Kinetic Study and Equilibrium Isotherm Analysis of Reactive Dyes Adsorption onto Cotton Fiber

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Abstract: This study was to evaluate the adsorption capability of cotton fiber to reactive dyes (C.I. Reactive Red 120 (RR120) and C.I. Reactive Black 5 (RB5)) in aqueous solution. The experiments were carried out in a batch system to optimise operation variables: dye concentration, pH, and temperature. In addition, adsorption of reactive dyes onto cotton fiber with using sodium edate (SE), sodium citrate (SC) and sodium sulphate (SS) was also investigated and the results obtained were compared. The results show that the presence of organic salts (SE and SC) significantly enhance the dye uptake (high Q, b and Q_f values) onto cotton fiber compared with the results obtained in aqueous and in the presence of sodium sulphate. Thus, presence of organic salts (SE and SC) is an alternative way to subsequently increase the affinity between RR120 and RB5 dyes and the cotton fiber. Moreover, the Langmuir and Freundlich adsorption models were applied to describe the equilibrium isotherms at different operation parameters and isotherm constants. The Langmuir model agreed very well with experimental data. The applicability of the Langmuir isotherm suggests monolayer coverage of the two reactive dyes on surface of cotton fiber. The kinetics of the adsorption with respect to the initial dye concentration, temperature, pH and different salts were investigated. The pseudo-first-order, second-order kinetic models and intraparticle diffusion model were used to describe the kinetic data and the rate constants were evaluated. The dynamical data fit well with the second-order kinetic model. Intra-particle diffusion studies revealed that, the adsorption rates were not solely controlled by the diffusion step. Further thermodynamic investigations showed that, the adsorption is an endothermic process. The activation energies (E_a) for the pseudo second-order kinetics and intraparticle diffusion kinetics for RR120 and RB5 are energetically favorable with different salts at different dye concentration and the adsorption process is a combination of chemical and diffusion processes [Nature and Science 2010; 8(11):95-110] (ISSN: 1545-0740).

Key words: Adsorption; Cotton fiber; Isotherm; Kinetics; Thermodynamics.

1. Introduction:

Cotton is an abundant natural fiber which consists of practically pure cellulose (about 88-96%) [1,2]. Natural cellulose fibers carry a small negative charge ($\zeta_{plateau}$ = -11 mV) due to the presence of some carboxylic acid groups from oxidation at the primary hydroxylic sites [3]. At a pH higher than 8, some of the hydroxyl groups on the hydroxymethyl side chains may also be ionized increasing the negative charge significantly [4]. The negative charges on the surface of cellulose repel anionic dyes and hence the efficiency of dye fixation on cellulosic fibers is generally low. To counter this problem, a number of studies on cotton dyeing have been carried out to improve the dye uptake and fastness properties [1]

Exhaustive dyeing of cotton with reactive dyes requires the presence of electrolytes (NaCl or Na_2SO_4), which suppresses negative charge build-up at the fiber surface and promotes increased dye-uptake [5, 6]. Progress has been made in reducing salt requirements for some newer reactive dyes, but salt concentrations are still too high [7]. Recently, reduced salt by the replacement of nonbiodegradable inorganic salt (sodium chloride) with biodegradable organic one (tetrasodium edate and trisodium citrate) in the exhaustive dyeing of cotton using reactive, direct and solubilised vat dyes has been reported [5, 8].

Moreover, high wet fastness in dyeing of cellulosic textiles is best gained by the use of reactive dyes; these are the only colorants which link covalently to cellulose. Fixation is invariably achieved in the presence of aqueous alkali. Under these conditions, nucleophilic cellulosate ion, Cell-O^-, is in competition with hydroxide ion, OH^-, for reaction with the electrophilic reactive group(s) of the dye [9].

It is shown that the dye fixation to the fabric is controlled by a solid–liquid interfacial process; however, the rate of this reaction is governed by the availability of sites for the adsorption of dye molecules on the fabric surface [10].

The adsorption of dye molecules on the fabric surface is basic step in the dyeing process. Consequently, the aim of this work is to evaluate the adsorption capacity of cotton fiber to reactive dyes, namely C.I. Reactive Red 120 (RR120) and C.I. Reactive Black 5 (RB5). The research focused on evaluating how the process operation parameters of initial dye concentration, pH, effect of nonbiodegradable inorganic salt (sodium sulphate) and biodegradable organic salts (tetrasodium edate and trisodium citrate) and temperature affect the adsorption capacity. The best-fit equilibrium isotherms are determined by Freundlich and Langmuir models. Adsorption kinetic models are employed to analyse the kinetics and mechanisms of RR120 and RB5 adsorption onto cotton fiber.

