Chapter 3

KINETICS OF METHYLENE BLUE ADSORPTION ON TREATED COCONUT CAKE

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KINETICS OF METHYLENE BLUE ADSORPTION ON TREATED COCONUT CAKE

3.1 Introduction

Monitoring a process as function of time is very important since it could give several information regarding the states of the system at different intervals of time. For a chemical reaction the concentrations of reactants and products vary with time, and the extent of variation with respect to time (rate of change) depend upon several system parameters. The factors that affect the rate of chemical processes include concentration of various species involved in the process, temperature, hydrogen ion concentration (pH), ionic strength, presence of catalysts or inhibitors, etc. A proper perspective of the effect of different properties on the nature of the system at different intervals of time and how it affects the rates is essential for understanding the mechanism of the process and for developing mathematical relationships between the system parameters.

Adsorption processes can be considered as processes where the reactants are the adsorption sites on the surface of the adsorbent and the adsorbate particles in the fluid medium. The force of attraction created between them, either physical or chemical, results in a bond (attachment) forming the product. Adsorption is accompanied by desorption, and as time proceeds rates of adsorption and desorption become equal resulting
in adsorption equilibrium. The rate of adsorption at various intervals of time and the related observations are important for industrial and other applications. Removal of pollutants from water by adsorption on suitable solid adsorbents can be applied in water pollution treatment, and kinetic studies related with this are ultimate requirement for optimizing the process.

Treated coconut cake (cc) is a mixture of cellulose and protein. The wide spectrum of functional groups on the surface of these biopolymers permits them to function as good adsorbents for a range of pollutants from water. These functionalities will not have equal adsorption capacities since they have different electronic environments. And also the electronic cloud and the related electronic densities change with respect to the medium parameters. The amount and nature of adsorption occurring depend on the ‘active’ adsorption sites available on the surface, which is a function of different system parameters and time. Hence temporal studies are very important in optimizing the application of adsorption phenomenon in water treatment techniques and for understanding the mechanisms involved.

3.2 Kinetics in general

Chemical Kinetics deals with the rates of chemical reactions and with how the rates depend on factors like concentration, pH, temperature etc. Such studies are important in providing essential evidence to the mechanisms of chemical processes (Laidler, 1987). From the study of the rate of a reaction and its dependence on several system factors, much can
be learned about the detailed steps by which the reactants are converted to products (Castellan, 1995).

The reaction rates depend on the concentrations of reactants (and products) in characteristic ways that can be expressed in terms of differential equations known as rate laws. The mathematical solutions of these rate laws are used to predict the concentrations of species at any time after the start of the reaction. The form of the rate law also provides insight into the series of elementary steps by which a reaction take place. The key task is the construction of a mechanism and its comparison with experiment (Atkins and de Paula, 2002).

The basic data in kinetics is the concentrations of reactants and products at different periods after a reaction has started. The rates of most chemical reactions are sensitive to temperature and must be held constant through out the course of the reaction. The methods used to monitor concentrations depend on the species involved and the rapidity with which their concentrations change. Spectrophotometry, the measurement of absorption of radiation in a particular spectral region, is used when one substance in the reaction mixture has a strong characteristic absorption in a conveniently accessible region of the electromagnetic spectrum (Atkins and de Paula, 2002).

3.2.1 Rate law, order and rate constant

The rate of a reaction will be a function of temperature, pressure, the concentration of the various species in the reaction, and may depend on the concentrations of species like catalysts or inhibitors that may not
appear in the overall reaction (Castellan, 1995). The relationship between the rate and the concentrations is called rate laws. Rate laws must be determined from experimental measurements (McQuarrie and Simon, 2001). Reaction rates depend on the composition and the temperature of the reaction mixture. The rate of a reaction is often found to be proportional to the concentration of the reactants raised to a power. An equation that expresses the rate of a reaction as a function of the concentrations of all the species present in the overall chemical equation for the reaction at some time is called the rate law (Atkins and de Paula, 2002).

\[ v = f([A], [B], \ldots) \]

\( v \) – Rate of the reaction.

\([A], [B]\) - Concentration of the species involved.

Many reactions have rate law of the form

\[ v = k[A]^a[B]^b \ldots \]

The proportionality constant ‘k’ is called the reaction constant or the specific rate of the reaction. Thus the rate law is an equation that expresses the rate of reaction as a function of the concentrations of all the species present in the overall chemical equation for the reaction at some time. The rate constant is independent of the concentration but depends on the temperature (Atkins and de Paula, 2002). In general the rate constant depends on temperature and pressure (Castellan, 1995).
The power to which the concentration of a species is raised in a rate law is the order of the reaction with respect to that species. The overall order of the reaction is the sum of the individual orders. The order of the reaction governs the mathematical form of the rate law and therefore the variation in concentration of all the species with time. The order of the reaction with respect to the various species must be discovered from experiment and it is one of the first objectives of a kinetic investigation (Castellan, 1995).

The rate law is determined experimentally, and cannot in general be inferred from the chemical equation for the reaction. An application of the rate law is that, from the law and the rate constant, one can predict the rate of reaction from the composition of the mixture at a later stage of the reaction. A rate law is also a guide to the mechanism of the reaction, because any proposed mechanism must be consistent with the observed rate law (Atkins and de Paula, 2002). For most chemical reactions, rate is related to the concentration of the various chemical species present in the system at that time.

3.2.2 Determination of rate laws and the related constants

In chemical kinetics one has to determine how rates depend on the concentrations of reacting substances. The rate law of a reaction can be determined from the concentrations of the reactants either by the differential method and or by the method of integration (Laidler, 1987).
1. **Differential method**

The differential method was first suggested by van’t Hoff. In this method, the rates \( v \) of chemical processes can be determined directly by measuring the slopes of concentration \( C \)–time \( t \) curves (van’t Hoff, 1884). If the reaction has an order ‘n’ with respect to a particular reactant,

\[
v = k C^n
\]

or

\[
\log v = \log k + n \log C
\]

\( v \) - Rate of the reaction

\( C \) - Concentration of the reactant at time ‘t’

\( k \) - Rate constant

\( n \) - Order of the reaction

A double logarithmic plot of ‘\( \log v \)’ versus ‘\( \log C \)’ gives a straight line of slope ‘n’. The y–intercept will be ‘\( \log k \)’.

The differential procedure can be done in two different ways. In one of them, experiments are carried out at different initial concentrations of the reactant, and initial rates are determined by measuring initial slopes. A double logarithmic plot of initial concentrations and rates is developed, from which the order and rate constant are determined. The order determined in this way is called the order with respect to concentration or true order \( (n_c) \). The method of initial rates might not reveal the full rate law, for the products may participate in the reaction.
and affect the rate (Atkins and de Paula, 2002). In the second method, the slopes of the time-concentration curve of a single experiment is determined at various concentrations of the reactant to get the rate of the reaction at different intervals of time. From the double logarithmic plot of rate and concentration, the order and rate constant can be determined. The order determined thus is called the order with respect to time \( (n_t) \). The two orders are not always the same for a given reaction (Laidler, 1987).

2. The method of integration

The kinetic data can be analyzed using integrated rate laws. The method of integration involves first making a tentative decision as to what the order of the reaction might be. The differential equation corresponding to that order is integrated, resulting in an expression for concentration as a function of time. The experimental time-concentration data is introduced into the expression to see whether it fit for the same. If not, other expressions with other orders is tested till the data fit, and from the characteristics of the graph rate constant is determined (Laidler, 1987).

3.2.3 Comparison of methods

The differential method is the most reliable one for investigating a reaction for which there is no previous information. The main reason is that it does not require a tentative decision as to what the order should be. Instead, it directly determines how the rate depends on concentration. The second reason is that it distinguishes clearly between the two orders of the reaction i.e. order with respect to concentration and time, \( n_c \) and \( n_t \). This distinction is helpful in understanding the influence of products on the rates. The method of integration is useful in getting accurate rate
constants when the order of a reaction is well established. Otherwise it has defects. It creates prejudice in favor of integral and half-integral orders, and deviations from such orders might escape notice. The inhibition of reaction by products is better understood by the differential method. The analysis of a given experimental data provides $n_e$, the order with respect to time. The rate constant for different reactant concentrations will be the same only if $n_c$ equals $n_t$. W. Lash Miller referred to the method of integration as “the method of guess and try” while the differential method he called as the “method of systematic exploration” (Laidler, 1987).

### 3.3 Kinetics of adsorption processes

Removal of pollutants from water by adsorption on suitable adsorbents is an effective technique being practiced for centuries. Presently the variety and percentage of pollutants in our water systems are large, and hence removal techniques like adsorption should be practiced in the most scientific pattern in so far as possible. Studies related with the adsorption of pollutants as a function of time is essential for effective implementation.

