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Kinetic Evaluation on the Adsorption of Reactive Black 5 on Used Black Tea Leaves

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Abstract

Kinetics of the adsorption of reactive black 5 from aqueous solution on used black tea leaves (UBTL) was studied in batch process. The influence of concentration and temperature on the kinetics of adsorption was investigated. The adsorption of reactive black 5 on UBTL follows pseudo second order kinetics at all concentrations. It also moderately follows the elovich model equation within the experimental range of concentrations. The adsorption equilibrium could not be attained during six hours of contact time. The equilibrium adsorption capacity and pseudo second order rate constant were calculated from the valid pseudo second order kinetics. The elovich model equation was used to calculate the desorption constant to evaluate the adsorption affinity. The amount adsorbed increases with increasing temperature, indicating the chemical nature of adsorption.

Keywords: Reactive Black 5, Adsorption kinetics, Used black tea leaves.

I. Introduction

Environmental pollution control and management is a common issue of 21st century. Globally high level production and uses of dyes in different industries generate a large amount of colored wastewaters, which gives a cause of economical concerns. Approximately 7×10^5 tons of 10000 different dyes and pigments are used every year over the world[1]. Among them, reactive dyes are largely used in textile industries. These dyes are chemically and photolytically stable, resistant to microbial degradation and highly persistent in natural environment. Azo dyes amounts to nearly 60% of textile dyes and displays adverse effect on the growth of methanogonic bacterial culture [2].

Various physicochemical and biological techniques may apply to remove dyes from wastewaters. They include the membrane filtration, coagulation/ flocculation, adsorption, ion exchange, advanced oxidation (chlorination, ozonation), flotation, chemical reduction, and biological treatment such as bacterial and fungal biosorption, biodegradation in aerobic or anaerobic conditions, etc. The technical and economic feasibility of each method depends on several factors such as wastewater composition, operation costs, generated waste products and finally types of dye.

From the economical point of view, adsorption is a suitable method. Again, the kinetics of adsorption is an important physicochemical tool to evaluate the basic quality and the proper use of an adsorbent. Very recently, high adsorption capacity of used black tea leaves (UBTLs) as a low cost adsorbent to Cr (VI) was reported [3]. The present study was carried out to investigate the adsorption characteristics of UBTLs to reactive black 5. The main focus of the present research is to study the kinetics of adsorption of reactive black 5 on UBTLs under various experimental conditions such as different initial concentrations of reactive black 5 and processing temperature.

II. Experimental

Materials and Methods

Fresh black tea leaves were collected form Bangladesh Tea Research Institute, Sylhet (CTC Manufacturing Process). Used black tea leaves (UBTLs) were obtained after extracting tea liquor from fresh black tea leaves by boiling with distilled water for 8 h. After extraction, the tea leaves were dried at room temperature and finally were dried in oven at 105 ^oC for 10 hours. Dried leaves were sieved through the metallic sieve of mesh size 0.25 mm and 0.50 mm and were stored in air-tight bottle for adsorption experiments. Characteristic features of the UBTLs are described in elsewhere [3].

All chemicals used in the study were either analytical or reagent grades. Reactive black 5 (RB-5) was collected from local market. Analysis of reactive black 5 in solution is very important for adsorption study. A stock solution of 500 mg/L (RB-5) was prepared by dissolving required amount of reactive black 5 in distilled water. Different concentrations of RB-5 solutions were prepared by required dilution of stock solution. The pH of each solution was adjusted at a definite value of 2.00 using either 0.1 M HCl or 0.1 M NaOH whichever was necessary. A UV-visible Spectrophotometer (UV-vis 160A, Shimardzu, Japan) was used to measure the absorbance of each solution at λ_{max} = 593.5 nm and calibration curve was constructed using measured absorbance as a function of concentrations. From the verification of Beer- Lambert law, the calibration limit and molar absorption coefficient (ε) of RB-5 at pH 2.00 were determined which were 0.5 to 25 mg/L and 2.78×10^4 L/(mol·cm), respectively.