2. Experimental :

2.1. Materials and chemicals

2.1.1. Cotton fiber preparation

Mill desized, scoured and bleached cotton fabric (Poplin) is supplied by Misr Company for spinning and weaving, Mehala El-Kubra, Egypt. To remove the wax and impurities, the cotton fiber was added to boiling water (2 l) which were added to a solution containing 4g/l sodium carbonate and 2g/l nonionic detergent (nastapon**)**. The mixture was then boiled for 4 hours. The cotton was then removed, washed with hot water and cold water and air dried at room temperature [11].

2.1.2. Dyestuffs and chemicals

Two reactive dyes (C.I. Reactive Red 120 (Procion HE3B, RR120) and C. I. Reactive Black 5 (Procion B, RB5)) are obtained from ICI (Imperical Chemical Industries Limited Dyestuffs Division Manchesester, England). The dyes are of commercial grade and are used as received (Scheme 1).

Other chemicals (Sodium Carbonate, Sodium Sulphate (SS), Tetrasodiumedate SE) Trisodiumcitrate (SC), Detergent nastapon, Sodium hydroxide, and Nitric acid) from BDH and Merk are used as received.

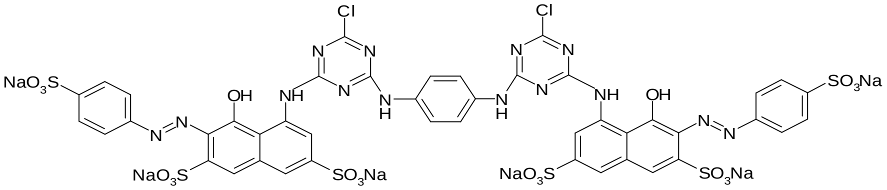
2.2. Instruments

The absorption spectra are recorded with JENWAY- 6300 UV-Visible spectrophotometer. The absorbance of solutions measured using a 1cm quartz cell. (U.K.).

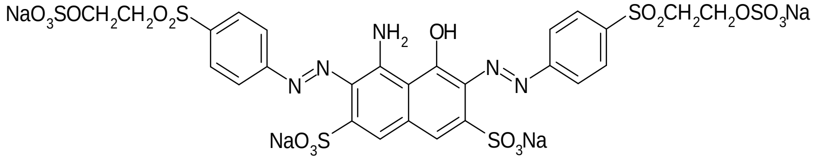
A pH meter (DATALOGGER 6209; JENCO ELECTRONICS – LTD, U.S.A.) is used to measure the pH values of the dye solutions.

A thermostatted shaker bath (Heto-Holten A/S Denmark, Type SBD-50 cold), operated at 75 rpm, and is used to study the kinetic adsorption of reactive dyes onto cotton fiber.

C.I. Reactive Red 120 (RR120):



C.I. Reactive Black 5 (RB5):



Scheme 1: Chemical structure of the studied dyes.

2.3. Adsorption experiment

Adsorption of RR120 and RB5 on cotton fiber is carried out in a batch system. A desired amount of cotton fiber (1g) is added to 30ml of known concentration of RR120 or RB5 solutions (L: R = 1:30). The dyes solutions are prepared to the desired concentrations using Milli-Q water. The pH is adjusted with 0.1M HNO3, and 0.1M NaOH. The mixture is agitated at 150rpm in a rotary shaker (Ratek OM 15 orbital mixer, Australia) at 30◦C. The experiments are carried out over 4 hours to ensure that adsorptive equilibrium is obtained. The samples are withdrawn from the experimental flask at pre-determined time intervals until adsorption equilibrium is achieved. Then, the cotton fiber is separated. The residual dyes concentrations are determined colorimetrically. All experiments are carried out in triplicate, and the average values are taken to minimise random error.

2.4. Analytical method

2.4.1. Dye concentration and removal capacity

Dye concentration is determined colorimetrically by measuring at maximum absorbance of the two dyes ((λ_{max} = 512 nm and 597 nm for RR120 and RB5, respectively)). Calibration curve is plotted between absorbance and concentration of the dye solution to obtain the absorbance-concentration profile for the two dyes.

