 (a and b) which shows that the adsorption of Basic violet 14 on UBTL partially follow the simple first order kinetic equation for different initial concentrations of BV-14 at pH 6.0 and at 30.0 ± 0.2°C and regression values are given in Table- 1.

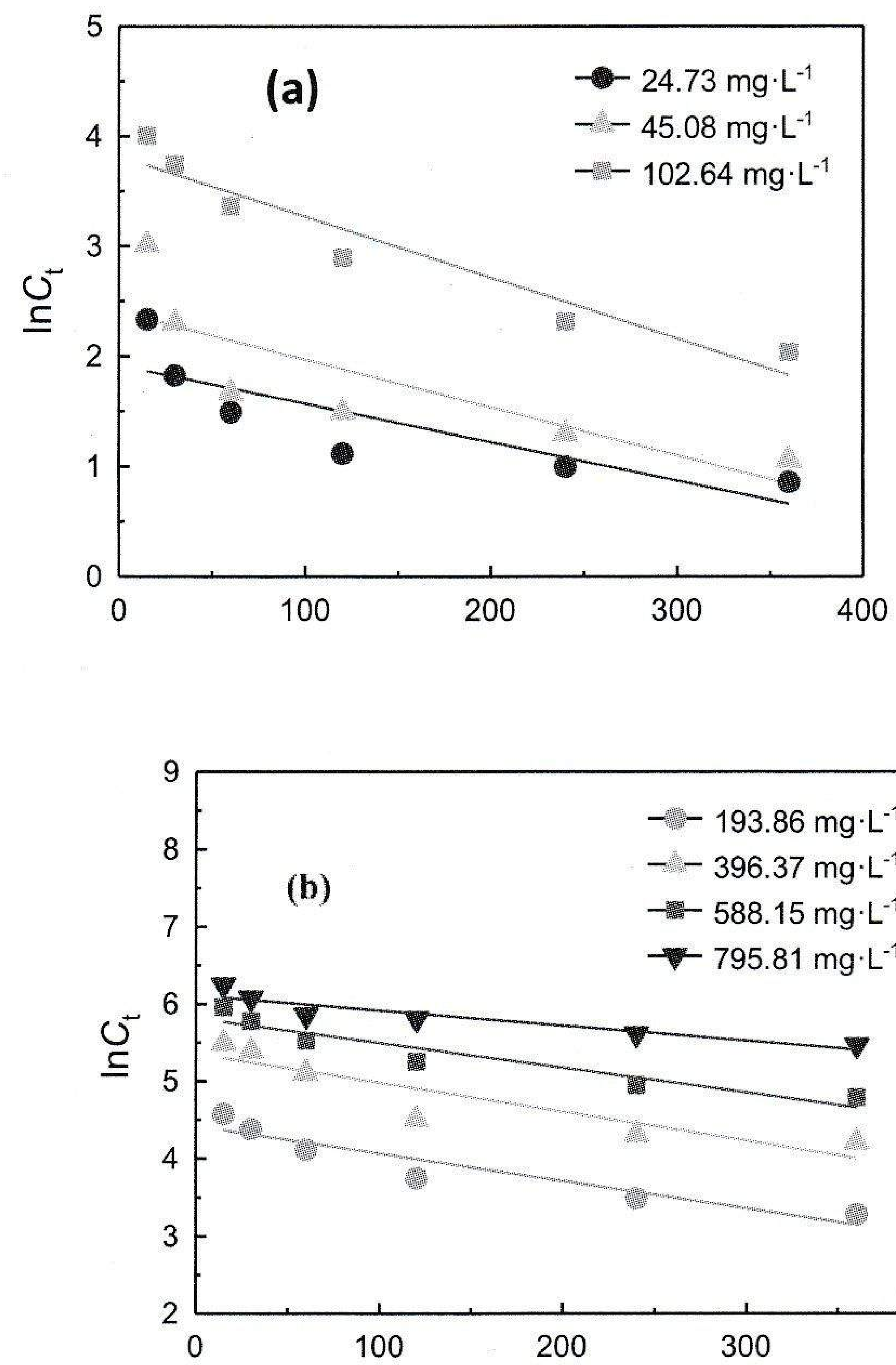


Fig. 4(a & b): First order kinetics of BV-14 on UBTL at various initial concentrations at pH 6.0 and temperature 30± 0.2°C.