Adsorption technique in water treatment involves the removal of pollutants from water by attaching them to the surface of solid adsorbents. The particles are attached to the surface of solids by physical or chemical forces (Mee and Speakman, 1962). The time dependence of the adsorption processes are important like the features of the system at equilibrium (Rudzinski and Panczyk, 2002). Understanding the time dependence of adsorption (kinetics) is important in designing treatment systems and plants (Vadivelan and Kumar, 2005). It will give information
regarding the changes one has to make in the system conditions so as to maximize the degree of adsorption. The study of adsorption dynamics describes the solute uptake rate and evidently this rate controls the residence time of adsorbate uptake at the solid-solution interface (Demirbas et al., 2004). The kinetics of the adsorbed process strongly influence the saturation or steady state of the adsorbed layer since the state of an adsorbed layer at a given time depends on its history (Michelle and Paul, 1999). The study of sorption kinetics in waste water treatment is significant as it provides valuable insights into the reaction pathways and into the mechanism of sorption processes (Ho and McKay, 1999; Yalcin et al., 2004). There are several factors, which determine the kinetics of adsorption. Knowledge of rate is a primary requirement for developing the rate law. The rate law is to be determined by experimentation and it cannot be inferred by examination of the chemical reaction (Ho and McKay, 1999). The rate at which the particles are attached to the surface may depend on factors like the number of vacant active adsorbent sites on the surface, concentration of the pollutant in the medium, pH of the medium (Karthikeyan et al., 2004), temperature (Ho, 2005) etc. Different investigators have used several integral models to examine the experimental results. It includes pseudo first order model, pseudo second order model, Elnovich equation, intermolecular diffusion model etc.

Adsorption Kinetics deals with the rate at which the sorption occurs, where the rate is defined as the change of a given quantity over specific period of time. After a period of time the sorption is reversible when enough sorbate had been sorbed and desorption will become active. At this point, the concentration of the sorbate depends on the rate
differences between the sorption and desorption reactions. If one neglects the desorption reaction the rate will depend only on the concentration of the adsorbate (Ho, 2004). The progress of adsorption can be followed by measuring the decrease in concentration of adsorption sites or by measuring the concentration of the adsorbate remaining in the mixture. It is practically difficult to measure the vacant adsorption sites and hence experimentalists are interested in measuring the decrease in concentration of the adsorbate to follow the process. The concentration of adsorbate can be monitored by titrimetric, gravimetric, spectrophotometric or some other analytical methods depending on the nature of the adsorbate. The data obtained can be utilized to test the authority of different models. These fundamental data will be useful for further applications in the treatment of practical waste or to process effluents (Ozacar, 2003).

3.3.1 Models in adsorption kinetics

Mathematical models are frequently used in scientific studies to test the suitability of experimental data. These models are equations relating the parameters of the system. These equations are derived on the basis of certain assumptions and the fitness of the data is an evidence for the validity of these assumptions. Presently there are different theoretical models for describing how chemical reactions occur. None is perfect, but each has its merits. Several of them provide a microscopic picture of how chemical reaction takes place (McQuarrie and Simon, 2001). To examine the mechanism of adsorption process such as mass transfer and chemical reaction, a suitable kinetic model is needed to analyze the rate data (Ozacar, 2003).
Kinetics of Methylene Blue Adsorption on Treated Coconut Cake

In kinetic studies, time and the concentration of reactants (or products) at different intervals of time are the experimental parameters. In adsorption systems the adsorbate concentration \( (C_t) \) data is used to calculate the extent of adsorption \( (x_t, \text{mg/g}) \) and these parameters are tested in different kinetic models. Adsorption of materials on solids can be considered as chemical reactions where some sort of bond is formed between the surface functionalities (adsorbent sites) and the adsorbate.

### 3.3.1.1 Experimental data in kinetics

Adsorption is a process in which the surface of the adsorbent is being covered by adsorbate particles by some kind of attraction. The attraction arises due to the residual forces on the surface, and the surface functional groups are responsible for the adsorption capability of coconut cake. The amounts of adsorbate that can be attached to the surface depend on the net surface force created when the adsorbent is in a fluid medium. For a specific adsorbent the residual surface force created may vary depending on the system conditions, since the medium conditions could alter the characteristics of the functional groups. Though many functional groups have the theoretical possibility for being an adsorption site, it need not function so due to several system limitations. The amount of adsorbate attached to the surface at a particular instant of time is a measure of the adsorption sites occupied at that time. The amount of adsorbate attached at equilibrium will be a measure of the maximum adsorption sites occupied in the given set of medium parameters. This amount can thus be taken as equivalent to the maximum adsorption sites available initially (at \( t = 0 \)) on the adsorbent in the specified system conditions.
The basic data in adsorption kinetics is the amount of the adsorbate remaining in the system at different intervals of time ($C_t$, mg/L). Knowing the initial concentration ($C_0$) of the adsorbate one can calculate the amount of adsorbate adsorbed at different intervals of time ($b$, mg). In adsorption study systems, the initial adsorbate concentration, adsorbent dose, pH, temperature etc. are frequently changed to optimize adsorption efficiencies, and hence the amount of adsorbate adsorbed per gram of the adsorbent at any time ‘t’ ($x_t$, mg/g or moles/g) is often calculated to standardize the results. The amount of adsorbate adsorbed at equilibrium (mg/g) varies from system to system and is termed ‘$x_e$’. The term ‘$x_e$’ is equivalent to the number of maximum adsorption sites becoming active on the adsorbent in the given system condition. ‘$x_i$’ represents the number of sites used at any time ‘t’. Thus ‘$x_e$’ may be considered as the maximum ‘active’ adsorption sites available on the adsorbent in the given set of conditions, and ($x_e-x_i$) as the ‘active’ adsorption sites vacant on the surface at time ‘t’. The kinetics of adsorption processes can be developed by studying the decrease in concentrations of active adsorption sites remaining on the adsorbent ($x_e-x_i$) as a function of time (t).

### 3.3.1.2 Lagergren pseudo first order model

A kinetic process in which the rate is proportional to the first power of a concentration term is called a first order reaction. The model developed by Lagergren is based on the solid capacity to adsorb particles (Ho and McKay, 1999). In Lagergren’s model the rate of adsorption, $\frac{dx}{dt}$, is assumed to be proportional to the first power of number of active sites vacant on the surface at time ‘t’. 

\[
\frac{dx_t}{dt} \propto (x_e - x_t) \tag{1}
\]

\(x_t\) – amount of adsorbate adsorbed at time ‘t’ (mg/g). \(\sim\) number of active sites occupied at time ‘t’.

\(x_e\) - amount of adsorbate adsorbed at equilibrium (mg/g). \(\sim\) total number of active sites on the surface.

\((x_e - x_t)\) - represents the total number of vacant active sites at ‘t’.

\[
\frac{dx_t}{dt} = k_L(x_e - x_t) \tag{2}
\]

\(k_L\) - First order rate constant (min\(^{-1}\)).

Integration of equation within limits and subsequent rearrangements give

\[
\log(x_e - x_t) = \log x_e - \frac{k_L t}{2.303} \tag{3}
\]

\[
(x_e - x_t) = x_e e^{k_L t} \tag{4}
\]

Plot of ‘\(\log (x_e - x_t)\)’ against ‘t’ will give a straight line if the adsorption process is first order with respect to the vacant active adsorption sites remaining on the surface of the adsorbent in the process of adsorption. The rate constant can be calculated from the slope, and the ‘y’ intercept will give the logarithm of theoretical equilibrium adsorption capability (mg/g, total active adsorption sites). Lagergren’s model is a first order
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integral model. Equation (4) shows that in a first order reaction the reactant concentration decreases exponentially with time with a rate determined by ‘kL’ (Atkins and de Paula, 2002).

When the adsorption process is following first order kinetics, the amount of adsorbate adsorbed at any instant of time (x_t, mg/g) can be determined using the relation ship,

$$x_t = x_e + x_e e^{-k_Lt}$$  \( (4) \)

3.3.1.3 Ho pseudo second order model

Second Order reactions are those in which the rates are proportional to the product of two equal concentrations or two different concentrations of reactants (Laidler, 1987). Ho and McKay (1999) developed an integrated kinetic equation based on the assumption that the rate of adsorption (dx/dt) is proportional to the second power of the vacant adsorption sites on the adsorbent.

$$\frac{dx_t}{dt} \propto (x_e-x_t)^2$$  \( (5) \)

$$\frac{dx_t}{dt} = k_H(x_e-x_t)^2$$  \( (6) \)

k_H - second order rate constant, L mol^{-1} min^{-1} (Laidler, 1987)

Integration of equation (6) followed by subsequent rearrangements give
\[
\frac{1}{(x_e-x_t)} = \frac{1}{x_e} + k_Ht
\]  

To test for a second order process one should plot \(1/(x_e-x_t)\) against \(t\) and expect a straight line. The slope of the graph will be the second order rate constant and the ‘y’ intercept is the reciprocal of the equilibrium adsorption.

### 3.4 Adsorption Kinetics- A Review

The Lagergren empirical equation proposed at the end of 19\(^{th}\) century to describe the kinetics of solute sorption at the solid/solution interfaces has been the most widely used kinetic equation until now. This equation has also been called the pseudo-first order kinetic equation because it was intuitively associated with the model of one-site occupancy adsorption kinetics governed by the rate of surface reaction. More recently, its generalization for the two-sites-occupancy adsorption was proposed and called the pseudo-second-order kinetic equation. However, the general use and the wide applicability of these empirical equations during more than one century have not resulted in a corresponding fundamental search for their theoretical origin. The first theoretical development of these equations is based on applying the new fundamental approach to kinetics of interfacial transport called the Statistical Rate Theory. It is shown that these empirical equations are simplified forms of a more general equation developed, when the adsorption kinetics is governed by the rate of surface reactions. The features of that general equation are shown by presenting exhaustive model investigations, and the applicability of that equation is tested by presenting a quantitative
analysis of some experimental data reported in the literature (Rudzinski and Plazinski, 2006).