The amount of dye uptake per gram of cotton (mg/g cotton) at any time (q_t) is calculated by a mass–balance relationship Eq. (1) as follows [12]:

$$q_t=(C_0-C_t)(V/W) \qquad (1)$$

where C_0 is the initial dye concentration (mg/l) and C_t is the dye concentration after dyeing time t (mg/l), V is the volume of dye solution (ml) and W is the weight of cotton fiber (g) used.

The adsorption capacity are determined at different operation parameters that affect the adsorption of RR120 and RB5 onto cotton fiber (initial dye concentration (24.166- 1183.400 mg/l for RR120 and 20.081 -1004.67 mg/l for RB5), pH (6.04 - 11.01), effect of inorganic salt (sodium sulphate [SS] = 0- 60g/l in presence of 20 g/l Na_2CO_3) and organic salts (sodium edate [SE] = 0- 60g/l and sodium citrate [SC]= 0-60g/l) and temperature(40-90ºC).

3. Results and Discussion:

3.1. Effect of contact time

Adsorption isotherms are usually determined under equilibrium conditions. A series of contact time experiments for the two reactive dyes have been carried out with initial dyes concentrations of 113.366mg/l and 110.011mg/l, L.R.1:30 and pH 10.02 and 11.01 in presence of 50g/l SS and 20g/l sodium carbonate used in fixation at temperatures 80 and 60^{o}C for RR120 and RB5, respectively (Figure 1). Moreover, adsorption in presence of 40g/l SE and 25g/l SC is also studied. Figures 1 and 2 show the contact time necessary for reactive dyes to reach saturation is >100 mins. As can be seen from Figure 1, the amount of the adsorbed dye onto cotton fiber increases with time and, at some point in time, reaches a constant value beyond which no more is adsorbed from solution. At this point, the amount of dye being adsorbed onto cotton fiber is in a state of dynamic equilibrium with the amount of the dye desorbing from the fiber. The time required to attain this state of equilibrium is termed the equilibrium time, and the amount of dye adsorbed at the equilibrium time reflects the maximum adsorption capacity of the cotton fiber under those operating conditions [13, 14].

3.2. Effect of temperature

The effect of temperature on the adsorption of RR120 and RB5 dyes on cotton is investigated in the temperature range of 40-90 ºC at initial dye concentration 113.366mg/l and 110.011mg/l, L.R.1:30 and pH 10.02 and 11.01 in presence of 50g/l SS and 20g/l sodium carbonate used in fixation for RR120 and RB5, respectively (Figure 1). Moreover, adsorption in presence of 40g/l SE and 25g/l SC is also studied.

Figures 1 and 2 show that the adsorption of RR120 and RB5 dyes on cotton enhanced with raising the temperature up to 80ºC and 60 ºC for both dyes indicating that a high temperature favored the dye adsorption onto cotton fiber. However, temperature higher than 80^{o}C and 60^{o}C for RR120 and RB5 dyes, respectively results in decrease in the adsorption, which may be attributed to decrease in dye molecule stability at higher temperatures [15].

The increase in temperature would increase the mobility of the large dye ions as well as produce a swelling effect with the internal structure of the fiber, thus enabling the large dye molecules to penetrate further [16, 17]. This may also be a result of an increase in the mobility of the dye molecule with an increase in their kinetic energy, and the enhanced rate of intraparticle diffusion of sorbate with the rise of temperature. It is clear that the sorption of RR120 and RB5 dyes onto cotton fiber is an endothermic process and RR120 and RB5 dyes sorption may involve chemical sorption [18].

3.3 Effect of initial dyes concentrations

The adsorption capacity of RR120 and RB5 dyes on cotton is a function of the initial dye concentration. As expected, under equilibrium conditions the amount of the dyes adsorbed on cotton increases with an increase in the initial concentration of dyes solutions (24.166- 1183.400 mg/l for RR120 and 20.081 -1004.67 mg/l for RB5, L.R.1:30 and pH 10.02 and 11.01 in presence of 50g/l SS and 20g/l sodium carbonate used in fixation at temperatures 80 and 60^{o}C for RR120 and RB5, respectively (Figure 2 for RR 120, similar behaviour is obtained in case of RB5). Moreover, adsorption in presence of 40g/l SE and 25g/l SC is also studied. It can be proposed that an increase in the initial dye concentration leads to an increase in mass gradient between the solution and adsorbent (cotton fiber), and thus acts as a driving force for the transfer of dye molecules from bulk solution to the fiber surface. The increase in the proportional dye adsorption is attributed to the equilibrium shift during the adsorption process [12, 19 and 20]. Moreover, RR120 has greater molecular weight than RB5; it gives better adsorption capacity. It is obvious that the dye fixation is related to dye molecule structure. Larger molecule usually means more intermolecular interaction due to van der Waals force between the dye and cotton fabric, contributed a great part in the dye fixation [21].

