



Research Journal of
**Environmental
Toxicology**

ISSN 1819-3420



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Linear and Non-Linear Kinetic Modeling for Adsorption of Disperse Dye in Batch Process

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ABSTRACT

Removal of disperse orange 25 dye by adsorption on activated carbon was experimentally investigated in a batch process in present study which revealed that the equilibrium data fitted better in the Langmuir isotherm, indicating monolayer coverage of disperse orange 25 dye molecules at the outer surface of activated carbon. Several forms of pseudo-first and second order kinetic models were employed to determine the best-fitting form of particular model on the basis of statistical analysis. The results concluded that the non-linear form of pseudo-second order kinetic model is best suited to explain the present adsorption study as compared to linear forms.

Key words: Activated carbon, disperse orange 25, adsorption isotherms, pseudo-first order kinetic model, pseudo-second order kinetic model

INTRODUCTION

Dyes and pigments are chemically complex compounds which are discharged into wastewater from various dye manufacturing and textile finishing industrial outlets. In the textile sector, 10-20% unexploited dyes remain as waste with residual liquors. These dyes are not completely exhausted during the processes and discharged into the rivers which inhibit sunlight penetration into the rivers (Gajare and Menghani, 2012). Nearly 0.1 million type of commercially available dyes are produced all over the world (Mondal, 2008). Major dyes cause skin diseases and cancer when discharged with the effluents. Hence, elimination of dyes before discharging effluents into the rivers and streams is an absolute necessity (Banerjee *et al.*, 2014).

Various processes including physical (dilution, floatation, filtration and reverse osmosis), chemical (coagulation-flocculation and precipitation, chemical oxidation) and biological (aerobic and anaerobic microbial degradation) treatments had been tested for dyes removal from industrial effluents. Compared to these processes, adsorption process is an efficient one for dyes removal from wastewater due to its clean and sludge-free operation. Further, adsorption has capability to remove dyes from wastewater having diluted concentrations (Yu and Hu, 2011).

Several commercially available adsorbents (e.g., activated carbon and zeolite) have previously been tried for treating textile wastewater containing dyes (Andersson *et al.*, 2012; Lian *et al.*, 2009). Khare *et al.* (1987) used complex mixture of coal and fly ash for adsorbing omega chrome Red ME. In this study, equilibrium data related to removal of disperse orange 25 dye by activated carbon has been analyzed for different isotherms (*viz.* Langmuir, Freundlich and Temkin). Kinetics of dye adsorption is important factor for adsorption rate of dye from solutions since it controls residence

time of dye in solid-liquid interface (El Saliby *et al.*, 2013). Pseudo-first order, second order (bulk transport of dye molecules in liquid phase) kinetic models and intra-particle diffusion model (film transport involving diffusion of dye molecules through a hydrodynamic boundary layer around adsorbent surface) were abundantly used in adsorption studies and have been used in present study also (Kisku *et al.*, 2015; Lange and Mendez-Sanchez, 2010). Different linear and non-linear forms of pseudo-first and second order kinetic models have been statistically compared to get best kinetic model describing the adsorption mechanism for removal of disperse orange 25 onto activated carbon.

MATERIALS AND METHODS

Analytical-grade chemical reagents and milli-Q water have been used in this study for preparing solutions. Disperse Orange 25 (DO) dye with 99.9% purity was procured from Siddheshwari Industries, GIDC, Gujarat, India. Figure 1 presents molecular formula and chemical structure of DO dye. Activated carbon was procured from Merck Ltd., Mumbai and directly used as adsorbent.

Dye solutions of different concentrations were prepared by mixing 10-100 mg dye in 1 L water. The batch adsorption kinetics was carried out using orbital incubator shaker (Model: GGT 1201, G.G. Technolies, New Delhi). Dye solutions were taken in flasks having adsorbent dose of 0.4 g L⁻¹ and pH of mixture was adjusted to 6.0 by adding 0.1 N H₂SO₄. The flasks were then subjected to agitation speed of 140 rpm and contact time was varied from 5-300 min. After adsorption, solution was filtered using filter paper (Whatman No. 42) and residual concentration of DO was measured at 456 nm wavelength using UV-Vis single beam spectrophotometer (Model: Halo SB-10, Dynamica).