The adsorption kinetics studies for a variety of adsorbates on a range of adsorbents can be found in the literature. It includes adsorption of several organic compounds like dyes, metallic ions etc. on a range of adsorbents like carbon from different sources, biomaterials etc. (Ho, 2005; Ho and Ofomaja, 2005; Ho and Ofomaja, 2006). Demirbas et al., (2004) found that the adsorption of Cr\textsuperscript{VI} on carbon prepared from agricultural wastes is following second order kinetics. Raghuvanshi et al., (2004) studied the adsorption kinetics of methylene blue on bagasse and found that there is an initial rise in rate of adsorption probably due to greater driving force. The diffusivity measurements (Chiang et al., 2002) in the adsorption of hydrogen sulphide on activated carbon showed that pore diffusion controlled the adsorption. The removal of orange G and acid green 25 by chitosan conjugated magnetic nano adsorbent is found to be following pseudo second order kinetics and found that the time required to reach equilibrium is relatively shorter due to large surface area (Yang - Chuang, 2005). In an attempt to study the (Ozacar, 2003) suitability of the first and second order equations and intra particle diffusion model, it is observed that the adsorption of phosphorous on calcined alunite is following intra particle diffusion in the early stages of adsorption. The phosphorous is slowly transported in to the particles and retained in the micro pores. For different initial concentrations of phosphorous, the data agrees with pseudo second order model. Carmo et al., (2004) found that the rate of adsorption of alcohol on starchy materials is dependant on temperature and length of the molecular chain of the
alcohol. The adsorption kinetic data of cetyl trimethyl ammonium bromide on powdered active carbon has been fitted to first order, second order and intra particle diffusion models. The data show that intra particle diffusion as well as boundary diffusion is playing significant role in the rate-controlling step. The adsorption process is following first order kinetics (Yalcin, 2004). A study conducted by Chiou et al., (2003) on the adsorption of certain acid dyes on chemically cross linked chitosan found that the data is not fitting the first order equation of Lagergren in the whole range of contact time and is generally applicable over the initial stage of the adsorption processes (Ho and McKay, 1999). The second order equation could predict the behavior over the whole range of adsorption and a chemisorption mechanism was assumed to be the rate-determining step (McKay and Ho, 1999). The rate constants for the second order model are found to be decreasing with increasing dye concentration (Chiou, 2003). The second order model was applied to the adsorption of lead on to palm kernel fiber (Ho and Ofomaja, 2006) to predict the rate constant and equilibrium capacity at different initial solution pH and fiber capacity. In another adsorption study using palm kernel fiber, Ho and Ofomaja (2005) found that intra particle diffusion is significant at low concentrations of lead. Adsorption of copper on palm kernel fiber is (Ho and Ofomaja, 2006) found to be obeying second order kinetics. Hameed et al., (2006) found that the adsorption of methylene blue on bamboo-based carbon is following second order kinetics. Agarwal et al., (2006) observed that the removal of Cr$^{VI}$ on certain seeds is following first order kinetics. Biosorption of Direct Yellow 12 from aqueous solution using green alga, Ulva lactuca, is consistent with the second order equation having high correlation coefficient. The adsorption
of lead on activated carbon from coconut and seed hull of palm tree is following first order kinetics with correlation coefficient greater than 0.97. The kinetic constants are varying in a random way and independently of the initial concentration verifying first order kinetics. The first order rate constants are found to be increasing as the temperature is increased, and there is a linear relationship between the rate constant and the temperature (Gueu et al., 2007). The first order rate constant is a measure of the rapidness of adsorption (Mathialagan, 2003). Removal of textile dyes by a fibrous biomass, Posidonia oceanica, followed first order kinetics in the initial period of adsorption while second order kinetics in the whole period (Ncibi et al., 2007). The adsorption of chromate on goethite is observed to be rapid and the rate of adsorption decreased with an increase in pH. The decrease is explained in terms of the formation of oxyanion molecule. In contrast to chromate, silicilic acid adsorption was characterized by biphasic kinetics. i.e. a rapid adsorption followed by a slower one. Silicic acid surface catalyzed polymerization on the ferric oxide surface may be responsible for the slow adsorption reaction. Biphasic kinetics have been observed for phosphate and several other metal cations and have been attributed to many processes including surface precipitation, intra and inter particle diffusion and change in the type of surface complex (Garman et al., 2004). A study on the adsorption of Zn (11) on chitosan showed that intraparticle diffusion constant is maximum for smaller particle size and high dose of the adsorbent (Karthikeyan, et al., 2004). Differential methods are used in chemical kinetic studies by Leal and Domingo (1990). The important parameters that govern the rate and extent of adsorption are the size of adsorbent particles, amount of adsorbent particles, chemical nature of adsorbate in
the aqueous system, concentration of the solution, temperature of the system, hydrogen ion concentration (pH) (Castellan, 1995) and so on.

3.5 Objectives of the Study

Treated coconut cake is a good adsorbent for the removal of methylene blue from aqueous solutions. The extent of adsorption is a function of several factors like pH, salt concentration, amount of adsorbent dose, temperature etc. The variation in adsorption capability with regard to the system parameters is primarily due to the modifications that occur on the adsorbent surface as well as the changes that occur for the states of the adsorbate in the medium. Studies related to the extent of adsorption as a function of time till equilibrium is reached is important since it can give much information regarding the rate of the process, order of the reaction, rate constants, diffusion constants etc. These parameters along with the related information help one to develop adsorption mechanisms and mathematical models. These studies are important for implementing the process when treatment systems are designed. The studies on the advancement of a reaction with respect to time are generally termed as chemical kinetics.

The kinetics of methylene blue adsorption on coconut cake has been studied with respect to three system parameters. The system parameters that have been changed in the present study are adsorbent dose, hydrogen ion concentration (pH), and the system temperature. Kinetic studies related to pH changes and temperature changes are significant since they are two important environmental parameters that
often vary in natural aquatic systems. Studies related to adsorbent doses are important since they are important in treatment design and techniques.

In this part of the work effort is made to analyze and interpret the observations related to the adsorption of methylene blue on coconut cake as a function of time,

1. By changing the adsorbent dose keeping the initial concentration of methylene blue and other parameters constant.

2. By changing the pH of the medium keeping adsorbent dose, adsorbate concentration and other parameters constant.

3. By changing the temperature of the medium keeping all other parameters constant.

3.6 Materials and Methods

3.6.1 Materials

**Adsorbent:** Treated coconut cake is powdered and sieved to get particle having size between 100 and 120 ASTM. This is used for the entire study.

**Adsorbate:** Methylene blue crystals (BDH) are recrystallised from acetone and dried at $110^\circ$ C (Kaewprasit *et al.*, 1998). 1000 mg is dissolved in 1000 ml of double distilled water to get the stock solution. The stock solution is diluted as per requirement using double distilled water.
3.6.2 Method

Kinetics of any process deals with rate of that process. The rate of a process can be followed by measuring the concentrations of the reactants or products as a function of time. In the adsorption phenomenon, the concentration of the adsorbate decreases with time while the fraction of active adsorption sites used for adsorption increases. The kinetics of methylene blue adsorption on treated coconut cake can be followed by measuring the decrease in concentration of methylene blue in the medium or the active adsorption sites on the adsorbent. It is practically difficult to follow the decrease in concentration of adsorption sites directly and hence the decrease in the concentration of methylene blue is followed spectrophotometrically by measuring the absorbance at 665 nm, which corresponds to the absorption maximum of methylene blue monomer (Bergman and O’Konski, 1963). The number of active sites on a specific amount of adsorbent used for adsorption will be proportional to the amount of methylene blue adsorbed at that time.

A definite volume (100 ml) of the adsorbate solution is stirred at constant speed with the required amount of the adsorbent in a 500 ml beaker on a magnetic stirrer at constant speed. The absorbance of the solution is measured initially and at different time intervals. 1 ml of adsorbate is pipetted out of the system for the purpose and diluted as required and the absorbance is measured at 665 nm using Genesys UV-Visible spectrophotometer. The absorbance data at different time intervals are used to generate the data required for kinetic analysis. The experiments are conducted separately by changing the mass of coconut cake (adsorbent dose), by varying the pH and at different temperatures.
For all the studies methylene blue solution having initial concentration 50 mg/L is used. For all the studies other than pH based studies, pH is kept at 6.5 +/- 0.3. The pH is changed using 0.1 N HCl (BDH) solutions or 0.1 N NaOH (BDH) solution prepared in double distilled water. The pH is measured using Systronics pH meter. In all studies other than temperature-based studies, temperature is kept at 28° C +/- 1° C. For the temperature-based studies, temperature is changed using the thermostat of the magnetic stirrer. For all studies other than adsorbent based studies, about 200 mg of adsorbent is used.