3.4. Effect of pH

The pH of a dye bath is an important influencing factor for the adsorption of RR120 and RB5 dyes on cotton. In this study, the pH of RR120 and RB5 dyes solutions is varied in the pH range of 6.04 to 11.01 with initial dye concentration 113.366mg/l and 110.011mg/l and L.R.1:30 for 2 hours dyeing time in presence of 50g/l SS and 20g/l sodium carbonate used in fixation at temperatures 80 and 60^{o}C for RR120 and RB5, respectively (Figure 3). Moreover, adsorption in presence of 40g/l SE and 25g/l SC is also studied. The maximum adsorption capacity is observed at high pH values (10.02 and 11.01) for RR120 and RB5 in presence of 50g/l SS and 20g/l sodium carbonate. In presence of 40g/l SE and 25g/l SC the maximum sorption capacity was observed at pH 9.52 and 8.31 for RR120 and RB5, respectively. The increase of RR120 and RB5 dyes adsorption onto cotton fiber with increasing pH values may be explained by the electrostatic interaction between dye molecules and negatively cotton fiber surface. This result emphasizes the fact that alkali is necessary for covalent bond fixation using SS as this salt is neutral electrolyte. Whereas SE and SC are alkaline polycarboxylic sodium salts.

Reactive dyes containing chlorotriazinyl groups (RR120) react with nucleophiles by an activated heteroaromatic nucleophilic substitution mechanism [9]. Chlorotriazine reactive dye fixation involves the formation of a covalent bond between a hydroxyl group, under alkaline conditions in the fabric, and the dye molecule, by the nucleophilic displacement of chloride ion [10].

Moreover, nucleophilic addition characterizes the dye-fabric reaction in which a nucleophilic group in the fabric adds across an activated carbon-carbon double bond in the reactive group contain a vinylsulphone moiety (RB5) [22].

3.5. Effect of sodium sulphate

Due to the presence of hydroxyl and some carboxylic acid groups, the natural cellulose fibers carry a negative charge [1, 3] whereas RR120 and RB5 dyes are also anion hence negatively charged; there is electrostatic anion-anion repulsion between dye and cellulose. This means that electrical repulsion between the RR120 and RB5 dyes and cellulose fibers in the dyeing process must be overcome by other forces of attraction. For this reason, electrolytes such as sodium chloride or sodium sulphate have been added into the dye bath to promote the adsorption of anionic dye on cellulose fibers [23].

Therefore, the effect of sodium sulphate (concentration range 0-60g/l) on the adsorption of RR120 and RB5 dyes on cotton is investigated in this study and the results are shown in Figure 4. It is found that an increase in the sodium sulphate concentration over the range 0-50 g/l led to an increase in the dye adsorbed on cotton and then remained constant in the concentration range 50-60 when cotton fiber is dyed with RR120 and RB5 dyes solution. The results obtained in our study can be explained by the Donnan model [24]. According to this model, cellulose fiber are negatively charged [3, 4], and dyeing occurs by the transfer of dye from the external to the internal solution. Upon addition of sodium sulphate (as an electrolyte) to the dye solution, the sodium ions (Na^+) distribute between the external solution and internal solution so that the negative charge on the cellulose surface is neutralized or shielded, allowing the dye molecules to be adsorbed on the cotton [3, 25].

3.6. Effect of sodium edate and sodium citrate

The generally accepted model for dyeing of reactive dyes into cellulosic fabrics consists of two phases i.e. adsorption and diffusion phase and fixation phase [26]. Electrolytes such as sodium chloride or sodium sulphate have been added into the dye bath to promote the adsorption of anionic dye on cellulose fibers [23]. Recently, reduced salt by the replacement of nonbiodegradable inorganic salt (sodium chloride) with biodegradable organic one (trisodium citrate) in the exhaustive dyeing of cotton using reactive, direct and solubilised vat dyes has been reported [8]. Moreover, the use of polycarboxylic acid salts have proved the most effective class evaluated, promoting higher exhaustion and fixation of reactive dyes on cotton than sodium chloride or sodium sulphat [5].