The dye removal percentage was calculated using the following equations:

$$\text{Percent removal} = \frac{(C_0 - C_t) \times 100}{C_0} \quad (1)$$

$$\text{Dye adsorbed (q}_e\text{)} = \frac{(C_0 - C_t) \times V}{M} \quad (2)$$

Where:

C₀ and C_t = Initial and final concentrations (mg L⁻¹) of dye, respectively

q_e = Amount of adsorbed concentration of dye (mg g⁻¹) on adsorbent

V = Volume of solution (L)

M = Mass of adsorbent used (g)

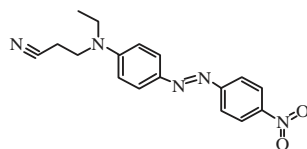


Fig. 1: Chemical structure of disperse orange 25 dye (C₁₇H₁₇N₃O₂)

RESULTS AND DISCUSSION

Adsorption isotherms: Observed data was tested for Langmuir (1916), Freundlich (1906) and Temkin and Pyzhev (1940) isotherms. Adsorption happens at specific homogeneous sites within the adsorbent in case of Langmuir isotherm. Adsorption sites are independent of the neighboring sites which accommodate only one dye molecule on each adsorption site in form of complexes of reactive functional groups present on surface of adsorbent. Linear form of Langmuir isotherm is shown below:

$$\frac{1}{q_e} = \frac{1}{q_m} + \left(\frac{1}{b q_m} \right) \frac{1}{C_e} \quad (3)$$

Where:

C_e = Concentration of adsorbate in solution at equilibrium (mg L^{-1})

q_m = Maximum capacity of adsorbent for adsorbate (mg g^{-1})

b = Constant for apparent energy of adsorption (L mg^{-1})

The experimental data was plotted ($1/q_e$ vs. $1/C_e$) to determine q_m and constant b .

Assumption of Freundlich isotherm is that heterogeneous surface has non-uniform distribution of adsorption heat over it. The linear form of the Freundlich isotherm is shown below:

$$\log q_e = \log K_F + \left(\frac{1}{n} \right) \times \log C_e \quad (4)$$

Where:

K_F = Freundlich constant related to adsorption capacity of adsorbents (mg g^{-1})

n = Freundlich exponent constant that represents the parameter characterizing Quasi Gaussian energetic heterogeneity of the adsorption surface.

The experimental data was plotted ($\log q_e$ vs. $\log C_e$) to determine the constant K_F and n .

The Temkin isotherm shown in Eq. 5 involves that the adsorption heat in layer's molecules decreases linearly due to adsorbent-adsorbate links. Such adsorption is distinguished by a uniform distribution of the bonding energies.

$$q_e = B_t \ln K_t + B_t \ln C_e \quad (5)$$

Where:

K_t = Equilibrium constant corresponding to maximum binding energy (L mg^{-1})

B_t = Variation of adsorption energy (kJ mol^{-1})

The experimental data was plotted (q_e vs. $\ln C_e$) to get values of B_t and constant K_t .

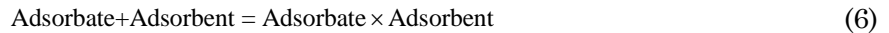
Parameters related to Langmuir, Freundlich and Temkin isotherms are given in Table 1. The coefficient of determination (R^2) is highest (0.990) in case of Langmuir isotherm which suggests that adsorption of DO dye on activated carbon is best described by Langmuir isotherm. Banerjee *et al.* (2014) also found that equilibrium data of adsorption of methylene blue dye on modified wheat husk surface is well fitted with Langmuir isotherm indicating monolayer adsorption. The low value of b (0.076 L mg^{-1}) in this study indicate a weak interaction between

Table 1: Isotherm parameters for adsorption of dispersive orange 25 dye on the activated carbon

Isotherm parameters	Values
Langmuir isotherm	
q_m (mg g ⁻¹)	200
b (L mg ⁻¹)	0.076
R^2	0.990
Freundlich isotherm	
K_F (L mg ⁻¹)	24.12
n	2.041
R^2	0.858
Temkin isotherm	
K_t (L mg ⁻¹)	1.393
B_t (kJ mol ⁻¹)	32.662
R^2	0.942

dye and activated carbon for ion-exchange mechanism (Hameed *et al.*, 2007). The maximum adsorption capacity of activated carbon, q_m , in present study has been found to be 200 mg g⁻¹ for DO dye (Table 1) which is comparable with 159 mg g⁻¹ in case of granular activated carbon used for the adsorption of maxilon goldgelb GL EC 400% dye (Meshko *et al.*, 2001).

Kinetic models: An empirical model, neglecting the mass transfer effects, can replace the kinetic modeling to resemble the observe data (Pagnanelli, 2011). According to Thomas (1948), the adsorption process is described by following reaction:



In the recent years, adsorption mechanisms are explained by involving kinetic-based models which describe the reaction order of adsorption systems based on solution concentrations viz. pseudo-first order (Febrianto *et al.*, 2009), pseudo-second order (Tiwari *et al.*, 2013; Ozacar and Sengil, 2006), kinetic models and intra-particle diffusion model (Shukla *et al.*, 2014). The kinetic models can be presented in different (linear and non-linear) forms having variable degree of complexity (Table 2).