3.6.3 Data analysis

The kinetics of adsorption has been followed by measuring the absorbance of methylene blue in the closed batch adsorption system as a function of time. From the absorbance of the solution, concentration of the methylene blue remaining in the solution at different time intervals \(C_t\) mg/L) are calculated applying the Beer- Lambert's Law (Williams and Fleming. 2004) and the amount of methylene blue adsorbed \((C_0 - C_t\), mg/L) is determined. The mass of methylene blue adsorbed per gram of coconut cake at time 't', \(x_t\) (mg/g), is calculated using the formula, \(x_t = \frac{(C_0 - C_t) V}{m}\), where 'V' is the volume of the solution in liters and ‘m’ is the mass of the adsorbent in grams(Cooney, 1999). \(x_e\) is the mass of methylene blue adsorbed per gram of coconut cake at equilibrium. In a given adsorption system the extent of adsorption will be maximum at equilibrium, and hence ‘\(x_e\)’ is proportional to the maximum ‘active’ adsorption sites on the adsorbent in that system conditions. The term ‘active’ refers to those sites on the adsorbent (coconut cake) capable of adsorbing the adsorbate (methylene blue cations) with respect to the
parameters of the system. Hence, ‘$x_e - x_0 = x_e$’, where ‘$x_0$’ is ‘$x_i$’ at $t = 0$, is a measure equivalent to the maximum adsorption sites available on one gram of the adsorbent in the system conditions. Though the actual number of possible adsorption sites is larger than this, it can be taken as a measure of the initial adsorption sites available on the adsorbent in the provided set of experimental conditions. Then ‘$(x_e - x_i)$’ will be proportional to the vacant adsorption sites at time ‘$t$’. These data are used to develop the various kinetic aspects.

The rate of adsorption (v) at each instant of time is the rate of disappearance of the active adsorption sites. This is determined by differentiating the active adsorption sites $(x_e - x_i)$ vs. time (t) data. For that ‘$x_e - x_i$’ vs. ‘$t$’ data is plotted and the graph is differentiated to get the slope. The slope at each instant of time is the rate of disappearance of the active adsorption sites which is equivalent to the rate of adsorption. From the rates and the corresponding concentrations, order and rate constants are determined using the differential method (Section 3.2.2). The experimental data is also used to test the suitability of the integrated first order and second order equations (Section 3.3.1).

3.7 Results and Discussion

3.7.1 Adsorption kinetics on changing the adsorbent dose

Adsorbent dose refers to the mass of adsorbent added to an adsorption system. A given mass of adsorbent with specific particle size will have a definite number of ‘possible’ adsorption sites. In the case of treated coconut cake, the adsorption sites are the functional groups and linkages on
cellulose and protein. Though increase in adsorbent dose results in proportionate increase in possible adsorption sites, the extent of adsorption need not have that trend. This is because the number of adsorbent sites becoming ‘active’ is significant and studies related to the concentration of active adsorption sites with respect to time are important.

Effort is made to study the kinetics of adsorption, keeping the adsorbate concentration constant at 50 mg/L but changing the mass of the adsorbent (adsorbent dose) added. All other system parameters like pH, temperature, shaking speed, size of the adsorbent etc. are kept constant. Experiments are carried out for adsorbent masses of 50 mg, 100 mg, 200 mg and 500 mg using 100 ml of the adsorbate solution prepared in distilled water.

### 3.7.1.1 Methylene blue adsorption as a function of time - Preliminary observations

The absorbance of methylene blue solutions are converted to the concentration (\(C, \text{ mg/L}\)) and from that methylene blue adsorbed is determined (\(b = C_0 - C_t\)). The graph representing the amount of methylene blue adsorbed (\(b, \text{ mg/L}\)) on different doses of coconut cake as a function of time is given in Fig. 3.1.

From the graph we understand that the amount of methylene blue adsorbed increases as the adsorbent dose is increased at all intervals of time, though not proportional. This is due to the fact that the number of adsorption sites (functional groups on the biopolymers) is directly proportional to the
Fig. 3.1 Mass of methylene blue adsorbed vs time for different adsorbent doses

adsorbent dose and hence more particles from the medium could attach to the surface as the dose is increased. In all cases, the major part of adsorption occurs in the initial stages as evident from the steep and straight part of the graph. The steepness of the initial part is larger for 500 mg and least for 50 mg. The time required for this initial instantaneous adsorption increases as the adsorbent dose is decreased. The initial rapid adsorption appears to be due to the surface process caused by the rapid diffusion of the dye from the bulk of the solution to the surface of the adsorbent (Karthikeyan et al., 2004). Initially the flow of dye cations towards the potential functional groups on the surface of the adsorbent is strong, may be due to high chemical affinity prevailing between the
vacant sites and the dye cations. As the more potent functional groups are occupied, the process becomes slow. Thus after the initial strong adsorption the systems slowly approach an equilibrium state.

The equilibration time decreases as the dose is increased. Since the numbers of adsorbate particles in all systems are constant (same solution concentration), the probability for these particles coming close to the adsorption sites is large as the adsorbent dose is increased. Hence more particles from the system will attach to the surface and attain equilibrium in a short time, as the dose is increased.

The amount of methylene blue adsorbed at equilibrium increases as the dose is increased. This is due to the proportionate increase in functional groups as the dose is increased, which allows more number of dye particles to get attached on the surface. But we can see that this increase in adsorption is not proportional to the adsorbent dose, which implies that mere increase in adsorbent dose alone will not produce proportionate increase in efficiency.

3.7.1.2 Active adsorption sites per gram of the adsorbent

To compare the efficiencies and to determine several parameters of adsorption processes it is convenient and conventional to express the amount of adsorbate adsorbed per gram of the adsorbent (x, mg/g). The graph showing the amount of methylene blue adsorbed per gram of coconut cake (xₜ, mg/gm) as a function of time is given in Fig. 3.2.
Fig. 3.2 Amount of methylene blue adsorbed (mg) per gram of coconut cake ($x_t$) at different time intervals for different adsorbent doses

It gives us an idea about the fraction (or percentage) of the total available adsorption sites that become ‘active’ under the given system conditions. It is observed that the amount of methylene blue ‘adsorbed per gram ($x_t$)’ at each instant of time is large when the adsorbent dose is less. This observation shows that, the fraction of sites (active sites per gram of adsorbent) on which the adsorbate is adsorbed increases as the adsorbent dose is decreased. Treated coconut cake is a mixture of cellulose and protein and it has several different functional groups on its surface. All these functional groups need not be equally efficient or ‘active’ under all conditions. In the present study systems, the number of adsorbate particles attacking the surface is kept constant (constant adsorbate concentration)
while the adsorbent dose is varied (or the available functional groups). When the adsorbent dose is low, the ratio of methylene blue cations in the medium to the total probable adsorption sites is large, and hence the frequency of particles approaching a particular site will be large. Thus the adsorbate could exert more ‘solution pressure’ on the adsorbent surface and this enhanced particle ‘pressure’ from the solution side results in the ‘activation’ of more sites. Therefore, at low adsorbent doses, though the total number of sites is comparatively low the fraction of sites covered is more. As the adsorbent dose is increased the ‘effective less solution pressure’ could ‘activate’ only lesser number of adsorption sites. The term ‘active’ refers to those functional groups or sites that are capable of adsorbing particles among the total sites in the given system conditions. As the dose is increased, though the number of probable sites is increasing, the density of particles approaching unit area is decreasing and hence the number of sites capable of adsorption (active) decreases.

The amount of methylene blue adsorbed per gram of coconut cake at equilibrium ($x_e$, mg/g) is a measure of maximum adsorption efficiency of the adsorbent in the given system conditions. The graph showing the equilibrium efficiency against adsorbent dose is given in Fig. 3.3. The amount adsorbed per gram is larger when the dose is less since the fraction of active sites is large at low doses, when the adsorbate concentrations are same.
Fig. 3.3 Amount of adsorbate adsorbed at equilibrium vs adsorbent dose

3.7.1.3 Rate of adsorption

The adsorption process can be represented by the following equation,

\[ A \rightarrow S \rightarrow AS \]

where ‘A’ is the adsorbate, ‘S’ is an active vacant site on the adsorbent, and ‘AS’ represents an adsorbed molecule of ‘A’ or an occupied site on the surface. ‘A’ and ‘S’ can be considered as the reactant species in the adsorption process. The amount of methylene blue adsorbed (in mg/g) at equilibrium \( x_e \) is a measure of (or equivalent to) the total initial active adsorption sites per gram of the adsorbent. The concentration of the active adsorption sites \( x_e - x_t \) (mg/g) at any time ‘t’ decrease as time proceed.
The plots of active adsorption sites ‘$x_e - x_t$’ per gram of coconut cake at different time intervals are given in Fig. 3.4.

**Fig. 3.4.** The active adsorption sites at different intervals of time for different adsorbent doses.

The figure shows that ‘$x_e - x_t$’, which is equivalent to the number of active sites per gram of the adsorbent at a particular time, decreases as the adsorbent dose is increased. This shows that the fraction of active adsorption sites is larger for small doses provided the concentration is kept constant.