Kinetic Experiments

Batch adsorption kinetic experiments were carried out in a series of 60 mL of reagent bottles at a specified temperature, by suspending 0.1g of the UBTLs in 50 mL of RB-5 solution at a fixed pH, decided by preliminary experiments[4]. The bottles were placed in a thermostatic shaker maintained at 30°C and were shaked continuously for different contact times. The reagent bottles were successively withdrawn after definite time of interval. Then the suspended UBTLs were separated from solutions and the pH of the supernatant was adjusted at 2.00 and measured the absorbance using UV-vis spectrophotometer at λ_{max} = 593.5 nm to determine the residual concentration of RB-5. The amount of RB-5 adsorbed on to UBTLs at time t were calculated from the previously measured initial concentration of RB-5, using the following Eq. (1)

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

where C_i and C_t are the concentrations of the RB-5 (mg/L) at a time 0 and t, respectively. V is the volume of the solution (L) and W the weight of the dry UBTLs(g).

Effect of concentration

A series of adsorption kinetic experiments were carried out using different initial concentrations of RB-5 ranging from 10 to 70 mg/L, with a fixed amount of UBTLs using constant pH, temperature and shaking rate. The amount adsorbed of RB-5 with different contact times was determined for different initial concentrations. Amount adsorbed *vs.* adsorption time plot are shown in Fig. 1.

Effect of temperature

To determine the effect of temperature on the adsorption kinetics, adsorption kinetic experiments were performed at 30 and 50 °C using initial concentration of 30 mg/L of RB-5 keeping other parameters constant. The change of concentration of RB-5 with time for different temperatures was determined.

III. Results and Discussion

Effect of Concentration

The effect of initial concentration of RB-5 on the rate of adsorption is presented in Fig. 1. Figure 1 shows that adsorption was very rapid during first 30 minutes and after this became slow. Initial adsorption rate increases with increasing initial concentration of RB-5. For a particular experiment, the rate of adsorption decreased with time approaching to minimum rate, indicating that the adsorbent became saturated. The kinetic experiments were continued up to six hours of contact time with different initial concentrations of RB-5. Figure 1 showed that the equilibrium was not achieved during six hours of contact time.

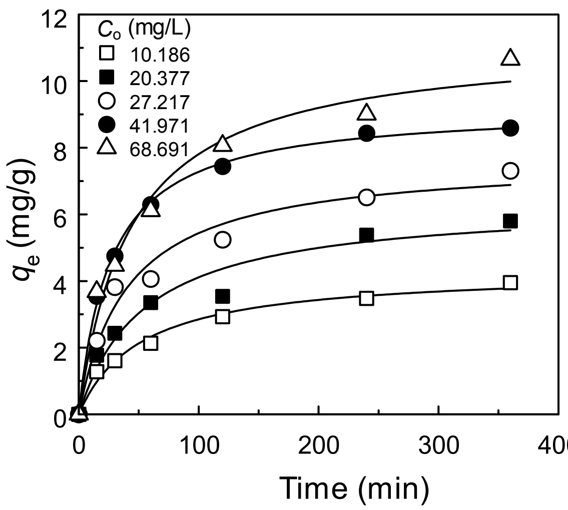

Fig. 1. Change of the amount adsorbed of reactive black 5 on UBTLs with time for different initial concetrations at pH 2 and 30 ± 0.5ºC.

Verification of Kinetic Equations

Kinetic evaluation of an adsorption process is very important for industrial application. It gives information for comparison among different adsorbents under various operational conditions[5]. This helps to design and optimize the operational conditions for practical application. Therefore, different kinetic rate equations were applied to the experimental data to evaluate the feasibility of the adsorption of reactive dye on UBTLs.

First order kinetics

Cimino et al. (2000)[6], Bhutani and Kumari (1994)[7] and Gupta et al. (2001)[8] described the adsorption of solid liquid system using the following simple first order kinetic equation (2) given as follows:

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

where, C_t is the concentration of reactant after time t (mg/L), C_o is the initial concentration of reactant (mg/L), k_1 is first order rate constant. For the present system, first order rate equation was verified by plotting $\ln C_t$ vs. t as shown in Fig. 2. Experimental results show that the adsorption of RB-5 on UBTLs follows simple first order kinetic equation only at lower concentration.

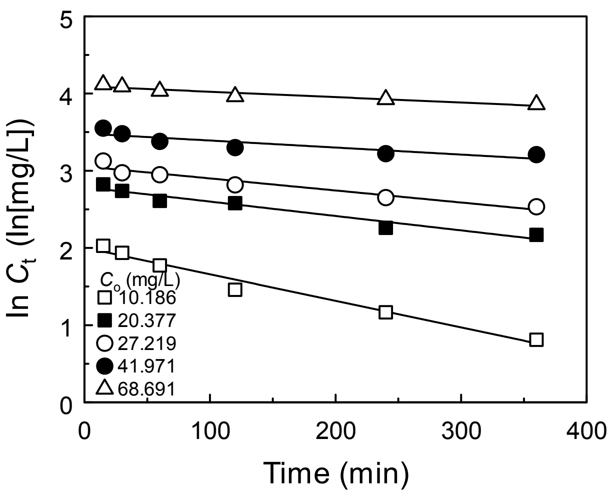

Fig. 2. First order kinetics for the adsorption of reactive black 5 on UBTLs at pH 2 and 30 ± 0.5 ºC.