Pseudo-first order kinetic model: Lagergren's rate equation of the first order describes the rate of adsorption based on adsorption capacity as:

$$\frac{dq}{dt} = k_1 (q_e - q_t) \quad (7)$$

Where:

q_t = Solid phase dye concentration (mg g⁻¹) at time t

Integration of Eq. 7 (boundary conditions: q varying from 0- q when t varies from 0- t) gives non-linear form of pseudo-first order kinetic model (Ho and Chiang, 2001) which can be transformed to linear form as shown in Table 2. Figure 2 shows plot of different linear and non-linear forms of pseudo-first order kinetic model.

The q_e and k_1 (Table 3) were determined by non-linear fitting (q_t vs. t) and linear fitting ($\log (q_e - q_t)$ vs. t) as well (Fig. 2). Pseudo-first order kinetic model has been applied to many adsorption kinetic studies (Febrianto *et al.*, 2009).

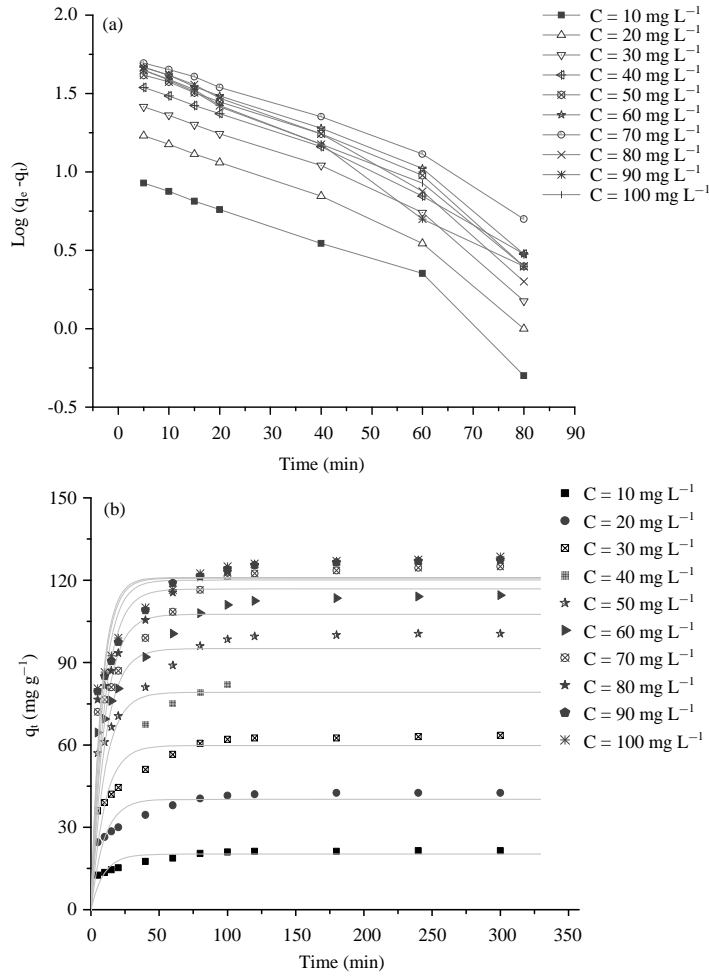


Fig. 2(a-b): Pseudo-first order kinetic model plots (a) Linear form and (b) Non-linear form for the adsorption of disperse orange 25 dye on activated carbon

Table 2: Pseudo-first order, second order and intra-particle diffusion model and their different forms

Kinetic models	Non-linear forms	Linear forms	Plots for linear forms	Constants
Pseudo-first order	$q_t = q_e (1 - \exp^{-k_1 t})$	$\log(q_e - q_t) = \log(q_e) - \frac{k_1 t}{2.303}$	$\log(q_e - q_t)$ vs. t	$k_1 = 2.303 \times M$
Type 1 pseudo-second order		$\frac{t}{q_t} = \left(\frac{1}{k_2 q_e^2} \right) + \frac{1}{q_e} t$	$\frac{t}{q_t}$ vs. t	$q_e = 1/M, k_2 = M^2/C$
Type 2 pseudo-second order	$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t}$	$\frac{1}{q_t} = \left(\frac{1}{k_2 q_e^2} \right) \frac{1}{t} + \frac{1}{q_e}$	$1/q_t$ vs. $1/t$	$q_e = 1/C, k_2 = C^2/M$
Type 3 pseudo-second order		$\frac{1}{t} = \frac{k_2 q_e^2}{q_t} - \frac{k_2 q_e^2}{q_e}$	$\frac{1}{t}$ vs. $\frac{1}{q_t}$	$q_e = -M/C, k_2 = C^2/M$
Type 4 pseudo-second order		$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t$	$1/(q_e - q_t)$ vs. t	$q_e = 1/C, k_2 = M$
Intra-particle diffusion		$q_t = k_{ip} \times t^{1/2} + C_i$	q_t vs. $t^{(1/2)}$	$k_{ip} = M, C_i = C$