The rates of adsorption processes at different intervals of time are important in developing the kinetic concepts. The instantaneous rate of chemical reactions can be determined by measuring the slope of the
Kinetics of Methylene Blue Adsorption on Treated Coconut Cake

concentration time - curve (Laidler, 1987). The rate of decrease in adsorption sites per gram \( \frac{d(x_e-x_i)}{dt}, \text{mg/g/min} \) of the adsorbent is obtained by differentiating the concentration of active adsorption sites \( (x_e - x_i) \) – time \( t \) data in Fig. 3.4. The rate of decrease of adsorption sites will be comparative to the rate of adsorption. The rate of decrease of adsorption site (or the rate at which the active adsorbent sites per gram are being occupied by the methylene blue) is given in Fig. 3.5. The initial rate with respect to the occupancy of the active adsorption sites for different adsorbent doses is given in Table. 3.1.

![Graph showing rate of adsorption at different intervals of time for different adsorbent doses](image)

**Fig. 3.5**  Rate of adsorption at different intervals of time for different adsorbent doses
Table 3.1 Initial rates of adsorption for different adsorbent doses (initial adsorbate concentration: 50 mg/L)

<table>
<thead>
<tr>
<th>Mass of the Adsorbent, (g)</th>
<th>Initial Active Adsorption Sites $x_e$, (mg/g)</th>
<th>Initial Rate of Adsorption, $v_0$, (mg/g/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>35.67</td>
<td>5.405</td>
</tr>
<tr>
<td>100</td>
<td>19.3</td>
<td>2.9042</td>
</tr>
<tr>
<td>200</td>
<td>16.2</td>
<td>2.5079</td>
</tr>
<tr>
<td>500</td>
<td>7.01</td>
<td>1.3825</td>
</tr>
</tbody>
</table>

The rate data show that the rate at which active sites are used (mg/g/min) is maximum for 50 mg and minimum for 500 mg. This trend is observed at all time intervals. The reason for this observation may be given in terms of the large fraction of active sites present on unit mass of the adsorbent for low adsorbent doses. The high initial rate in all cases may be due to the large chemical affinity between the comparatively large numbers of adsorbate particles and active adsorbent sites initially present, which causes a rapid flow of the adsorbate particles towards the surface resulting in fast adsorption. As time advances the flow towards the surface decreases since the fraction of vacant active sites comes down resulting in decreased rate of adsorption.

An interesting observation is that there is a linear relationship between the initial active adsorption sites (mg/g) and the initial rate (mg/g/min) with respect to active adsorption sites (Fig. 3.6) with a correlation coefficient of 0.99902. This shows that the initial adsorption
rate is a direct function of the initial active sites available on the adsorbent under the given system conditions. The corresponding relationship can be given as, Initial rate = $0.1356 \times \text{Initial active sites} + 0.3541$, for the studied adsorbent dose range.

![Graph showing initial adsorption rate as a function of initial active adsorption sites.]

**Fig. 3.6** Initial adsorption rate as a function of initial active adsorption sites

### 3.7.1.4 Order of adsorption

The order of adsorption is the sum of the powers to which the concentration terms in the rate equations are raised. The order of the reaction gives us information regarding the dependence of rate on the concentration of different reactant species present in the system. The order of the reaction is determined by analysing the concentration-time
data of kinetic experiments by proper methods. The order can be determined by differential methods and integral methods.

### 3.7.1.4.1 Differential method to determine order

The differential method is based on the relationship,

\[
\text{Rate} = k \times (\text{concentration})^n,
\]

where ‘k’ is the rate constant and ‘n’ is the order of the process. The concentration of the active adsorption sites \((x_e-x_t)\) and the rate of decrease of adsorption sites \((v = d (x_e-x_t)/dt)\) determined in the previous section are used to determine the order of adsorption. The order with respect to concentration \((n_c)\) can be determined by using the initial rate and initial concentration of active adsorbent sites for different adsorbent doses. The order with respect to time \((n_t)\) can be determined separately for each experiment using the rate and concentration of vacant adsorption sites at different intervals of time.

The order with respect to concentration or true order \((n_c)\) is determined by plotting the logarithm of the initial concentration of active adsorption sites \((\log x_e)\) against the logarithm of the initial rates \((\log v_0)\), (Fig. 3.7) (Laidler, 1987).

The rate equation will have the form:

\[
\log v_0 = \log k + n_c \log x_e
\]

Hence the slope of the curve is the true order and the y-intercept is the logarithm of the rate constant.
The order with respect to concentration or true order is 0.8713 and the rate constant is 0.2296. The correlation is very high ($R = 0.9964$) and we can assume that the order of adsorption with respect to initial adsorption sites is a fraction less than one. In the initial conditions the number of adsorption sites is very high and dependence of adsorption rate on the concentration of active adsorption sites is low. Under these conditions the rate may depend more on the concentration of adsorbate particles and thus on the frequency of adsorbate particles approaching the surface.
The order of the process with respect to time \( (n_t) \) is determined separately for all adsorbent doses by plotting the logarithm of the adsorption sites remaining at different time intervals \( \log (x_e - x_t), \text{mg/g} \) against the logarithm of the respective adsorption rates \( \log v_t \). The related equation is

\[
\log v_t = \log k + n_t \log (x_e - x_t)
\]

The orders and rate constants calculated for the different adsorbent doses are given in Table 3.2.

**Table 3.2** Order \((n_t)\) and rate constants \((k)\) determined for different adsorbent doses with respect to time

<table>
<thead>
<tr>
<th>Adsorbent Dose, (mg)</th>
<th>Order w.r.t. Time, ( (n_t) )</th>
<th>Rate Constant, ( (k) )</th>
<th>Correlation coefficient ( (R) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>0.5531</td>
<td>0.7901</td>
<td>0.9813</td>
</tr>
<tr>
<td>100</td>
<td>0.9147</td>
<td>0.2311</td>
<td>0.9311</td>
</tr>
<tr>
<td>200</td>
<td>1.2377</td>
<td>0.1100</td>
<td>0.9027</td>
</tr>
<tr>
<td>500</td>
<td>2.0783</td>
<td>0.0362</td>
<td>0.9270</td>
</tr>
</tbody>
</table>

The results show that the order of adsorption with regard to time increases from 0.5531 to 2.0783 as the adsorbent dose is increased from 50 mg to 500 mg. This shows that the dependence of adsorption rate on the vacant sites \( (x_e-x_t) \) becomes prominent as we go to higher doses. As the dose mass increases the relative number of active sites decreases in a system of constant adsorbate concentration, and hence the dependence increases. The rate constants are high for small doses and decreases as the
dose is increased. The large rate constant at low doses is responsible for the comparatively high rate observed.

The mathematical models for the four adsorbent doses (50, 100, 200 and 500 mg respectively) can be written as,

\[
\text{Rate} = 0.7901 \times (x_e - x_t)^{0.5531}
\]

\[
\text{Rate} = 0.2311 \times (x_e - x_t)^{0.9147}
\]

\[
\text{Rate} = 0.1100 \times (x_e - x_t)^{1.2377}
\]

\[
\text{Rate} = 0.0362 \times (x_e - x_t)^{2.0783}
\]

3.7.1.4.2 Integral method to determine order

Integrated equations are often used in kinetics to determine the order and rate constants. In this method the experimental data are tested for previously developed equations assuming a certain order for the process. Two important integral models being used in adsorption kinetics are pseudo first order (Lagergren Model) and pseudo second order (Ho Model) models. Both models assume the rate of adsorption to be function of the active adsorption sites available on the adsorbent \((x_e - x_t)\). In the first order model the rate is supposed to be proportional to the first power of the concentration \((x_e - x_t)\) while in the second order model, it is considered to be proportional to the second power of concentration.

The experimental data is analyzed for the suitability of both models and is given in Fig. 3.8, Fig. 3.9, Fig. 3.10 and Fig.3.11. The correlation coefficients for the data are given in Table 3.3. The results
show that the adsorption process is predominantly following first order kinetics in the earlier stages of adsorption and second order kinetics at the later stages with respect to the concentration of vacant adsorption sites. In the initial stages the availability of vacant sites is large and the observed rate may depend on other factors like the probability of methylene blue particles attacking the active sites. As time proceeds, the fraction of vacant active sites decreases and the rate of adsorption depends much on the concentration of vacant sites rather than other factors operating in the system.

**Fig. 3.8** Lagernren 1\textsuperscript{st} order and Ho 2\textsuperscript{nd} order graphs (adsorbent dose-50 mg)
Fig. 3.9  Lagergren 1\textsuperscript{st} order and Ho 2\textsuperscript{nd} order graphs (adsorbent dose-100 mg)

Fig. 3.10  Lagergrens 1\textsuperscript{st} order and Ho 2\textsuperscript{nd} order graphs (adsorbent dose - 200 mg)
**Fig. 3.11** Lagergren's 1st order and Ho's 2nd order graph (adsorbent dose - 500 mg)

**Table 3.3** Correlation coefficients (R) for different adsorbent doses, Integral approach

<table>
<thead>
<tr>
<th>Adsorbent Dose (mg)</th>
<th>50</th>
<th>100</th>
<th>200</th>
<th>500</th>
</tr>
</thead>
<tbody>
<tr>
<td>‘R’ for 1st Order (Initial Stages)</td>
<td>0.9953</td>
<td>0.9841</td>
<td>0.9672</td>
<td>0.9939</td>
</tr>
<tr>
<td>‘R’ for 2nd Order (Final Stages)</td>
<td>0.9965</td>
<td>0.9648</td>
<td>0.9999</td>
<td>0.9832</td>
</tr>
</tbody>
</table>

The general conclusion is that, dependence of rate on the concentration of active vacant sites is high (high order) when the number of active sites are comparatively less, while the dependence of rate on the
concentration of active vacant sites is low (low order) when the number of active sites is large.