Sodium edate, ethylenediaminetetraacetic acid, tetrasodium salt is a sequestering agent that works by a complexation mechanism. The resulting complex remains soluble and innocuous under the condition of processing. This phenomenon has been widely exploited in textile industries such as in dyeing to prevent precipitation of dyes by calcium and magnesium salts present in hard water and thus producing brilliant dyed goods

The effect of SE and SC concentration on the adsorption of RR120 and RB5 onto cotton fabrics are conducted at different concentrations (0-60 g/l). The adsorption capacity on cotton fiber increases with increasing SE and SC concentration (Figure 5). It is clear that increasing the salt concentration from 0 to 50 g/l leads to a pronounced effect on the dye uptake for both dyes and further increases, however, leads to a marginal increase. This result reflects the findings that SE and SC acts as fixing agent. The results show that better adsorption capacity can be obtained using sodium edate and sodium citrate.

3.7. Adsorption isotherms

The Langmuir isotherm which has been successfully applied to many other real sorption processes can be used to explain the sorption of RR120 and RB5 onto cotton fiber. A basic assumption of the Langmuir theory is that sorption takes place at specific sites within the adsorbent [27,28].

The most widely used two-parameter equation describing the adsorption process has the linear form [26]:

$$C_e/q_e=1/Qb+(1/Q)C_e \qquad (2)$$

For lower concentrations, the following form of the Langmuir equation is found to be more satisfactory [20, 27, 33]:

$$1/q_e=(1/Q)+(1/QbC_e) \qquad (3)$$

In the above equations, Q is the maximum amount of the dye absorbed per unit weight of fiber to form a complete monolayer coverage on the surface bound at high equilibrium dye concentration C_e, q_e is the amount of dye adsorbed per unit weight of fiber at equilibrium, and b is the Langmuir constant related to the affinity of the binding sites. The value of Q represents a practical limiting adsorption capacity when the surface is fully covered with dye molecules and assists in the comparison of adsorption performance [21]. The values of Q and b are calculated from the intercepts and slopes of the straight lines of plot of $1/q_e$ versus $1/C_e$.

The data obtained from the adsorption experiment conducted during the present investigation is fitted using different temperature (40-90ºC) and different salts (SS, SE and SC) into the isotherm equation. A plot of ($1/q_e$ versus $1/C_e$) results is a linear graphical relation indicating the applicability of the above model for different temperature in presence of 50 g/l SS and 20 g/l sodium carbonate as shown in Figure 6 and for different salts (SE and SC). The values are calculated from the slope and intercept of different straight lines representing the different temperature and different salts. The observed linear relationship is statistically significant as evidenced by the *r* values (which are close to unity). This indicates the applicability of the isotherm (Langmuir isotherm) and the surface. The Langmuir isotherm constants along with correction coefficients are reported in Table 1. Data in Table 1 shows that Q and b values increase with increasing temperature confirming the endothermic nature of the adsorption. Increasing the temperature reduces the viscosity of the solution and increases the rate of diffusion of dye molecules [29].

The essential characteristic of the Langmuir isotherm can be expressed in terms of a dimensionless equilibrium parameter, such as the separation factor (or) equilibrium factor (R_L) used in the following equation [30]:

$$R_L=1/(1+bC_o) \qquad (4)$$

where b is the Langmuir constant and C_o is the initial concentration of the adsorbate in solution. This parameter indicates that isotherm will be shaped according to the following adsorption characteristics: RL > 1 unfavourable; RL = 1 corresponds to linear; 0 < RL < 1 is favourable and RL =0 is irreversible [30] as given in Table 1. It can be seen that the adsorption of RR120 and RB5 onto cotton fiber will be favorable.

The Freundlich isotherm model is also used to fit the experimental data for the adsorption of RR120 and RB5 dyes on cotton at pH 10.02 and 11.01, respectively at different temperatures (40-90 ºC) and in presence of different salts (SS, SE and SC).

The empirical Freundlich equation based on a heterogeneous surface is given by Eq. (5)[31]:

$$q_e=Q_fC_e^{1/n} \qquad (5)$$

where Q_f is roughly an indicator of the adsorption capacity and $1/n$ of the adsorption intensity.

The linear form of the model can be expressed as follows:

$$\ln q_e=\ln Q_F+1/n(\ln C_e) \qquad (6)$$

C_e, q_e are the dye concentration (mg/l) and the amount of dye adsorbed per gram of cotton (mg/g cotton) at equilibrium, respectively. Q_f and n are the Freundlich constants which are related to adsorption capacity and intensity, respectively.