q_e : Measured values of equilibrium adsorbate concentration in solid phase (mg g^{-1}), q_t : Amount of dye adsorbed (mg g^{-1}) at time t , C_i : Initial dye concentration (mg L^{-1}), t : Time (min), k_1 : Rate constant of the pseudo-second order kinetics (min^{-1}), k_2 : Rate constant of the pseudo-second order kinetics ($\text{g mg}^{-1} \text{min}^{-1}$), k_{ip} : Intra-particle rate constant ($\text{mg/g min}^{1/2}$), M : Slope, C : Intercept of plot

Table 3: Pseudo-first order kinetic model parameters for disperse orange 25 dye adsorption by activated carbon

Concentration (mg L ⁻¹)	Pseudo-first order (Linear form)					Pseudo-first order (Non-linear form)			
	q _{e,exp} (mg g ⁻¹)	q _{e,cal} (mg g ⁻¹)	k ₁ (L min ⁻¹)	χ ²	R ²	q _{e,cal} (mg g ⁻¹)	k ₁ (L min ⁻¹)	χ ²	R ²
10	21.011	11.310	3.224	8.302	0.933	20.221	0.108	0.027	0.952
20	41.500	22.860	3.455	15.199	0.964	40.184	0.104	0.038	0.964
30	62.002	35.157	3.455	20.501	0.958	59.795	0.101	0.073	0.961
40	82.051	43.448	2.994	34.203	0.987	79.191	0.099	0.087	0.976
50	98.504	55.852	3.455	32.570	0.954	95.094	0.099	0.104	0.959
60	111.011	60.678	3.224	41.729	0.962	107.592	0.101	0.093	0.978
70	121.508	62.378	2.764	56.030	0.976	116.781	0.102	0.156	0.981
80	123.051	65.769	3.915	49.799	0.969	120.061	0.115	0.061	0.979
90	124.043	58.614	3.915	72.954	0.991	120.021	0.129	0.113	0.992
100	125.502	56.372	3.455	83.556	0.976	120.971	0.135	0.114	0.987

q_{e,exp}: Experimental dye concentration at equilibrium, q_{e,cal}: Calculated dye concentration at equilibrium

Pseudo-second order kinetic model: Pseudo-second order kinetic model is derived by assuming a second order dependence of the adsorption rate on available sites (Ozacar and Sengil, 2006) and can be written as:

$$\frac{dq}{dt} = k_2 (q_e - q_t)^2 \tag{8}$$

On integration of Eq. 8 with boundary conditions: q_t varying from 0-q_e when t varies from 0-t, we get:

$$q_t = q_e \left(1 - \frac{1}{1 + k_2 q_e t} \right) \tag{9}$$

Equation 9 can be converted to varying linearity forms (Table 2). Linear forms (t/q_t vs. t, 1/q_t vs. 1/t, 1/t vs. 1/q_t and 1/(q_e-q_t) vs. t) of this model are plotted in Fig. 3(a-d), whereas non-linear form (q_t vs. t) is plotted in Fig. 3e. For non-linear forms, ‘origin’ software (version 9.0) was employed to determine constants of kinetic models. Pseudo-second order constants (q_e and k₂) are given in Table 4.

Different linear forms of the same kinetic model significantly affect the modeling data due to the differences in the error function that varied upon linearizing the non-linear equation. The error distribution, varying from one linear form to other, depends on the way of linearization of kinetic models. Even though non-linear forms were proven to be the best way to regress model parameters, most of adsorption studies used the linear forms of equations.