3.7.2 Adsorption kinetics on changing the pH

One of the important parameters that vary in different environmental aquatic systems is the hydrogen ion concentration (pH). The pH of a natural system depends upon the geological conditions and on the anthropogenic activities of the region. pH has great effect on the various chemical, physical and biological activities occurring in aquatic systems since it could affect the processes in several ways. In adsorption processes it may affect the medium conditions, adsorbate structure and the adsorbent surface, causing changes in the extent of adsorption, mechanism, kinetics etc. The studies described in chapter 2 have shown that both surface characteristics of treated coconut cake and agglomerations of methylene blue are influenced by pH causing changes in the extent of adsorption and equilibration time. In this part of the work effort is made to understand the different aspects related to the time dependence of methylene blue adsorption on treated coconut cake at different pH, keeping all other parameters constant. The studies are done at pH 3.23, 4.17, 5.42, 8.57 and 10.95.

3.7.2.1 Methylene blue adsorption as a function of time –Preliminary observations

The amount of methylene blue adsorbed per gram of treated coconut cake ($x_t$, mg/g) at different time intervals, for various pH studied, are given in Fig. 3.12.
Fig. 3.12  Amount of methylene blue adsorbed per gram of coconut cake at different pH

The results show that the amount of the dye adsorbed increases as the pH is increased from 3.23 to 10.95. This can be explained in terms of the rise in the number of negative adsorption sites on the surface as the pH is raised. Better adsorption at high pH is observed at all intervals of time.

The amount of methylene blue adsorbed at equilibrium \( (x_e) \) is a measure of the total active adsorbent sites initially present on the adsorbent under the system conditions. Hence \( x_e-x_t \) is proportional to the active adsorbent sites remaining vacant on the adsorbent surface at time\( 't' \). Graph showing the variation of \( x_e-x_t \) against\( 't' \) is given in Fig. 3.13.
The graphs reveal that the number of active adsorption sites increases as the pH is increased from 3.23 to 10.95. This is due to the changes occurring to the functional groups of the surface as the system moves from acidic to alkaline conditions. The increasing concentration of hydroxide ions enhances the removal of protons from the surface groups resulting in more negative sites. It is also observed that most of the sites are occupied by the dye cations in an initial short time, may be due to the high affinity and solution pressure existing at these conditions. Very low concentration of active adsorption sites at pH 3.23 is due to the high positive charge density created on the adsorbent surface by the attachment of protons from the medium.

Fig. 3.13 The fraction of active adsorption sites (mg/g) at different intervals of time.
3.7.2.2 Comparison of reaction (adsorption) rates at different pH

The rate of adsorption process (v) is followed by studying the rate at which the active adsorption sites are being occupied by the adsorbate particles. The rate of decrease of adsorption sites at different time (equal to the rate of adsorption) intervals is determined by differentiating the concentration of adsorbent site (x_e-x_t) vs time (t) graph (Fig.3.13). The rates of the adsorption process \[v = \frac{d (x_e-x_t)}{dt}\] vs time are given in Fig.3.14.

The results show that the rates of the processes are functions of pH. The rate at each instant of the process is large for high pHs and small for low pHs. The large number of active sites along with the greater affinity of dye particles towards the surface due to enhanced electrostatic force of attraction is the reason for increase in rate, as pH is increased.

![Graph showing rate of adsorption at different pH](image)

**Fig. 3.14** Rate of adsorption at different time intervals for different pH of the medium
3.7.2.3 Order and Rate constants

The order of the process at different pH is determined by both differential method and integral method. The results are used to determine the corresponding rate constants.

3.7.2.3.1 Differential approach

The rates of adsorption (v) as a function of the active sites remaining (x_e-x_t) on the adsorbent at different pH is given in Table. 3.4. This data is used to determine the order of the process with respect to time (n_t) at different pH using the equation

\[ v = k \ C^{n_t} \]

\[ \log v = \log k + n_t \log C \]

where ‘C’ is the concentration of the reactant species at different intervals of time [here, the concentration of active adsorption sites on the adsorbent surface(x_e-x_t)], ‘v’ the corresponding rate of adsorption, ‘n_t’ order of adsorption with respect to time and ‘k’ the rate constant.

Table 3.4 Rates of adsorption at different concentrations of active adsorbent sites in the course of the process, for different pH

<table>
<thead>
<tr>
<th>pH</th>
<th>C = (x_e-x_t) mg/g</th>
<th>v mg/g/min</th>
<th>1.1610</th>
<th>0.8514</th>
<th>0.387</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.23</td>
<td></td>
<td></td>
<td>0.1548</td>
<td>0.1064</td>
<td>0.05805</td>
</tr>
<tr>
<td>4.17</td>
<td>18.5891</td>
<td>8.2876</td>
<td>3.0207</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.1508</td>
<td>3.1021</td>
<td>1.0534</td>
<td></td>
</tr>
<tr>
<td>5.42</td>
<td>19.0327</td>
<td>10.8422</td>
<td>5.9514</td>
<td>1.3553</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>8.1905</td>
<td>5.3180</td>
<td>1.6823</td>
<td>0.9192</td>
</tr>
<tr>
<td>8.57</td>
<td>20.1890</td>
<td>10.0944</td>
<td>6.8644</td>
<td>2.0977</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>10.0946</td>
<td>5.5856</td>
<td>1.0148</td>
<td>0.61106</td>
</tr>
<tr>
<td>10.95</td>
<td>21.4445</td>
<td>10.5793</td>
<td>4.4319</td>
<td>2.6448</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>10.8642</td>
<td>6.9695</td>
<td>1.7156</td>
<td>0.3717</td>
</tr>
</tbody>
</table>
Double logarithmic plots of rates against the concentration of active sites are developed to study the order and to determine rate constants, for different pH. The order, rate constant and correlation coefficient for each set is given in Table 3.5.

**Table 3.5** The order, rate constant and correlation coefficient at different pH obtained by differential method

<table>
<thead>
<tr>
<th>pH</th>
<th>Order ($n_t$)</th>
<th>Rate Constant (k)</th>
<th>Correlation Coefficient(R)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.23</td>
<td>0.8686</td>
<td>0.1301</td>
<td>0.9939</td>
</tr>
<tr>
<td>4.17</td>
<td>0.8815</td>
<td>0.4216</td>
<td>0.9899</td>
</tr>
<tr>
<td>5.42</td>
<td>0.8437</td>
<td>0.5992</td>
<td>0.9499</td>
</tr>
<tr>
<td>8.57</td>
<td>1.2950</td>
<td>0.3860</td>
<td>0.9162</td>
</tr>
<tr>
<td>10.95</td>
<td>1.5868</td>
<td>0.1154</td>
<td>0.9648</td>
</tr>
</tbody>
</table>

The results show that the order of the adsorption process vary with respect to pH. In acidic conditions the order is less than one while in basic conditions it is between 1 and 2. On the whole, we see that the rate of adsorption depends increasingly on the concentration of adsorption sites as the pH is increased. The enhancement in order means that the contribution of the adsorption sites to keep the adsorbate ions on the surface increases as the pH is increased. This is against the previous observation that the order of adsorption decreases as the effective concentration of adsorption sites is increased. The noted discrepancy may be explained in terms of the higher aggregations that the adsorbate cations acquire as the pH is increased (Chapter 2, 2.3.1.1.2.). Higher associations
of the adsorbate require the contribution from more adsorption sites to keep it stable on the surface by electrostatic force of attraction

### 3.7.2.3.2 Integral approach

The experimental data is tested for suitability to Lagergren’s first order equation and Ho second order equation. The integrated form of the first order equation is based on the assumption that the rate of adsorption \((dx_c/dt)\) is proportional to the concentration of the active adsorption sites present at time ‘t’.

\[
\text{Rate} = k_L \times (x_c-x_t) \quad \text{(A)}
\]

The integrated form of the second order equation is based on the hypothesis that the rate \((dx_c/dt)\) is proportional to the square of the concentration of active adsorption sites present on the surface.

\[
\text{Rate} = k_H \times (x_c-x_t)^2 \quad \text{(B)}
\]

The rate constants \((k_L \text{ and } k_H)\) and the maximum equilibrium capacity \((x_c)\) are calculated for the first order model and second order model by plotting \(\log (x_c-x_t)\) and \(1/(x_c-x_t)\) against time ‘t’ respectively. The initial rate of the reaction \((v_0)\) with respect to first order rate constant and second order rate constants are calculated using equations ‘A’ and ‘B’ setting \((x_c-x_t) = x_c\). The appropriateness of the model is determined by comparing the calculated maximum adsorption capability \((x_c)\) and initial rate \((v_0)\) with the experimental one, and by considering the correlation coefficient\((R)\) and nearness to the order determined by differential
method. The various parameters determined for the first order model and second order model are given in Table 3.6 and Table 3.7 respectively.

