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Der Chemica Sinica, 2012, 3(3):576-581

Der Chemica Sinica
Pelagia Research Library
ISSN: 0976-8505
CODEN (USA) CSHIA5

Development of New Rate Model for the Adsorption of Direct Blue 86

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ABSTRACT

The present investigation had been focused on the insights of the theoretical aspects of pseudo-second-order kinetic equation which is typically used for a solid-liquid adsorption system. The basic principal of this developed kinetic equation was found to be in line with universal rate law. Based on this principal a pseudo-second order equation had been proposed for the adsorption of direct blue 86 on the microwave assisted carbon surface. The proposed rate equation could be used as an alternative of the universal rate equation which is quite complex in nature. The rate of adsorption was expressed in the form of a power law equation where the adsorption capacity (mg/g) was assumed to be a function of time (min). The values of various coefficients namely A, B, C and D used in the rate law expression were also determined at different initial concentrations (32 – 100 mg/l) and temperatures (13.5 – 35 °C). It was observed that the values of A remained almost constant with varying experimental conditions whereas, the values D was increased with increase in initial concentration but the values of C was decreased with increase in concentration. Besides, the values of B were increased with increase in temperature. The activation energy and frequency factor were also determined and the corresponding values were found to be 78.34 kJ/mol and 0.83 min^{-1}.

Keywords: Adsorption, Kinetics, Rate constant, Rate expression, Activation energy.

INTRODUCTION

Adsorption is one of the most widely used techniques for removal of various pollutants from waste water [1, 2]. In order to know the insights of the adsorption process the kinetic aspects should be studied in detail [3]. Expect the isotherm studies; the adsorption characteristics could also be well defined with the help of kinetic study as it gives the adsorption capacity of a given adsorbent with respect to time [4, 5]. The kinetic study also gives a fair idea about the time required for completion of an adsorption reaction i.e. the time required to reach to the pseudo steady state [6]. Therefore with the help of the adsorption kinetics experimental data could be successfully correlated at the solid/solution interfaces [7]. Several mathematical models have been proposed so far to describe adsorption characteristics such as adsorption reaction models and adsorption diffusion models. Both of these models have been applied successfully to predict the kinetic behavior of adsorption process [8]. The adsorption reaction model mainly depends upon the type of adsorbent and the time required for a given adsorption process to reach to its' completion whereas the diffusion models depends upon the various resistances exists across the liquid film surrounding the adsorbent particles and resistance offered by the adsorbent pore itself 9]. However, the adsorption reaction models originating from its theoretical aspects involve the use of many complex equations [10]. Therefore the use of these complex equations can be avoided by introducing some simple polynomial equations which are in line with the universal rate law [11]. This newly introduced rate law not only offers the simplified rate expressions but also describe the adsorption behavior very successfully. In most of the cases the integral form of these rate equations are applied and according to it the amount adsorbed is a linear function of time [12]. Such type of linear equations are already been studied for a wide variety of adsorption systems [13 -14]. But it is quite surprising to know that very little effort has been made to study the theoretical background of the pseudo-second order kinetic equation [15]. Azizian (2004) [16] has already studied the classical theory adsorption. Therefore in the present investigation a rate expression was developed based on the theoretical aspects of adsorption kinetics to predict the rate of adsorption of direct blue 86 onto the surface of microwave assisted activated carbon. In this rate expression the adsorption capacity was expressed as a function of time. The rate of adsorption was also determined at varying the initial concentrations and temperatures. The values of activation energy and the frequency factor were also calculated.

1. Theoretical aspects of pseudo second order kinetics

The pseudo second order kinetic equation which is used to describe the adsorption under non equilibrium conditions can be expressed in the following way: [17]

$$\frac{dq_t}{dt} = k(C_e - C_t)^2 \tag{1}$$

Where, q_t is the amount of adsorbate adsorbed at time *t*, C_e and C_t are the concentrations at equilibrium and at any time t (min). On the other hand, the instantaneous dye uptake capacity (mg/g) can be calculate by using the Eqn. (2)

$$q_t = \frac{(C_0 - C_t)}{m} V \tag{2}$$

Where C_0, m and V are the initial dye concentration (mg/l), amount of adsorbent required in g and the adsorbate volume (ml) taken for a particular adsorption reaction.