Statistical analysis: Error functions are required to assess the kinetic model describing the experimental results in a best possible way. The R² and chi-square tests (Chowdhury and Saha, 2011) are performed to find out suitability of various forms of kinetic models in case of present study.

$$R^2 = \frac{(q_{e,exp} - q_{e,cal})^2}{\sum (q_{e,exp} - q_{e,cal})^2 + (q_{e,exp} - q_{e,cal})^2} \tag{10}$$

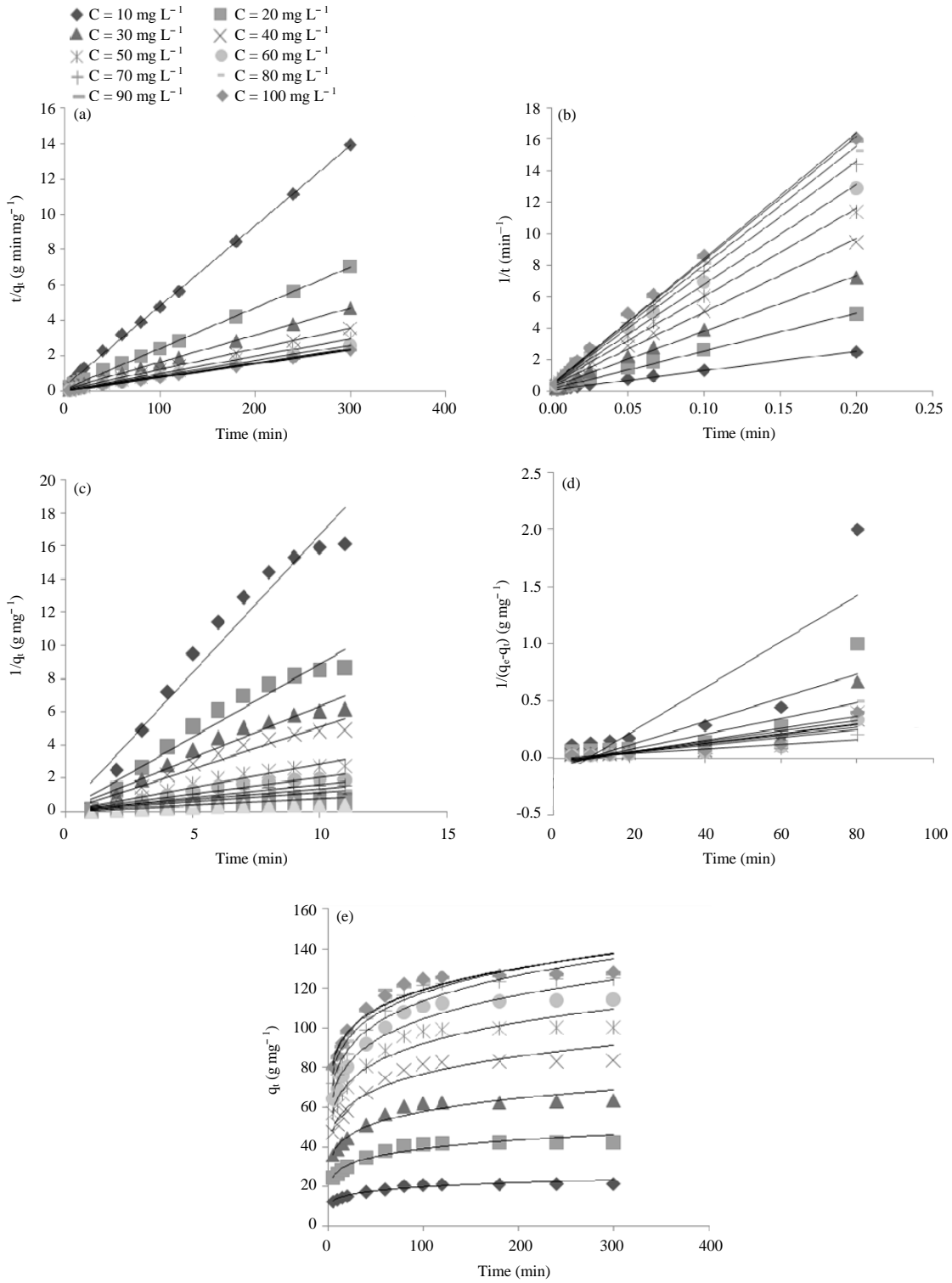


Fig. 3(a-e): Pseudo-second order kinetic model plots (a) Type 1 linear form, (b) Type 2 linear form, (c) Type 3 linear form, (d) Type 4 linear form and (e) Non-linear form for the adsorption of DO dye on activated carbon