Second order kinetics

A second-order reaction depends on the concentrations of two reactants. The integrated second-order rate laws is given by

$$\frac{1}{C_t} = kt + \frac{1}{C_o} \qquad (3)$$

where, C_t = Final concentration after time t (mg·L^{-1}), C_o = Initial concentration (mg·L^{-1}), k = Second order rate constant (g·mg^{-1}.min). The adsorption of Basic violet 14 on UBTL for different initial concentrations was verified by using equation (3) as a simple second order kinetics and the plot of $1/C_t$ versus t is shown in Fig. 4 (a) and 4 (b) which shows that the simple second order kinetics is not applicable for the adsorption of BV-14 on UBTL for low concentration but for high concentration of BV-14 partially follow the simple second order kinetics at pH 6.0. The regression values are given in Table- 1.

Pseudo second order kinetics

Ho and McKay's pseudo second order rate equation [11] (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).

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

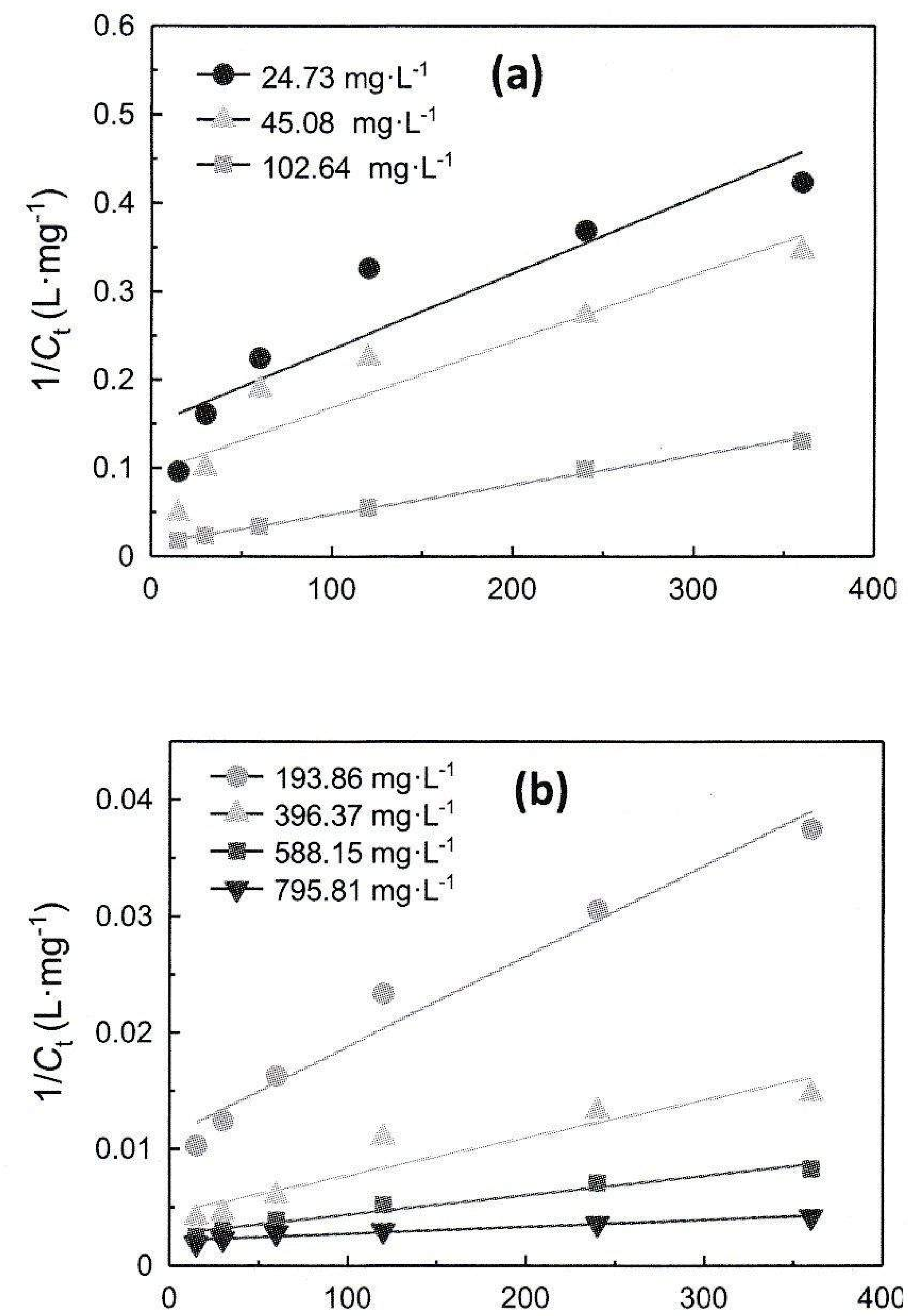


Fig. 5(a & b). Second order kinetics of BV-14 on UBTL at various initial concentrations at pH 6.0 and temperature 30± 0.2°C.