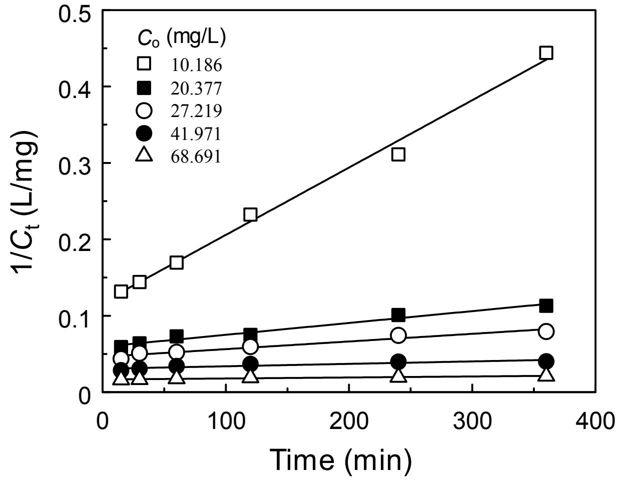

Fig. 3. Second order kinetics for the adsorption of reactive black 5 on UBTLs at pH 2 and 30 ± 0.5 ºC.

Second order kinetics

Generally, a second-order reaction depends on both the reactants. To verify the dependency of the concentration of RB-5 and UBTLs on the adsorption process, the integrated form of second-order rate equation (3) was applied to our experimental results[8].

$$1/C_t = k_2 t + 1/C_o \quad (3)$$

where C_o and C_t are the concentration (mg/L) of RB-5 at initial stage and after time t, respectively. Second order rate constant is presented by k_2. Figure 3 shows the applicability of the second order rate equation by plotting $1/C_t$ as a function of time t. The figure shows that the adsorption of RB-5 on UBTLs follows second order kinetics satisfactorily at lower concentration and its fitness is better than that of first order kinetics.

Pseudo second order kinetics

Several studies on adsorption using heterogeneous surface like tea leaves[9], moss peat[10], clay-wood sawdust[11], rice husk[12], peanut hull carbon[13], etc reported that adsorption follows pseudo second order kinetics. In the present study, Ho and McKay's pseudo second order rate eqution[10] was applied. The linearized from of Ho and McKay's pseudo second order rate eqution is shown in eq. (4)

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

where q_t is the amount adsorbed at time t (mg/g), q_e is the equlibrium amount adsorbed (mg/g) and k is the pseudo second order rate constant (g/mg.min). The verification of pseudo second order kinetics was performmed by plotting $1/q_t$ vs. t as shown in Fig. 4. This figure shows the satisfactory fitness of data to the straight line. From the straight lines obtained equilibrium amount adsorbed at different initial concentrations of RB-5 were calculated and the values are given in Table 1.

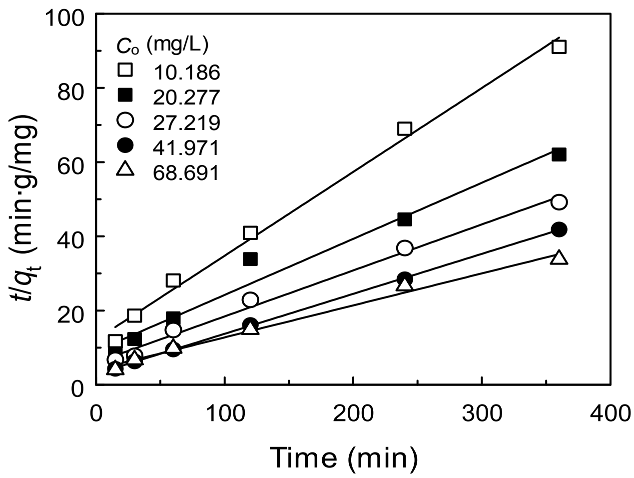

Fig. 4. Pseudo second order kinetics for the adsorption of reactive black 5 on UBTLs at pH 2 and 30 ± 0.5 ºC.