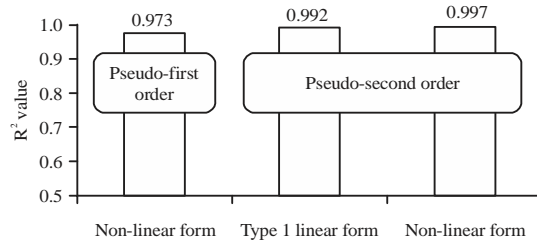


Fig. 4: R² values of experimental data fitting in kinetic models

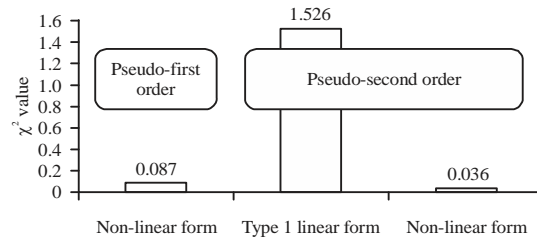


Fig. 5: χ² values of experimental data fitting in kinetic models

$$\chi^2 = \sum \frac{(q_{e,\text{mean}} - q_{e,\text{cal}})^2}{q_{e,\text{cal}}} \quad (11)$$

where, $q_{e,\text{exp}}$ and $q_{e,\text{cal}}$ (mg g^{-1}) are experimental and calculated dye concentration at equilibrium, respectively and $q_{e,\text{cal}}$ (mg g^{-1}) is average value of $q_{e,\text{cal}}$.

R² and χ² values of linear and non-linear forms of kinetic models are plotted in Fig. 4 and 5, respectively. For the best fit kinetic model in any adsorption study, three conditions should be satisfied: (i) the $q_{e,\text{exp}}$ values should reasonably match with the $q_{e,\text{cal}}$ values at all initial concentrations of adsorbate, (ii) the values of R² should be maximum and (iii) the values of χ² should be minimum.

From Table 3 and 4, it can be observed that kinetic model constants (k_1 , k_2) and calculated dye concentration at equilibrium ($q_{e,\text{cal}}$) vary with $q_{e,\text{exp}}$ (experimental dye concentration at equilibrium). The $q_{e,\text{exp}}$ values are always increasing with the increases of initial dye concentration and $q_{e,\text{cal}}$ values should also follow the similar trend. In case of linear form of pseudo-first order kinetic model, the $q_{e,\text{cal}}$ values show increasing trends ($11.310\text{-}65.769 \text{ mg g}^{-1}$) when initial dye concentration is increased from $10\text{-}80 \text{ mg L}^{-1}$. At higher initial concentrations of dye ($90\text{-}100 \text{ mg L}^{-1}$), the $q_{e,\text{cal}}$ values show the decreasing trends and are even lower ($58.614\text{-} 56.372 \text{ mg g}^{-1}$) than those obtained at initial dye concentration of 80 mg L^{-1} . In the entire range of initial dye concentrations, $q_{e,\text{cal}}$ values are about 50% of $q_{e,\text{exp}}$ values which makes linear form of pseudo-first order kinetic model unfit for present study.

In case of linear form of type 2 pseudo-second order kinetic model, the $q_{e,\text{cal}}$ increases when initial dye concentration is increased from 10 mg L^{-1} onwards but reverses the trend as soon as initial dye concentration is more than 40 mg L^{-1} . The $q_{e,\text{cal}}$ again show increasing trend when initial dye concentration goes beyond 70 mg L^{-1} . Further the $q_{e,\text{cal}}$ values are varying from 50-25% of $q_{e,\text{exp}}$ values. These observations suggest that linear form of type 2 pseudo-second order kinetic model is not explaining the adsorption process well.

Table 4: Pseudo-second order kinetic and intra-particle diffusion model parameters for disperse orange 25 adsorption by activated carbon

Concentration (mg g ⁻¹)	Type 1 pseudo-second order (Linear form)					Type 2 pseudo-second order (Linear form)				Type 3 pseudo-second order (Linear form)			
	q _{e,exp} (mg g ⁻¹)	q _{e,cal} (mg g ⁻¹)	k ₂ (L min ⁻¹)	χ ²	R ²	q _{e,cal} (mg g ⁻¹)	k ₂ (L min ⁻¹)	χ ²	R ²	q _{e,cal} (mg g ⁻¹)	k ₂ (L min ⁻¹)	χ ²	R ²
10	21.011	22.222	6.193	0.067	0.990	10.638	5.339	4.831	0.953	139.886	20.01	0.629	0.996
20	41.500	45.455	2.969	0.344	0.992	12.821	6.889	18.101	0.952	133.944	10.21	1.344	0.996
30	62.002	66.667	2.009	0.301	0.990	12.048	10.987	37.431	0.947	130.184	7.31	2.089	0.995
40	82.051	90.909	1.407	0.873	0.994	30.303	2.148	29.402	0.951	129.391	3.23	2.790	0.996
50	98.504	111.110	1.141	1.431	0.992	20.833	8.170	54.292	0.940	129.169	4.02	3.352	0.996
60	111.011	125.010	0.985	1.568	0.991	19.608	12.813	66.820	0.928	127.843	3.21	3.880	0.995
70	121.508	142.862	0.790	3.193	0.994	17.544	20.563	75.650	0.915	142.955	2.43	3.456	0.997
80	123.051	142.863	0.980	2.760	0.992	20.000	19.380	74.261	0.909	147.937	5.43	3.441	0.996
90	124.043	142.863	1.167	2.489	0.994	23.810	16.183	70.270	0.909	155.754	4.54	3.236	0.996
100	125.502	142.864	1.140	2.232	0.992	37.037	9.998	54.166	0.909	158.410	4.58	3.175	0.996