Now if we differentiate the Eqn. (2) with respect to time Eqn. (3) will be obtained:

$$\frac{dq_t}{dt} = \frac{V}{m}\frac{dC_t}{dt} \tag{3}$$

Therefore, $$\frac{dC_t}{dt} = \frac{m}{V}\frac{dq_t}{dt} \tag{4}$$

On the other hand, the rate expression can be written in the form of a polynomial equation where the concentration was expressed as a function of time t. Some assumptions had been made during the development of these polynomial expressions. They are as follows:

i) The initial adsorbate concentration was kept constant during a particular reaction.
ii) The order of the reaction was three.
iii) The reaction temperature was also kept constant during the course of a particular reaction

The polynomial rate equation correlating the instantaneous dye adsorption capacity (q_t, mg/g) and reaction time t (min) are as follows:

$$C_t = A + Bt + Ct^2 + Dt^3 \tag{5}$$

Differentiating Eqn. (5) with respect to time t give:

$$\frac{dC_t}{dt} = B + 2C + 3Dt^2 \tag{6}$$

Comparing Eqn. (4) and (6) we get Eqn. (7)

$$\frac{dq_t}{dt} = \frac{V}{m}(B + 2Ct + 3Dt^2) \tag{7}$$

Now if the rate of adsorption is denoted by $-r_{AD}$ then Eqn (7) can be written as

$$r_{AD} = -\frac{dq_t}{dt} = -\frac{V}{m}(B + 2Ct + 3Dt^2) \tag{8}$$

MATERIALS AND METHODS

3.1. Materials

The scrap wood of Acacia Auriculiformis was collected from local saw mill of Kharagpur. Direct blue-86 (DB-86), hydrochloric acid, sulphuric acid and ammonia were procured from Merck Specialities Private Limited, Mumbai, India.

3.2. Preparation of activated carbon

The wood scraps were first cut into small pieces of 2 mm width and 40 mm of length, cleaned with distilled water and was sun dried for 24 h prior to the carbonization process. The wood pieces were kept on a ceramic boat which was placed at the center of a 40-mm i.d tubular furnace. The material was then heated from ambient temperature to the carbonization temperature of 750 °C at the rate of 4 °C/min in a continuous flow of N_2 (300 ml/min) and then it was kept at this temperature for 1h for subsequent activation. The product was then allowed to cool to ambient temperature in presence of N_2 flow and sieved to obtain the desired size fractions. It was further stored in a desiccator over silica gel. The char was further activated in a domestic microoven (IF20PG3S) for five minutes at a constant input power of 800 W and a frequency of 2450 MHz. to enhance its surface properties [18].

RESULTS AND DISCUSSION

4.1. Prediction of kinetic parameters at different experimental conditions

The coefficients of the polynomial equation can be determined by using the polynomial fitting curve at various experimental conditions. For this purpose the initial dye concentration was varied from 32 – 100 mg/l whereas the temperature of the adsorption reaction was varied from 13 – 35 °C. The values of different parameters at varied initial concentrations and temperatures are shown in Table 1 and 2. It was seen from Table 1 that the values of parameter D was increased with increase in initial concentration whereas the values of C was decreased with increase in concentration. But the rate of increase of D was much higher than rate of decrease of C. As a result the total dye uptake capacity was increased with increase in initial concentration. As the initial concentration increase the difference between initial and instantaneous dye concentration increase which acts as a driving force for mass transfer and increases the dye adsorption capacity [19, 20]. The effect of temperature on the instantaneous dye uptake capacity is shown in Table 2. It was seen from Table 2 that with increase in temperature the value of temperature the values of B was increased. But the increase of this value was nullified by the values of C and D. Therefore the overall rate of reaction did not change so much. This type of behavior was also obtained by [21, 22].

Table1: values of different parameters at various initial concentrations

Concentration (mg/l)	A $\times 10^{-4}$	B	C	D
100	-1	0.0370	-2.94	93.48
80	-1	0.0323	-2.61	74.66
60	-1	0.0252	-1.94	55.71
40	-1	0.0177	-1.38	39.22
32	-1	0.0144	-1.08	29.42

Table 2: values of different parameters at various temperatures

Temperature (°C)	A $\times 10^{-4}$	B	C	D
35	-1	0.0370	-2.94	93.48
16	-1	0.0318	-2.52	94.25
13	-1	0.0283	-2.20	94.95

4.2. Prediction of rate of reaction at different conditions

The rate of adsorption reaction was determined at various temperatures and initial concentrations (Table 3 and Table 4). It was seen from Table 3 that initially the rate of reaction was increased very rapidly but as the time progressed it increased at a comparatively slower rate. This phenomenon may be ascribed to the fact that initially more active sites were available on the adsorbent surface but with the passage of time the active sites got saturated which retards the rate of adsorption [23].