where, q_t is the amount adsorbed at time t (mg·g^{-1}), q_e is the equilibrium amount adsorbed (mg·g^{-1}) and k is the pseudo-second order rate constant (g mg-

^{1} min^{-1}). To investigate the feasibility of adsorption BV-14 on UBTL, equation (4) was verified by plotting t/qt vs. t in the whole range of concentration indicating the fitness of pseudo second order rate equation as shown in Fig. 5(a & b). These figures show that each plot gives straight line with adsorption of Basic Violet 14 on UBTL in both at low and high concentration of Basic Violet 14.

A comparison of the regression factor for the fitness of first order, second order and pseudo- second order model to the adsorption of BV-14 on UBTL at pH 6.0 is given in Table 1.

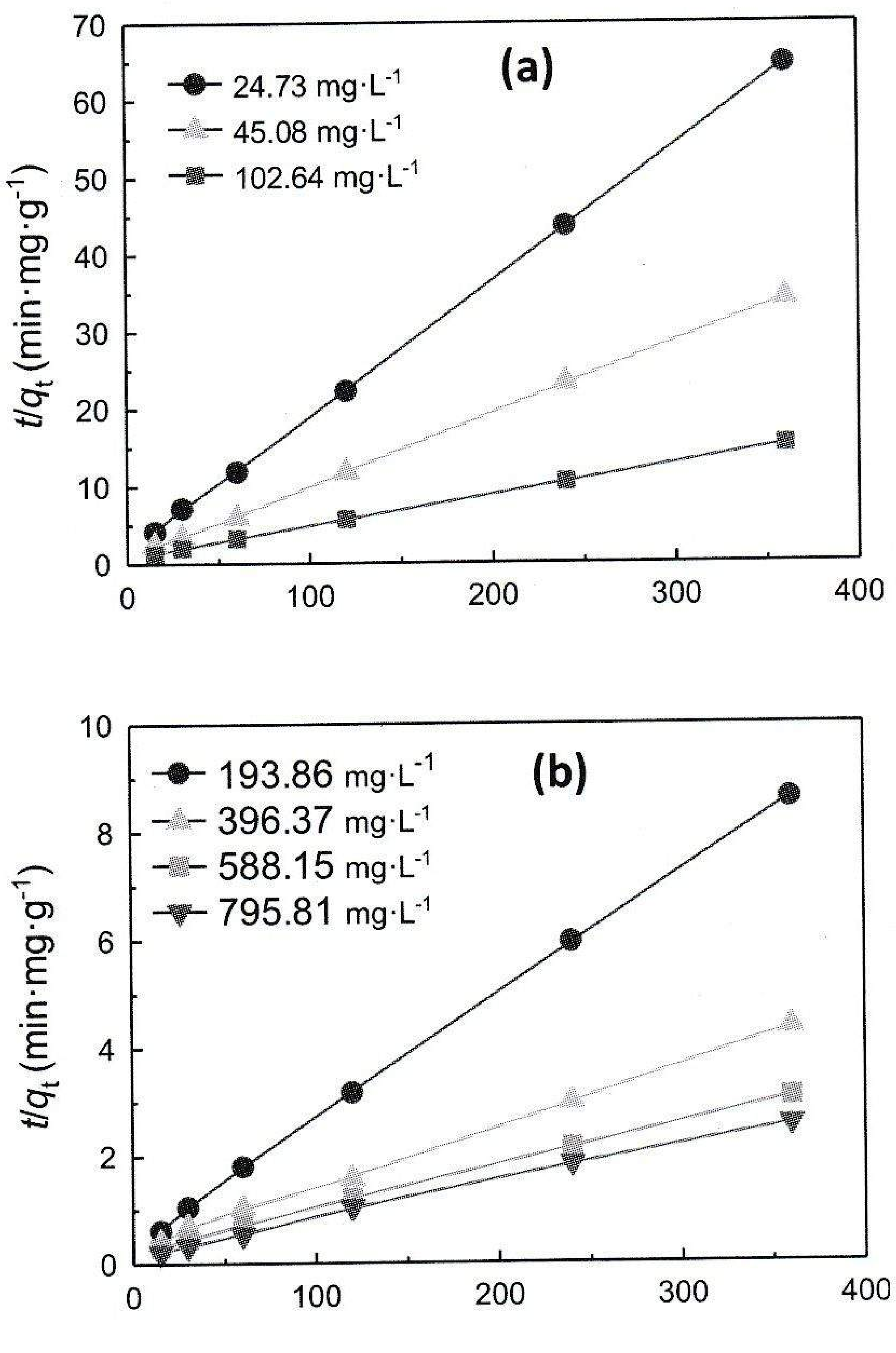


Fig. 6(a & b) Pseudo second order kinetics of BV-14 on UBTL at various initial concentrations at pH 6.0 and temperature 30± 0.2°C.

Effect of Temperature

The effect of temperature plays a vital role on the adsorption kinetics. In order to observe the effect of temperature on the adsorption kinetics, different kinetic experiments was carried out at different temperatures using same concentration of Basic Violet 14 solution at pH 6.0. Pseudo second order kinetic equation was also applied for the system at kinetic equation was also applied for the system at different temperatures which is shown in Fig. 7 (a). The equilibrium amount adsorbed was calculated from the slope of each straight line. The plot of equilibrium amount adsorbed *vs* temperature shown in Fig. 7(b), which shows that the mount adsorbed decreased with increase in temperature suggesting favorable adsorption at low temperature i.e. the process is exothermic which is the common feature of physical adsorption.

Thermodynamic parameters