Linear plots of ln q_e versus ln C_e (Figure 7) showed that the adsorption follows the Freundlich isotherm model well with high correlation coefficients ($r > 0.99$) (Table 1).

The various constants associated with the isotherm are the intercept, which is roughly an indicator of sorption capacity (Q_f) and the slope ($1/n$) sorption intensity. The values are recorded in Table 1. The Freundlich isotherm has been illustrated to be a special case of heterogeneous surface energies but it can be easily extended to this case. The magnitude of the exponent $1/n$ gives an indication of the favorability and capacity of the adsorbent/adsorbate system. Values where $n > 1$ represent favorable adsorption conditions. In most cases the exponent between $1 < n < 10$ shows beneficial adsorption [30, 32, 33].

Based on the correlation coefficient (r_2) shown in Table 1 the adsorption isotherm can be better described by Langmuir equation. Also, the Langmuir equation yields a better fit of the experimental data than the Freundlich equation. The applicability of the Langmuir isotherm suggests monolayer coverage of the two reactive dyes on surfaces of cotton fiber.

Moreover, Table 1 shows that the presence of organic salts (SE and SC) significantly enhance the dye uptake (high Q, b and Q_f values) onto cotton fiber compared with the results obtained in aqueous and in the presence of inorganic salt (SS). Thus, presence of organic salts (SE and SC) is an alternative way to subsequently increase the affinity between RR120 and RB5 dyes and the cotton fiber.

3.8. Adsorption kinetics

In order to investigate the mechanism of adsorption and potential rate controlling steps such as mass transfer and chemical reaction, processes are used to test experimental data. Many models such as homogeneous surface diffusion model (also known as pore and diffusion model) have been extensively utilized for batch reactors to describe the transport of solutes inside adsorbent particles; however, the mathematical complexity of there models makes them inconvenient for practical use. Any kinetic or mass transfer representation is likely to be global. From a system design viewpoint, a lumped analysis of kinetic data is hence sufficient for practical operation [14, 19, 21, 34-36]. The Lagergren's equation, pseudo first-order equation, is given as [36]:

$$(dq_t/dt)=k_1(q_e-q_t) \qquad (7)$$

after integration by applying the boundary conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, Eq. (7) becomes:

$$\ln(q_e/(q_e-q_t)=k_1t \qquad (8)$$

Eq.(8) can be rearranged to obtain a linear form:

$$\ln(q_e-q_t)=\ln q_e-k_1t \qquad (9)$$

where (q_e)and (q_t) are the amounts of dye sorbed at equilibrium and at time (t) (mg/g cotton), respectively, and (k_1) is the equilibrium rate constant of pseudo-first-order sorption (min^{-1}).

A straight line of ln(qe-qt) versus t (Figure 8) in presence of 50 g/l SS and 20 g/l sodium carbonate, suggests the applicability of this kinetic model to fit the experimental data. The data obtained from the adsorption experiment conducted during the present investigation is fitted using different temperature (40-90ºC), different organic salts (SE and SC) and different dye concentrations (24.16 - 1183.40mg/l for RR120 and 20.08 - 1004.67mg/l for RB5).

The rate constants (k_1) using the Lagergren equation, the equilibrium adsorption density (q_e) calculated from the plots and its corresponding regression correlation coefficient values are shown in Tables 2 and 3.

The equilibrium adsorption capacity, q_e, is required to fit the data, but in many cases q_e remains unknown due to slow adsorption processes. For this reason, it is necessary to obtain the real equilibrium adsorption capacity, q_e, by extrapolating the experimental data to $t = \infty$ or by using a trial and error method. Also, in many cases, the first-order equation of Lagergren does not fit well for the whole range of contact time and is generally applicable over the initial stage of adsorption processes [19, 21, 37].

On the other hand, a pseudo second-order equation based on equilibrium adsorption [19, 21, 35, 37 and 38] is expressed as:

$$dq_t/dt=k_2(q_{e2}-q_t)^2 \qquad (10)$$

Integrating Eq. (10) for the boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$ gives [39]:

$$1/(q_{e2}-q_t)=1/q_t+k_2t \qquad (11)$$

where k_2 (g/mg min) is the rate constant of second-order adsorption. If second-order kinetics are applicable, the plot of t/qt versus t should show a linear relationship. There is no need to know any parameter beforehand and q_{e2} and k_2 can be determined from the slope and intercept of the plot (Figure 9). Also, this procedure is more likely to predict the behavior over the whole range of adsorption and is in agreement with chemical sorption being the rate-controlling step [21, 37], which may involve valency forces through sharing or exchange of electrons between dye anions and adsorbent. The calculated q_{e2} and k_2 values for RR120 and RB5 at different temperature, different dye concentration and different salts are listed in Tables 2 and 3.