**Table 3.6** Lagergren’s first order model, different pH

<table>
<thead>
<tr>
<th>pH</th>
<th>(x_e) (calculated) mg/g</th>
<th>(x_e) (experimental) mg/g</th>
<th>(k_L)</th>
<th>(v_o) (calculated) mg/g/min</th>
<th>(v_o) (experimental) mg/g/min</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.23</td>
<td>1.112</td>
<td>1.161</td>
<td>0.107</td>
<td>0.1189</td>
<td>0.1548</td>
<td>0.9962</td>
</tr>
<tr>
<td>4.17</td>
<td>16.331</td>
<td>18.589</td>
<td>0.249</td>
<td>4.6286</td>
<td>5.1508</td>
<td>0.98407</td>
</tr>
<tr>
<td>5.42</td>
<td>17.704</td>
<td>19.033</td>
<td>0.314</td>
<td>5.559</td>
<td>8.1905</td>
<td>0.99131</td>
</tr>
<tr>
<td>8.57</td>
<td>17.65</td>
<td>20.189</td>
<td>0.3749</td>
<td>6.617</td>
<td>10.094</td>
<td>0.9853</td>
</tr>
<tr>
<td>10.95</td>
<td>14.521</td>
<td>21.445</td>
<td>0.233</td>
<td>3.383</td>
<td>10.865</td>
<td>0.9685</td>
</tr>
</tbody>
</table>

**Table 3.7** Ho second order model, different pH

<table>
<thead>
<tr>
<th>pH</th>
<th>(x_e) (calculated) mg/g</th>
<th>(x_e) (experimental) mg/g</th>
<th>(K_H)</th>
<th>(v_o) (calculated) mg/g/min</th>
<th>(V_o) (experimental) mg/g/min</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.23</td>
<td>1.1815</td>
<td>1.161</td>
<td>0.1734</td>
<td>0.2421</td>
<td>0.1548</td>
<td>0.9998</td>
</tr>
<tr>
<td>4.17</td>
<td>20.713</td>
<td>18.589</td>
<td>0.04007</td>
<td>17.19</td>
<td>5.1508</td>
<td>0.99886</td>
</tr>
<tr>
<td>5.42</td>
<td>N</td>
<td>19.032</td>
<td>0.0839</td>
<td>N</td>
<td>8.1905</td>
<td>0.94155</td>
</tr>
<tr>
<td>8.57</td>
<td>18.86</td>
<td>20.189</td>
<td>0.0384</td>
<td>13.66</td>
<td>10.094</td>
<td>0.9993</td>
</tr>
<tr>
<td>10.95</td>
<td>15.89</td>
<td>21.445</td>
<td>0.0411</td>
<td>10.38</td>
<td>10.865</td>
<td>0.98408</td>
</tr>
</tbody>
</table>

N - The parameter cannot be determined since the y-intercept has a negative sign. ‘- \(x_e\)’ is meaningless.

Comparison of parameters like initial rate and equilibrium adsorption capacity observed in the experiment and those calculated from derived data (by fitting the data to integrated models) along with correlation coefficient
show that in acidic conditions the order of adsorption is near ‘one’ while in basic conditions it approaches ‘two’. This observation is in accordance with the order determined by differential method. The reason for the greater dependence of rate on the concentration of adsorption sites \((x_e-x_i)\) may be due to increase in concentration of associated adsorbate cations as pH is increased, though the number of active adsorption sites is increased.

3.7.3 Adsorption kinetics on changing the temperature

The temperature of a system is a measure of its heat content (Glastone, 1947). The amount of heat preset in a system could modify the medium parameters as well as the structure and properties of the reactant species. These changes will make alterations in reaction mechanisms and kinetics. The heat content of different environmental aquatic systems depends on the geology, climate and anthropogenic activities of the region. Thus temperature is an important factor to be considered in environmental aquatic chemistry. In adsorption processes temperature will change the mechanisms and kinetics by altering the adsorption - desorption processes in a variety of ways. To understand the effect of heat content of the system on the kinetics of adsorption of methylene blue on coconut cake, experiments are done at four different temperatures, and the data analyzed.

3.7.3.1 Preliminary observations

The amounts of methylene blue adsorbed per gram of coconut cake (mg/g) as a function of time at four different temperatures \((27^0 \text{ C}, 42.5^0 \text{ C}, 51^0 \text{ C} \text{ and } 59.5^0 \text{ C})\) are given in Fig. 3.15.
The amount of methylene blue adsorbed per gram of coconut cake (x, mg/g) decreases as the temperature is increased. This tendency is observed at each interval of time. As the temperature is increased, the heat energy entering the system will enhance the kinetic, vibrational, rotational, electronic, etc. energies of the components of the system. Thus at elevated temperatures the adsorbate particles adsorbed on the surface will get detached by the enhanced vibrations leading to more desorption. This observation also gives the message that the force operating between the surface functional groups and the cations are physical in nature, since physical forces like van der Waals forces of attraction decreases as the temperature is increased. But the equilibration time is inversely related to temperature. Temperature rise will be accompanied by increase in the mobility of dye cations and electronic energies of the surface functional groups, which allows the equilibrium to be attained at an earlier time.

The amount of active adsorption sites at different intervals of time \((x_e-x_i)\) plotted against time \((t)\) is given in Fig. 3.16. The number of active adsorption sites on coconut cake decreases as the temperature of the medium is increased. This trend is followed at all intervals of time in the course of the process. It can be assumed that at elevated temperatures some of the functional groups on the cellulose and/ or protein surface are excited to some electronic states such that their sticking capacity is reduced. Also at higher temperatures the adsorbed particles will vibrate at higher frequencies causing more desorption.
Fig. 3.15  Amount of methylene blue adsorbed vs time at different temperatures

Fig. 3.16  Active adsorption sites at different temperatures as a function of time
3.7.3.2 Rate of adsorption at different temperatures

To determine the rate of adsorption at different time intervals for different temperatures, ‘x(t)-x(t)’ against ‘t’ graph (Fig. 3.16) is differentiated. The slopes obtained at different time intervals are the rates of occupancy of active adsorption sites, which is equal to the rate of adsorption with opposite sign. The rates of adsorption are given in Fig. 3.17. The initial rates of adsorption at the temperatures studied are given in Fig. 3.18. Though a decrease in adsorption rate with respect to rise in temperature is normally expected since the number of active sites per gram of the adsorbent is decreasing as temperature is raised, the observed rate is higher at higher temperatures at all intervals of time. The observed larger rate may be explained in terms of the enhanced mobility that the adsorbate particles have acquired so that the probability for them to reach surface in unit time (or frequency of attachment) is increased, resulting in more adsorption per unit time.

![Graph showing rate of adsorption at different temperatures](image)

**Fig. 3.17** Rate of adsorption (v) at different time intervals for different temperatures
3.7.3.3 Reaction order and Rate constants

Attempt is made to get an idea about the order of the adsorption process at different temperatures. Both differential and integral methods are used. The results are used to determine the rate constants and the equilibrium concentration of adsorption sites. The rate constants obtained by the differential method are analyzed to see their temperature dependence, and from that Arhenius parameter and activation energy are determined.

3.7.3.3.1 Differential method

Double logarithmic plots of reaction rates (log v) and active adsorption sites (log x_t-x_e) at different time intervals for all the four medium temperatures are developed. The slope of the curve and the y-intercept are used to determine the order with respect to time (n_t) and rate constants (k) respectively. The parameters calculated are given in Table. 3.8.
Table 3.8 Kinetic parameters obtained by the differential method at different temperatures

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Order ((n_i))</th>
<th>Rate Constant ((k))</th>
<th>Correlation Coefficient ((R))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(27^\circ\text{C})</td>
<td>1.2835</td>
<td>0.1455</td>
<td>0.9678</td>
</tr>
<tr>
<td>(42.5^\circ\text{C})</td>
<td>1.5903</td>
<td>0.1351</td>
<td>0.9591</td>
</tr>
<tr>
<td>(51^\circ\text{C})</td>
<td>1.0031</td>
<td>0.7497</td>
<td>0.9868</td>
</tr>
<tr>
<td>(59.5^\circ\text{C})</td>
<td>0.8047</td>
<td>1.5627</td>
<td>0.9349</td>
</tr>
</tbody>
</table>

The order at \(27^\circ\text{C}\) and \(42.5^\circ\text{C}\) are well above ‘one’ with almost equivalent rate constants. The comparable rate constants suggest that the behaviour of the systems and mechanism of adsorption at these two temperatures is not much different. The order of the process decreases as we go to higher temperatures showing that the dependence of rate on active adsorbent sites is becoming less important. At high temperature the rate may depend more on the mobility of the adsorbate particles and the vibrational energy of the adsorbed system, than on the number of active sites. An increase in rate constants is also observed showing the profound influence of temperature on the process (Castellan, 1995).