Thermodynamic parameters such enthalpy (ΔH_{ads}), entropy (ΔS_{ads}) and free energy (ΔG_{ads}) of adsorption is very important to know the nature of adsorption. The equilibrium adsorption constant values, K_d, for Basic Violet 14 on the UBTL were also calculated at different temperatures by using equation (5) [12] (Yu *et al.*, 2001).

$$K_d = \frac{q_e}{C_e} \quad (5)$$

where, q_e (mg·g^{-1}) is the dye concentration in the adsorbent at equilibrium, C_e (mg·mL^{-1}) is the dye concentration in solution at equilibrium. These values were used to calculate the free energy (ΔG_{ads}) and enthalpy (ΔH_{ads}) of adsorption by using the equation (6) and (7) [13] (Ada *et al.*, 2009) [14] (Nandi *et el.*, 2008).

$$\Delta G^{o} = -RT \ln K_d \quad (6)$$

$$\ln K_d = \frac{\Delta S^{o}}{R} - \frac{\Delta H^{o}}{RT} \quad (7)$$

where, ΔG^{o} is the standard free energy change (kJ mol^{-1}) and ΔH^{o} is the standard enthalpy change (kJ mol^{-1}), R is the molar gas constant (8.314 J K^{-1} mol^{-1}) and T is the absolute temperature. The value of ΔG^{o} was calculated from equation (6). The values of ΔH^{o} and ΔS^{o} were obtained from the slope and intercept of the linear plot of lnK_d versus $1/T$ which is shown in Fig. 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 [15] (Fathi *et al.*, 2014).and the negative value of ΔH_{ads} indicates that the adsorption of Basic Violet 14 is exothermic. The positive value of entropy change means fragmentation of adsorbed FG molecule might be occurred on UBTL [16, 17] (Hossain *et al*, 2011; Hossain and Hasan 2013).

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

Initial concentration, C_o (mg·L^{-1})	First order kinetics R^2 (-)	Second order kinetics Model R^2 (-)	Pseudo second order kinetics R^2 (-)
24.73	0.368	0.246	0.999
45.08	0.768	0.918	0.999
102.64	0.922	0.996	0.999
193.86	0.891	0.970	0.999
396.37	0.821	0.893	0.998
588.15	0.899	0.968	0.999
795.81	0.869	0.935	0.998