In order to analyze the adsorption kinetics for the two reactive dyes, the pseudo first- and second-order kinetic models are used to analyze the data. Figure 8 shows a plot of linearised form of the pseudo first-order model at 113.366mg/l and 110.011mg/l concentrations of RR120 and RB5, respectively in presence of 50g/l SS and 20g/l sodium carbonate concentration used for fixation for the initial 120 min of adsorption. The slopes and intercepts of plots of ln(qe - qt) versus t are used to determine the first-order rate constant k_1 and equilibrium adsorption density q_{e1}. Tables 2 and 3 list the calculated results with the correlation coefficients. The calculated q_e values obtained from the first-order kinetic model do not give reasonable values, which are different from experimental q_e values. This finding suggests that the adsorption of reactive dyes onto cotton fiber is not a first-order reaction.

The plot of the linearised form of the second-order model at 113.366mg/l and 110.011mg/l concentrations of RR120 and RB5, respectively in presence of 50g/l SS and 20g/l sodium carbonate concentration used for fixation are shown in Figure 9. The straight lines in plot of t/qt versus t show good agreement of experimental data with the second-order kinetic model for the two dyes. The slopes and intercepts of plots of the t/qt versus t are used to calculate the k_2 and q_{e2}. The values of the parameters k_2 and calculated and experimental q_e and of correlation coefficients are also presented in Tables 2 and 3. The correlation coefficients for the second-order kinetic model are greater than 0.998 for the two dyes. The calculated q_{e2} values also agree very well with the experimental data in the case of pseudo second-order kinetics. These results suggest that each of the dye sorption systems is not a first-order reaction and that the second-order model, based on the assumption that the rate limiting step may be chemisorption involving valence forces through sharing or exchange of electrons [12].

3.9.Adsorption mechanism

The dye sorption is usually governed by either the liquid phase mass transport rate or the intra-particle mass transport rate [12]. However, most of the adsorption processes may be described by either the external mass transfer (boundary layer diffusion) or intraparticle diffusion model. The later is given by the Weber–Morris equation [40, 41].

$$q_t=k_i t^{1/2} \qquad (12)$$

where the parameter k_i is the diffusion coefficient value, t the time and q_t is the amount of dye adsorbed. Figure 10 shows the data fitting to the above equation for RR120 and RB5 dyes, whereas, the diffusion coefficient rate values, k_i, obtained from this equation are tabulated in Tables 2 and 3 for the two dyes investigated in the present study.

The intraparticle diffusion constants (k_i) values are obtained from the slope of the straight line portions of plot of q_t versus $t^{1/2}$ for various RR120 and RB5 concentrations and solutions temperatures as shown in Figure 10 and Tables 2 and 3. It is observed that intraparticle rate constant values (k_i) increase with initial dye concentration. The observed increase in k_i values with increasing initial dye concentration in different salts (SS, SE, and SC) at pH 10.02 and 11.01 and L:R 1:30 can be explained by the growing effect of driving force resulted in reducing the diffusion of dye species in the boundary layer and enhancing the diffusion in the solid [42]. Also, as show in Tables 2 and 3, increasing the temperature promote the pore diffusion in sorbent particles (cotton fabric) and enhance the intraparticle diffusion rate. It is likely that a large number of ions diffuse into the pore before being adsorbed [29].

Figure 10 shows that the adsorption plots of cotton fiber are not linear over the whole time range and can be separated into a few linear regions. This may reveal that there are two or three adsorption stages taking place. Lorenc-Grabowska and Gryglewicz [43] explained such multi-linearity stages that the initial portion can be attributed to external surface adsorption that the adsorbate diffuses through the solution to the external surface of the adsorbent or the boundary layer diffusion of solute molecules, where the adsorption rate is high. The second portion illustrates the gradual adsorption stage, where intra-particle diffusion rate is rate-controlling. The last portion refers to the final equilibrium stage in which the intra-particle diffusion starts to slow down and level out as the extremely low dye concentration remains in the solution or maximum adsorption was attained. Generally, when adsorption steps are not dependent of one another; the plot of q_t against $t^{1/2}$ should give two or more intercepting lines depending on the actual mechanism [44]. The intra-particle diffusion plots of the two dyes provide a linear relationship; however, none of the lines passed through the origin. This indicates that the intraparticle diffusion is involved in the adsorption process but not the only rate-controlling step. That is, some other mechanisms such as complexation or ion-exchange may also control the rate of adsorption [45, 46].