Table. 1. Veriation of equilibrium amount adsorbed and equilibrium concentration with initial concentration determined from the pseudo second kinetic plotting.

Initial concentration C_o (mg/L)	Eulibrium amount adsorbed q_e (mg/g)	Equilibrium concentration C_e (mg/L)
10.186	4.425	1.336
20.377	6.623	7.917
27.219	8.064	11.091
41.971	9.345	23.281
68.691	10.640	47.187

The Elovich equation

General expression of the elovich model equation is shown[14] as eq. (5)

$$\frac{dq_t}{dt} = \alpha \exp(-\beta q_t) \quad (5)$$

where dq_t/dt is the initial adsorption rate (mg/g·min) and β is the desorption constant (g/mg) of any experiment. To simplify the elovich equation Chien and Clyton assumed $\alpha\beta t >> t$ and by applying boundary conditions $q_t= 0$ at $t = 0$ and $q_t = t$ at $t = t$, the equation becomes-

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

The elovich equation was applied to the present study as a plot q_t vs $\ln t$ as shown in Fig. 5. All the plots give straight lines with the slope $\frac{1}{\beta}$ and an intercept of $\frac{\ln \alpha\beta}{\beta}$ indicating the validity of elovich equation. Different parameters of the elovich equation for the adsorption of RB-5 on UBTLs are given in Table 2. Decrising of desorption constant, β with increasing initial concentration of RB-5 indicates the favorable adsorption at higher concentration of adsorbate. A comparison of the regragration factor for the application of different kinetic equations has been shown in Table 3. It can be concluded that the best fitted equation for the adsorption of RB-5 on UBTLs is pseudo second order kinetics.

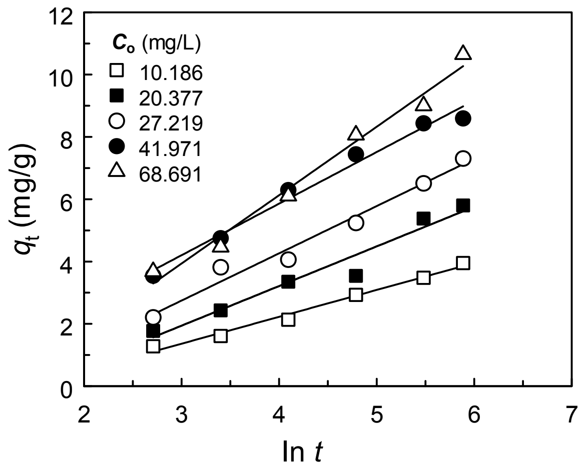

Fig. 5. Elovich model equation for the adsorption of reactive black 5 on UBTLs at pH 2 and 30 ± 0.5 ºC.

Table. 2. Elovich equation parameters for the adsorption of reactive black 5 on UBTLs.

Initial concentration C_o (mg/L)	Elovich equation parameters		R^2
	α	β	
10.186	0.284	1.159	0.985
20.377	0.291	0.786	0.951
27.219	0.461	0.659	0.971
41.971	0.655	0.604	0.982
68.691	1.040	0.455	0.982

Table. 3. A comparison of the data fitness to the first order, second order, pseudo second order and elovich model kinetic equations.

Initial concentration C_o (mg/L)	R^2			
	First order	Second order	Pseudo second order	Elovich model
10.186	0.975	0.999	0.992	0.985
20.377	0.947	0.974	0.972	0.951
27.219	0.937	0.953	0.990	0.971
41.971	0.792	0.819	0.999	0.982
68.691	-	-	0.990	0.982

Effect of Temperature

The effect of temperature on the adsorption kinetics was performed to identify the nature of adsorption. Figure 6 shows the variation of change of concentration of RB-5 with time for same initial concentration of RB-5 and UBTLs, for two different temperatures. The concentration of RB-5 solution decreases rapidly at higher temperature than lower temperature suggesting the amount adsorbed increases at higher temperature. It may be due to the temperature dependent chemical interaction between RB-5 molecules and UBTLs. As the temperature increases the activation energy of interacting species increases [9, 15] due to the increased velocity of the solute [2] and the adsorption rate also increases.