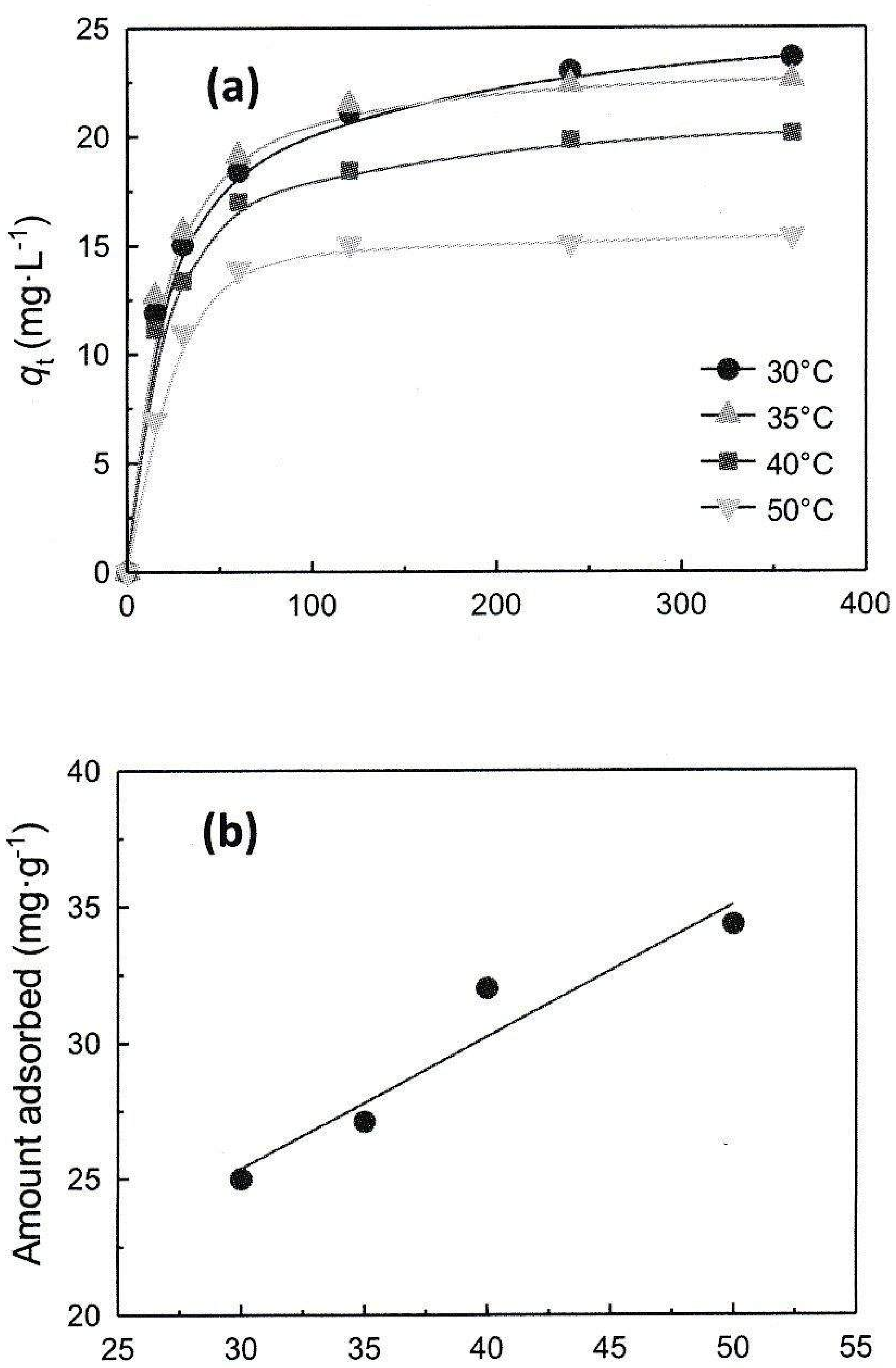


Fig 7(a) Change of the amount adsorbed with time during the adsorption of BV-14 on UBTL at pH 6.0 for different temperatures, (b) Variation of equilibrium amount adsorbed with temperature for adsorption of BV-14 on UBTL at pH 6.0.