Table 3: The rate of adsorption at different temperatures

Run	Concentrations (mg/l)	Rate of Adsorption (gmol/g-sec) ×10^3 13.5 °C	16 °C	35 °C
1	0	0	0	0
2	20	0.0024	0.0024	0.0023
3	40	0.0097	0.0097	0.0094
4	60	0.0219	0.0217	0.0213
5	80	0.0389	0.0386	0.0382
6	100	0.0608	0.0604	0.0598
7	120	0.0876	0.0869	0.0861

Table 4: The rate of reaction at various initial concentrations

Run	Concentrations (mg/l)	Rate of Adsorption (gmol/g-sec) ×10^3 32 (mg/l)	40 (mg/l)	60 (mg/l)	80 (mg/l)	100 (mg/l)
1	0	0	0.00	0.00	0.00	0.0
2	20	0.75	1.00	1.42	1.91	2.3
3	40	3.02	4.02	5.71	7.65	9.5
4	60	6.79	9.05	12.85	17.2	21.5
5	80	12.07	16.09	22.84	30.6	38.3
6	100	18.85	25.14	35.70	47.84	59.9
7	120	27.15	36.20	51.4	68.9	86.2

4.3. Development of rate equation at various experimental conditions

The rate equations generally expressed instantaneous dye adsorption capacity (q_t, mg/g) as a function of time t (min). The rate equation correlating q_t and t are given by Eqns. (10) - (15). Integrating Eqn (8) with respect time (t) Eqns (10) were obtained:

$$q_t = -\frac{V}{m}(Bt + Ct^2 + Dt^3) \qquad (9)$$

Now substituting the values of various parameters in Eqn (10) we obtained:
For 100 mg/l and 35 °C:

$$q_t = 0.037t - 2.94t^2 + 93.48t^3 \qquad (10)$$

For 80 mg/l:

$$q_t = 0.0323t - 2.61t^2 + 74.66t^3 \qquad (11)$$

For 60 mg/l:

$$q_t = 0.0252t - 1.94t^2 + 55.71t^3 \qquad (12)$$

For 40 mg/l:

$$q_t = 0.0177t - 1.38t^2 + 39.22t^3 \qquad (13)$$

For 32 mg/l:

$$q_t = 0.0144t - 1.08t^2 + 29.42t^3 \qquad (14)$$

For 16 °C:

$$q_t = 0.0318t - 2.52t^2 + 94.25t^3 \quad (15)$$

For 13 °C:

$$q_t = 0.0283t - 2.20t^2 + 94.95t^3 \quad (16)$$

4.4. Calculation of activation energy

The activation energy is the energy that must be overcome in order for a chemical reaction to occur [24]. Activation energy may also be defined as the minimum energy required to start a chemical reaction. The activation energy of a reaction is usually denoted by E_a, and given in units of kilojoules per mole. The activation energy can be expressed as:

$$k = Ae^{-E_a/RT} \quad (17)$$

Where, A is the frequency factor for the reaction, R is the universal gas constant, T is the temperature (in kelvins), and k is the reaction rate coefficient. While this equation suggests that the activation energy is dependent on temperature, in regimes in which the Arrhenius equation is valid this is cancelled by the temperature dependence of k. In the present investigation, the activation energy was calculated from the values of coefficients taken at different temperatures (286 - 308 K). The value of frequency was also calculated and these values are shown in Table 5.

Table 5: Values of the activation energy and frequency factor

Parameters	Values
Ea (kJ/mol)	78.34
A (min^{-1})	0.8298

CONCLUSION

The rate of adsorption reaction can be well described with the help of power law expression. The adsorption capacity was expressed as a function of time. The values of different coefficients were also determined by comparing the rate law expression with the conventional rate law. The adsorption reaction was assumed to be of third order. New rate equations were also developed by using the calculated values of various coefficients. The rate of adsorption in gmol/g-sec was also determined for varying initial concentrations (32 – 100 mg/l) and temperatures (13.5 – 35 °C). The basic principal of this developed kinetic equation was found to be in line with universal rate law. The values of activation energy and frequency factor were also calculated.

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