Concentration (mg g ⁻¹)	Type 4 pseudo-second order (Linear form)					Pseudo-second order (Non-linear form)				Intra-particle diffusion model		
	q _{e,exp} (mg g ⁻¹)	q _{e,cal} (mg g ⁻¹)	k ₂ (L min ⁻¹)	χ ²	R ²	q _{e,cal} (mg g ⁻¹)	k ₂ (L min ⁻¹)	χ ²	R ²	C _i	k _{ip}	R ²
10	21.011	5.208	2.020	47.880	0.702	22.638	2.020	0.119	0.993	12.760	0.632	0.823
20	41.500	10.101	10.000	97.604	0.751	41.821	10.000	0.010	0.992	25.110	1.271	0.816
30	62.002	14.925	7.128	148.500	0.740	62.048	7.128	0.001	0.997	37.000	1.914	0.811
40	82.051	50.001	3.010	20.480	0.845	83.303	3.010	0.034	0.991	48.670	2.563	0.817
50	98.504	26.316	4.016	198.000	0.733	98.833	4.016	0.004	0.990	58.250	3.087	0.812
60	111.011	34.483	3.086	169.790	0.751	112.608	3.086	0.075	0.998	71.710	3.818	0.839
70	121.508	55.560	2.020	78.259	0.814	122.544	2.020	0.020	0.995	66.120	3.492	0.825
80	123.051	16.393	5.016	693.260	0.742	124.000	5.016	0.061	0.999	78.360	3.555	0.816
90	124.043	23.812	4.008	421.600	0.879	124.810	4.008	0.027	0.999	82.870	3.251	0.792
100	125.502	26.316	4.000	370.070	0.768	125.037	4.000	0.005	0.999	84.050	3.202	0.806

q_{e,exp}: Experimental dye concentration at equilibrium, q_{e,cal}: Calculated dye concentration at equilibrium

In type 3 linear form of pseudo-second order kinetic model, q_{e,cal} decreases from 139.886-127.843 mg g⁻¹ when initial dye concentration is increasing from 10-60 mg L⁻¹. However, at higher initial dye concentrations (70 mg L⁻¹ onward), the q_{e,cal} values show increasing trends (142.955-158.410 mg g⁻¹) and further increases (5.280-50.001 mg g⁻¹) with increasing initial dye concentration (10-40 mg L⁻¹) in case of type 4 linear form of pseudo-second order kinetic model. Thereafter when initial dye concentration further increases (40-70 mg L⁻¹), q_{e,cal} shows decreasing trend which is again reversed when initial dye concentration increases beyond 80 mg L⁻¹. Overall q_{e,cal} does not follow any definite trend with respect to q_{e,exp} values suggesting that type 4 linear form of pseudo-second order kinetic model also is not fit to explain the adsorption process of present study. Kumar (2006) studied on sorption kinetics of methylene blue onto activated carbon and found that as initial concentration of dye increase, the q_{e,cal} values were sometimes increasing and sometimes decreasing as in the case of present findings.

From above discussion, it is observed that linear forms of pseudo-first order and type 2, type 3, type 4 pseudo-second order kinetic models are violating theory of adsorption in case of adsorption of DO dye onto activated carbon mainly for two reasons: (i) the values of q_{e,cal} do not follow increasing trend with increasing initial concentration of dye, as observed for q_{e,exp} and (ii) q_{e,cal} values range from 25-90% of q_{e,exp} values. Hence, it can be concluded that linear forms of pseudo-first order and type 2, type 3, type 4 pseudo-second order kinetic models are not the suitable models for explaining the adsorption process happening in present study. Suitability of rest of the linear and non-linear forms of pseudo-first and second order kinetic models are discussed next so as to decide the best fit kinetic model and its form for present study.