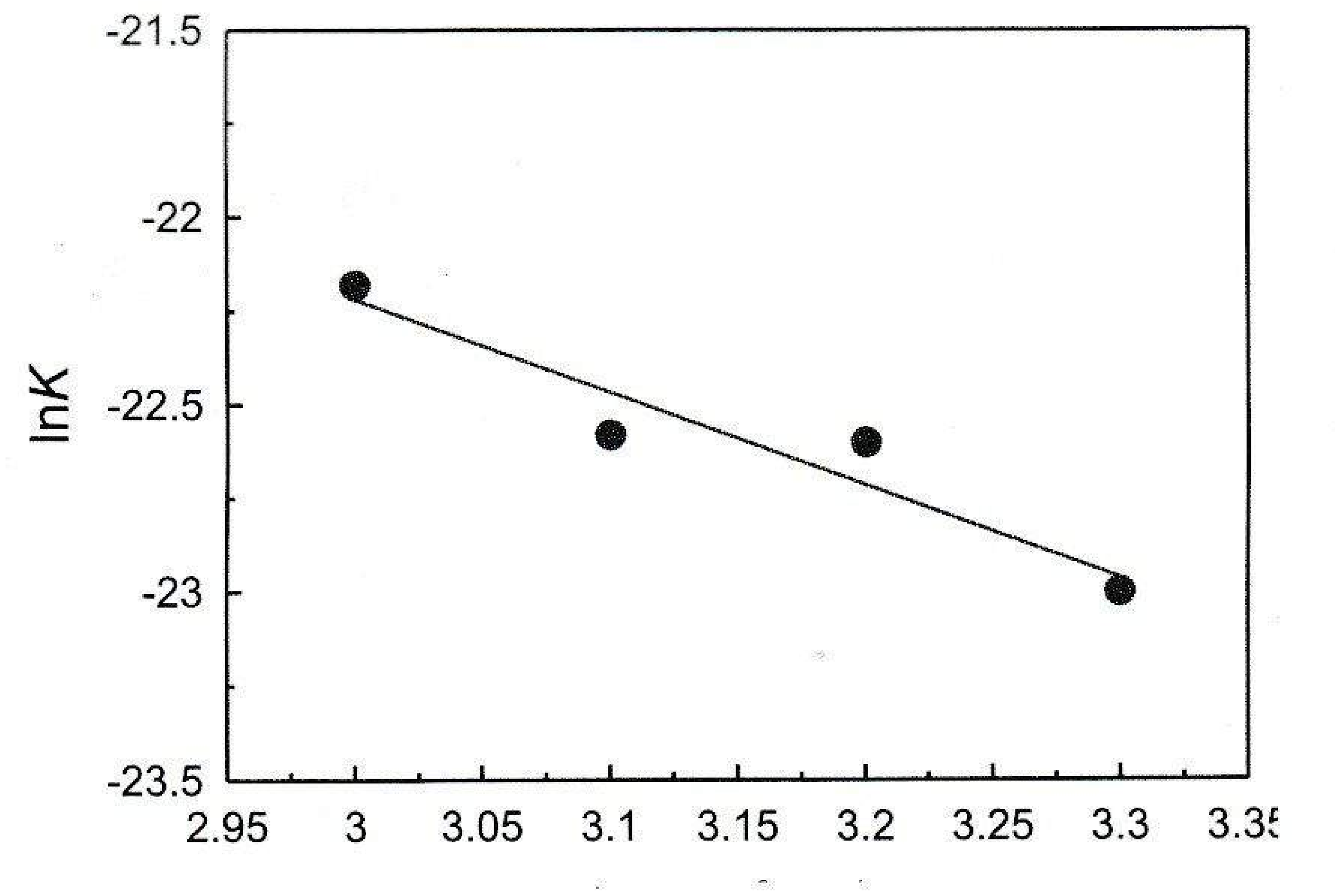


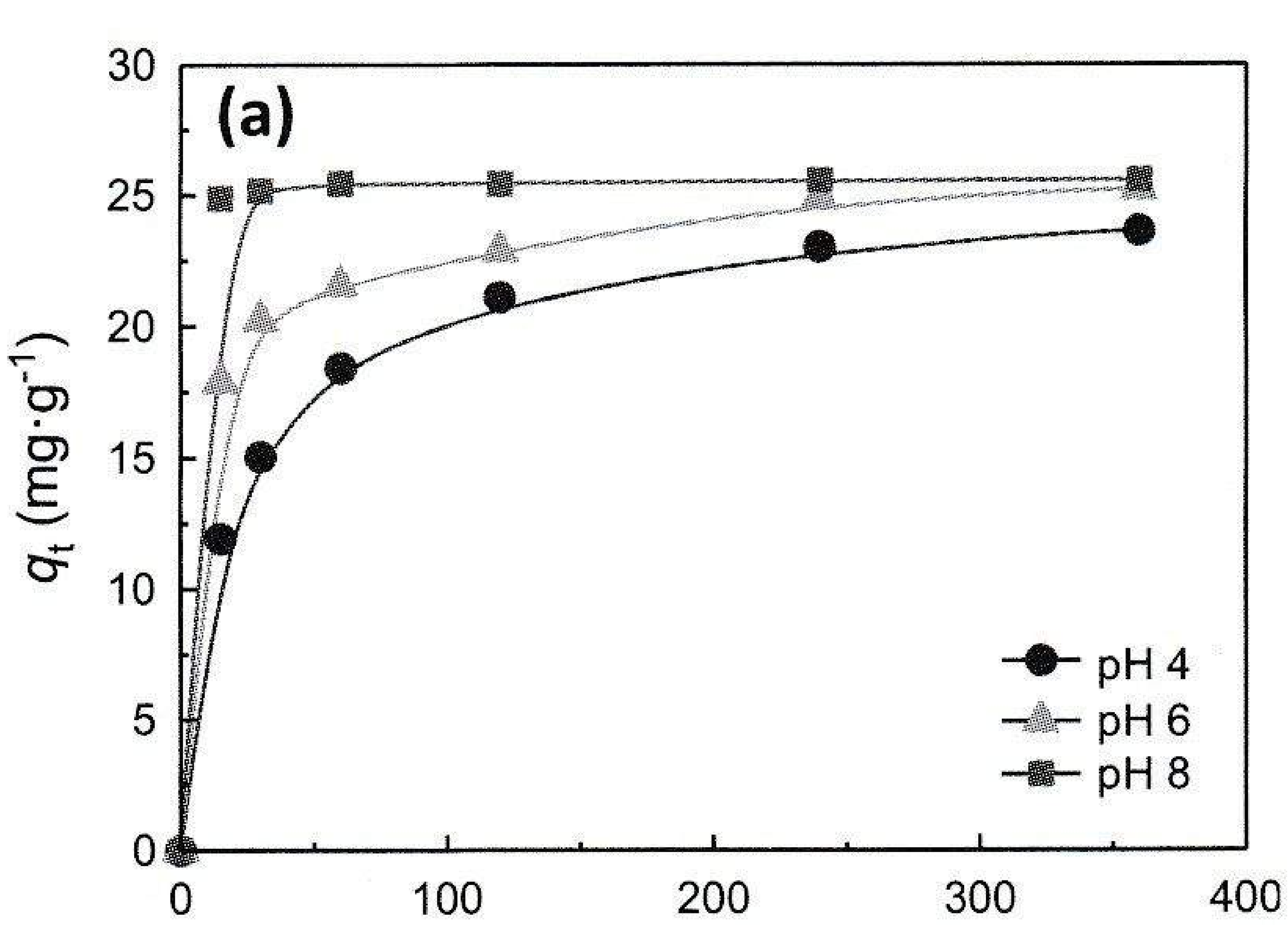
Fig. 8: A plot of lnK vs 1/T for the determination of thermodynamic parameter during the adsorption of BV-14 on UBTL.

Table 2. Adsorption equilibrium constant and thermodynamic parameters for BV-14 adsorption on UBTL at different temperatures.

T (*K*)	C_o (mg/L)	C_e (mg/L)	K_d (mL/g)	lnK_d	ΔG^o (kJ/mol)	ΔH^o (kJ/mol)	ΔS^o (kJ/K·mol)
293	25.0	2.25	1111.10	7.013	-17.65		0.072
303	23.80	1.69	1408.28	7.250	-18.86	- 4.24	0.073
313	21.27	1.01	2105.94	7.652	-19.59		0.077
323	16.12	1.07	1606.50	7.317	-19.65		0.074

Effect of pH

The effect of solution pH on the adsorption of BV-14 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 Fig. 9(a). Pseudo-second