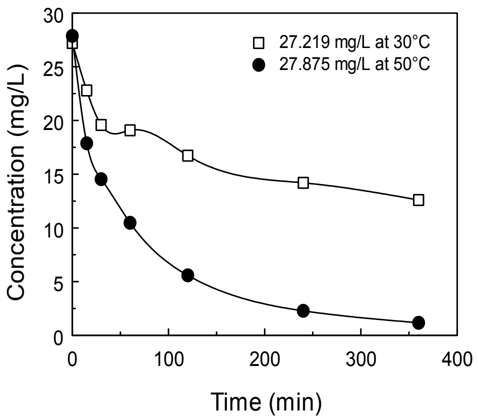

Fig. 6. Change of the concentration of reactive black 5 with time for the adsorption on UBTLs at pH 2 and different temperatures.

IV. Conclusions

From the comparison of regragration factors, it can be concluded that the adsorption of RB-5 on UBTLs follows pseudo second order rate equation at pH 2. Using the best-fitted equation one can calculate the equilibrium concentration of residual RB-5, which is very important for evaluating the adsorption efficiency. The desorption constant, β was calculated by using elovich model equation and the value is decreased with increase in initial concentration of RB-5 indicates the favorable adsorption at higher concentration of adsorbate. From temperature dependences of the adsorption of RB-5 on UBTLs at pH 2 it can be concluded that the adsorption involves chemical interaction which needs activation energy.

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1. Daniela, S. and D. Bilba, 2005. Equilibrium and Kinetics Study of Reactive Dye Brilliant Red HE-3B Adsorption by Activated Charcoal, *Acta Chim. Solv.* **52**, 73-79.
2. Hu, T. and S. C. Wu, 2001. Assessment of the Effect of Azo Dye RP2B on the Growth of Langmuir, I. *J. Am. Chem. Soc.* **38**, 2221-2228.
3. Hossain, M. A., 2006. Study on Process Development for removal of Cr(VI) From Waste Water by Sorption on Used Black Tea Leaves, *Ph. D Thesis,* Kanazawa University, Japan.
4. Zubair Hasan, 2007. Kinetic Study on Adsorption of Reactive Black 5 on Used Black Tea Leaves, *BS Project,* Department of Chemistry, University of Dhaka, Bangladesh.
5. Benguella, B. and H. Benasissa, 2002. Cadmium Removal from Aqueous Solutions by Chitin: Kinetics and Equilibrium Studies, *Water Res*. **36**, 2463-2467.
6. Cimino, G., A. Passerini and G. Toscano, 2000. Removal of Toxic Cations and Cr(VI) from Aqueous Solution by Hazelnut Sheel, *Water Res.* **34**, 2955-2962.
7. Bhutani, M. M. and R. Kumari, 1994. Adsorption of Low Level 51 Cr(VI) from Aqueous Solution by Bismuth Trioxide: Kinetic and IR Study, *J. Radioanal. Nucl. Chem.* **180**, 145-153.
8. Gupta V. K., M. Gupta and S. Sharma, 2001. Process Development for the Removal of Lead and Chromium from Aqueous Solutions Using Red Mud-an Aluminium Industry Waste, *Water Res.* **34**, 735-742.
9. Hossain, M. A., M. Kumita, Y. Michigami and S. Mori, 2005. Kinetics of Cr(VI) Adsorption on Used Black Tea Leaves, *J. Chem. Eng. Jpn*. **38**, 402-406.
10. Ho, Y. S and G. McKay, 2000. Kinetics of Sorption of Divalent Metal Ions onto Sphagnum Moss Peat, *Water Res.* **34**, 735-742.
11. Yeddou, N. and A. Bensmaili, 2005. Kinetic Models for the Sorption of Dye from Aqueous Solution by Clay-wood Sawdust Mixture, *Desalination.* **185**, 499-508.
12. Allen, S. J. and B. Koumanova, 2005. Decolourisation of Water/Waste Water Using Adsorption (Review), *J. Univ. Chem. Technol. and Metallur*. **40(3)**, 175-192.
13. Amin, N. K., 2008. Removal of Reactive Dye from Aqueous Solutions by the Adsorption onto Activated Carbons Prepared from the Sugarcane Bagasse Pith, *Desalination.* **223(9)**, 152-161.
14. Dong-Jin, J., I. Gye, H. L. Chang, A. Gab-Hwan and T. J. Park, 2006. Biosorption Characteristics of Reactive Dye on to Red Activated Sludge, *Water Practice and Technol.* **1**, 20-28.
15. Hossain, M. A., M. Kumita, Y. Michigami and S. Mori, 2005. Optimization of Parameter for Cr(VI) Adsorption on Used Black Tea Leaves, *Adsorption*. **11**, 61-68.