Based on the criteria that q_{e,cal} should follow similar trend as of q_{e,exp} and their values should reasonably match, only linear form of type 1 pseudo-second order and non-linear forms of both

kinetic models qualify to be best fit model. These forms have been further compared based on error parameters i.e. R^2 and χ^2 (Fig. 4 and 5). R^2 values in case of non-linear form of pseudo-second order kinetic model ranged from 0.990-0.999 (average value 0.997) followed by 0.990-0.994 (average value 0.992) for type 1 pseudo-second order (linear form) and 0.952-0.992 (average value 0.973) for pseudo-first order (non-linear form) kinetic model (Fig. 4), indicating that non-linear form and type 1 (linear form) of pseudo-second order kinetic model explain adsorption process of present study well as compared to non-linear form of pseudo-first order kinetic model (Table 3 and 4). The mean χ^2 values of pseudo-second order (non-linear form) kinetic model vary from 0.001-0.119 followed by 0.067-3.193 and 0.027-0.156 for type 1 pseudo-second order (linear form) and pseudo-first order (non-linear form) kinetic models respectively indicating that non-linear forms of pseudo-first order and second order represent the experimental data better as compared to other linear forms of kinetic models (due to smaller χ^2 values). These observations indicate that transforming non-linear form of kinetic model to linear forms can alter the distribution error and twist model parameters. Finally, considering both error functions χ^2 and R^2 together, it is concluded that the best fit kinetic model to explain adsorption of DO dye onto activated carbon is non-linear form of pseudo-second order kinetic model. Kumar (2006), studied on sorption of methylene blue onto activated carbon, results suggested that non-linear form of kinetic model better than linear forms.

Intra-particle diffusion model: The experimental observations were further investigated by the diffusion (intra-particle) model to explain the diffusion mechanism. According to Hameed *et al.* (2009), the plots (q_t vs. $t^{1/2}$) represent multi-linearity, which indicates two or more steps occurring in the adsorption process. The relationship between q_t vs. $t^{1/2}$ is plotted in Fig. 6. The intra-particle diffusion constant was calculated using linear equation (Table 2).

If plot (q_t vs. $t^{1/2}$) is straight line passing from origin, then intra-particle diffusion becomes rate-limiting step. The adsorption data indicated that removal of dye from aqueous phase is a complex process, involving both boundary layer diffusion as well as intra-particle diffusion.

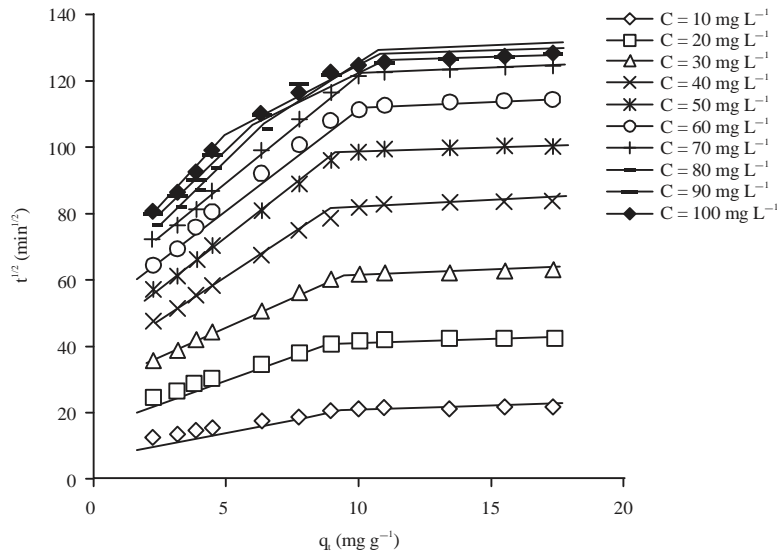


Fig. 6: Intra-particle diffusion kinetics model for the adsorption of disperse orange 25 dye on activated carbon

Hameed *et al.* (2009) also studied removal of cationic dye (methylene blue) from aqueous solutions using pineapple stem (a novel agricultural waste) as adsorbent and observed the more than one step affected the adsorption process.

CONCLUSION

Present study of adsorption process, removing disperse orange 25 dye from aqueous solution by the activated carbon, concludes that Langmuir isotherm describes the equilibrium data better than the Freundlich and Temkin isotherms. The maximum DO dye binding capacity (q_m) of activated carbon is found as 200 mg g^{-1} . A comparative statistical analysis of various linear and non-linear forms of pseudo-first and second order kinetic models shows that non-linear form of pseudo-second order kinetic model was best fitting the experimental data for the adsorption of disperse orange 25 dye onto activated carbon as $q_{e,cal}$ matched with $q_{e,exp}$ in terms of trends and values. Further the mean values of error function R^2 was maximum and χ^2 was minimum in non-linear form of pseudo-second order kinetic model. The varying stages of adsorption rates showed that the rate of adsorption was faster in the beginning but later slowed down as the time progresses.

ACKNOWLEDGMENT

The first author is grateful to World Bank sponsored Technical Education Quality Improvement Programme (TEQIP-II), Uttar Pradesh, for providing support for this study.

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