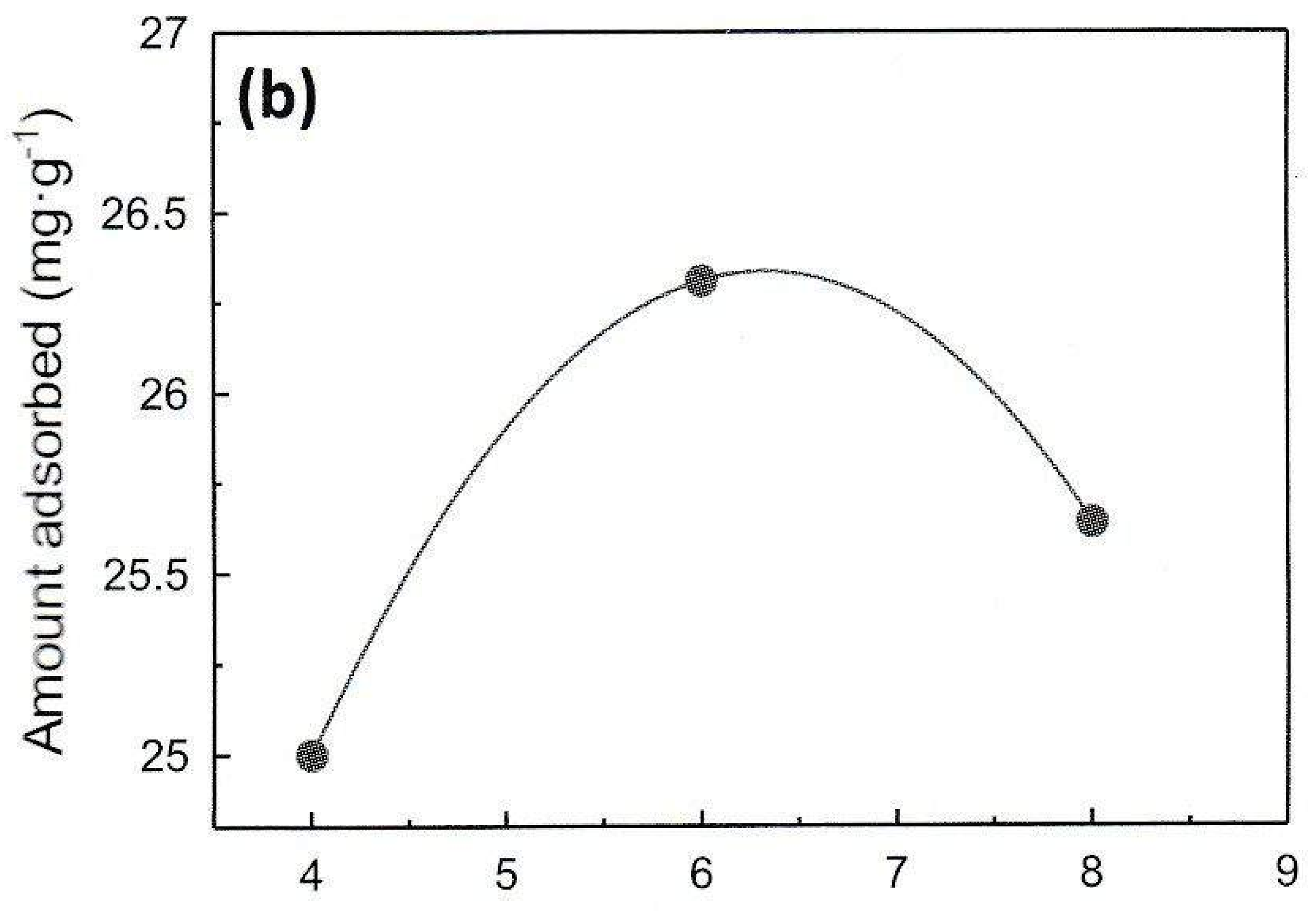


Fig. 9 (a). Change of the amount adsorbed of BV-14 with time for different pH with initial concentration of 50 mg/L at 30±0.2°C, (b) Variation of equilibrium amount adsorbed with pH for adsorption of BV-14 on UBTL at 30±0.2°C.

order rate equation was verified for different pH by plotting t/qt 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 Fig. 9(b) which indicated the increase of equilibrium amount adsorbed with increase of solution pH from 4.0 to 6.0, then decrease from 6.0 to 8.0.

5 Conclusion

The adsorption of Basic violet 14 on UBTL follows pseudo-second order kinetic equation for different initial concentrations at pH 6.0. The equilibrium amount adsorbed obtained from pseudo second order kinetic plots for different temperatures were found to be decreased with increase in temperature i.e. the process is exothermic. The calculated standard enthalpy change of the adsorption is -4.24 kJ mol^{-1}. 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 4.0 to 6.0 and decrease with increase of solution pH from 6.0 to 8.0. This observation might be due to the amphoteric nature of Basic violet 14 and zero point charge pH of UBTL (pH_{zpc}=4.2).

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