3.7.3.3.1.1 Temperature dependence of rate constants: Arrhenius equation

The effect of temperature on the rate constants is studied by fitting the rate constants at different temperatures to the Arrhenius equation.

\[
k = A e^{-\frac{E}{RT}}
\]

\[
\ln k = \ln A - \frac{E}{RT}
\]
log k = log A - E/2.303 RT

where ‘k’ is the rate constant, ‘A’ is the Arrhenius frequency factor or the pre-exponential factor, ‘E’ is the activation energy, ‘R’ is the universal gas constant and ‘T’ the temperature on absolute scale.

It is found that the rate constants are obeying the Arrhenius equation from 42.5°C to 59.5°C, and the graph obtained by plotting ‘log k’ against ‘1/T’ is given as Fig. 3.19. From the slope and y-intercept the activation energy and Arrhenius frequency factor are determined.

Fig. 3.19 Temperature dependence of rate constants, determination of Arrhenius parameters
The frequency factor calculated is $1.827 \times 10^{20}$ s$^{-1}$ and the activation energy is 127.1439 KJ. High activation energy signifies that the rate constant depends strongly on temperature. The activation energy is the minimum amount of energy that the adsorbent site and the adsorbate should possess so that the collision between them results in bond formation. The fraction of collisions with a kinetic energy in excess of the activation energy is given by the Boltzmann Distribution as $e^{-E/RT}$. Hence the exponential factor in Arrhenius equation can be interpreted as the fraction of collisions that have enough kinetic energy which lead to reaction. The pre-exponential factor is a measure of the rate at which the collision occurs irrespective of their energy (Atkins and de Paula, 2002).

In an adsorption process, the particles from the medium are transferred to the surface by diffusion and a reaction occurs on the surface. In the processes being studied, the chemical reaction is the binding of methylene blue cations on the surface by some force of attraction. The reaction is said to be kinetically controlled when the rate of diffusion is fast and diffusion controlled when the rate of chemical binding is fast. The same process, depending on the condition like temperature at which it is conducted, may be kinetically controlled or diffusion controlled. The dependence of the logarithm of rate constant (k) on the inverse of temperature (1/T) could give information regarding this control (Fig. 3.20.).
Fig. 3.20 1/T vs log k from 27°C to 59°C

The section CD of Fig. 3.20, for a practically constant value of ‘k’ (‘k’ does not depend on the temperature in this range), corresponds to a diffusion-controlled process. This corresponds to temperature 27°C to 42.5°C. The section AC (42.5°C to 59.5°C) of the curve corresponds to a kinetically controlled process. This section is usually characterized by a considerable value of the activation energy (Gerasimov et al., 1978). We can thus conclude that at low temperatures diffusion is the slow step, while at high temperatures attachment to the surface is the slow step, in the of process of adsorption. The slow step of a process is the rate-determining step. At low temperatures the diffusion process may be slow due to the comparatively less kinetic energy available, and at high temperatures slow binding is observed may be due to the process of
desorption occurring at a higher rate as a result of the greater vibrations of the functional groups at elevated temperatures.

3.7.3.3.2 Integral method

The integral methods are used to test the validity of 1st order and 2nd order equations. The results are given in Table 3.9 and Table 3.10. Comparison of the experimental and calculated parameters (maximum adsorption at equilibrium, $x_e$ and initial rate, $v_o$) along with the correlation coefficients is considered for analysis.

Table 3.9 Experimental and calculated parameters for Lagergren’s first order equation - Temperature dependent studies

<table>
<thead>
<tr>
<th>Temperature</th>
<th>$x_e$ (calculated)</th>
<th>$x_e$ (experimental)</th>
<th>$k_L$</th>
<th>$v_o$ (calculated)</th>
<th>$v_o$ (experimental)</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>27°C</td>
<td>18.39 mg/g</td>
<td>18.44 mg/g</td>
<td>0.2897</td>
<td>5.327 mg/g/min</td>
<td>5.147 mg/g/min</td>
<td>0.9992</td>
</tr>
<tr>
<td>42.5°C</td>
<td>15.68 mg/g</td>
<td>18.11 mg/g</td>
<td>0.4513</td>
<td>7.07 mg/g/min</td>
<td>9.88 mg/g/min</td>
<td>0.9833</td>
</tr>
<tr>
<td>51°C</td>
<td>12.83 mg/g</td>
<td>15.92 mg/g</td>
<td>0.5290</td>
<td>6.787 mg/g/min</td>
<td>10.15 mg/g/min</td>
<td>0.9847</td>
</tr>
<tr>
<td>59.5°C</td>
<td>14.56 mg/g</td>
<td>15.33 mg/g</td>
<td>1.254</td>
<td>19.22 mg/g/min</td>
<td>11.58 mg/g/min</td>
<td>0.9975</td>
</tr>
</tbody>
</table>

Table 3.10 Experimental and calculated parameters for Ho second order equation - Temperature dependent studies

<table>
<thead>
<tr>
<th>Temperature</th>
<th>$x_e$ (calculated)</th>
<th>$x_e$ (experimental)</th>
<th>$K_H$</th>
<th>$v_o$ (calculated)</th>
<th>$v_o$ (experimental)</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>27°C</td>
<td>19.48 mg/g</td>
<td>18.44 mg/g</td>
<td>0.0277</td>
<td>10.511 mg/g/min</td>
<td>5.147 mg/g/min</td>
<td>0.998</td>
</tr>
<tr>
<td>42.5°C</td>
<td>20.19 mg/g</td>
<td>18.11 mg/g</td>
<td>0.0795</td>
<td>32.40 mg/g/min</td>
<td>9.88 mg/g/min</td>
<td>0.999</td>
</tr>
<tr>
<td>51°C</td>
<td>44.66 mg/g</td>
<td>15.92 mg/g</td>
<td>0.2015</td>
<td>401.89 mg/g/min</td>
<td>10.15 mg/g/min</td>
<td>0.996</td>
</tr>
<tr>
<td>59.5°C</td>
<td>102.25 mg/g</td>
<td>15.33 mg/g</td>
<td>0.3681</td>
<td>3848.50 mg/g/min</td>
<td>11.58 mg/g/min</td>
<td>0.968</td>
</tr>
</tbody>
</table>
At $27^0 C$ and $42.5^0 C$ the calculated and experimental values are comparable along with correlation coefficients both for first order and second order equations. Hence we may conclude that the adsorption process is following some order between 1 and 2 at these temperatures supporting the evidence from the differential methods. At $51^0 C$ and $59.5^0 C$ the calculated equilibrium capacity ($x_e$) and initial rate ($v_o$) are very large compared to the experimental results for second order analysis. Hence it may be assumed that at these higher temperatures adsorption is following an order near to one with respect to vacant adsorption sites, again in agreement with the differential results.

3.8 Summary and Conclusion

Kinetic studies carried out using different masses of the adsorbent (adsorbent dose) keeping all other parameters constant, showed that the fraction of adsorption sites becoming active is a function of the adsorbent dose. As the adsorbent dose is increased, the fraction of sites becoming active is reduced. The data is then used to determine the rates of the process initially and at other intervals of time. Attempt is made to interpret the initial rate differences and the rate at different intervals of time. The initial rates for different adsorbent doses are used to determine the order of the process with respect to concentration. The rates at different time intervals are used to determine the order of the process with respect to time. Also the fitness of the data is checked for the Lagergren first order equation and Ho second order equation. The order determined by the differential and integral methods is compared. In general it is observed that the order of the process gradually increases as the adsorbent dose is increased. The order of the process depends much on the availability of the active sites. As the fraction
of the adsorbent sites is low the rate depends much on its concentration, as observed by increase in order.

Studies are done to understand the rates, order, rate constants etc. at different hydrogen ion concentrations (pH) of the medium, keeping other parameters constant. Experiments done at pH 3.23, 4.17, 5.42, 8.57 and 10.95 showed that the rates of adsorption are high at high pH, which is explained in terms of the large number of negative sites available as the pH is increased. The order is determined by both integral and differential methods, and compared. Differential approach showed that the order is less than one in acidic conditions and it is between 1 and 2 in basic conditions. Integral methods also provide supporting evidences for this observation. The results are explained in terms of the changes in methylene blue aggregations with respect to pH changes.

To study the effect of temperature on adsorption kinetics experiments are conducted at 27° C, 42.5° C, 51° C and 59.5° C. It is observed that the amount of adsorbate in milligram adsorbed per gram of the adsorbent decreases as the temperature is increased. This may be due to the enhanced vibrational energies of the functional groups at higher temperatures resulting in decreased number of active adsorption sites. The rates of the process are found to be increasing with increase in temperature which is explained in terms of the enhanced mobility that the adsorbate particles acquire as the temperature is increased. The order determined by the differential method showed that the dependence of adsorption on active sites decreases as the temperature is increased. The temperature dependence of the rate constants are analysed using
Arrhenius equation and Arrhenius parameters are determined. Studies related to the dependence of rate constants on temperature also showed that the process is diffusion controlled at low temperatures while it is kinetically controlled at high temperatures. The data is also analyzed for the soundness of integrated equations.

References


Van’t Hoff, J.H. 1884. *Etudes de dynamique chimique*, Muller, Amsterdam, 84.