3.10. Activation Parameters

The pseudo second-order model and intraparticle diffusion model are identified as the best kinetic models for the adsorption of RR120 and RB5 onto cotton fabric. Accordingly, the pseudo second-order rate constants (k_2) and intraparticle diffusion rate constants (k_i) are adopted to calculate the activation energy of the adsorption process of reactive dyes onto cotton fabric using Arrhenius equation (13) [29, 47]:

$$\ln k=\ln A-E_a/RT \qquad (13)$$

where k, refer to either the rate constants (k_2) of pseudo second- order model or intraparticle diffusion rate constants (k_i) of intraparticle diffusion model, E_a is the activation energy of sorption (kJ/mol), R is the gas constant (8.314 J/mol K), T is the absolute temperature (^{o}K) and A the Arrhenius factor which is a temperature independent factor, respectively. The activation energy is determined from the slope of the plot of $\ln k_2$ or $\ln k_i$ versus $1/T$ at pH 10.02 and 11.01 and L: R 1:30 in aqueous medium and in presence of optimum concentration from different salts (SS), (SE) and (SC) with constant initial dye concentrations 113.366 and 110.011 for RR120, and RB5 respectively (Figures 11 and 12). The calculated activation energy values are listed in Tables 4 and 5.

Moreover, the enthalpy ($\Delta H^{\#}$) and entropy ($\Delta S^{\#}$) of activation are calculated using the Eyring Equation (14) [48, 49]:

$$\mathrm{Ln}(k/T)=\ln(K_b/h)+\Delta S^{\#}/R-\Delta H^{\#}/RT \qquad (14)$$

where (k_b) and (h) refer to Boltzmann's constant and Planck's constant, respectively. The enthalpy ($\Delta H^{\#}$) and entropy ($\Delta S^{\#}$) of activation are calculated from the slope and intercept of the plot of ln(k/T) versus 1/T.

Gibbs energy of activation ($\Delta G^{\#}$), can be written in terms of enthalpy and entropy of activation (Equation 15) [50- 52]:

$$\Delta G^{\#}=\Delta H^{\#}-T\Delta S^{\#} \qquad (15)$$

The calculated values of ($\Delta G^{\#}$), ($\Delta H^{\#}$) and ($\Delta S^{\#}$) for RR120 and RB5 with initial dye concentrations 113.366mg/l and 110.011mg/l and L.R. 1:30 in aqueous medium, in presence of 50g/l salt concentration (SS) and 20g/l sodium carbonate concentration used for fixation at pH 10.02 and 11.01 and in presence of 40g/l add at pH 9.52 and 25g/l add at pH 8.31 for SE and SC, respectively (Figure 13 and 14) are listed in Tables 4 and 5. From Tables 4 and 5, the positive $\Delta G^{\#}$ value suggests that adsorption reactions require energy to convert reactants into products. The positive value of $\Delta H^{\#}$ confirms the endothermic process, meaning the reaction consume energy. The negative value of $\Delta S^{\#}$ indicates that the adsorption leads to order through the formation of activated complex suggesting that RR120 and RB5 adsorption on cotton fiber surface is an associated mechanism. Also the negative value of $\Delta S^{\#}$ normally reflects that no significant change occurs in the internal structure of the adsorbent during the adsorption process [53, 54].

The magnitude of the activation energy (E_a) yields information on whether the adsorption process is mainly physical or chemical. Unuabonah *et al.* [55] reported that the activation energy of physisorption is normally not more than 4.20kJ/mol. Consequently, the activation energies (E_a) for the pseudo second-order kinetics and intraparticle diffusion kinetics listed in Tables 4 and 5, for RR120 and RB5 are energetically favorable with different salts and the adsorption process is a combination of chemical and diffusion processes [56].

4. Conclusion

This investigation examined the equilibrium and the dynamic adsorption of two reactive dyes (C.I. Reactive Red 120 (RR120) and C. I. Reactive Black 5 (RB5)) onto cotton fiber. The adsorption capacity is determined at different operation parameters that affect the adsorption of RR120 and RB5 onto cotton fiber (initial dye concentration, pH, effect of inorganic salt (sodium sulphate (SS)) and organic salts (sodium edate (SE) and sodium citrate (SC)) and temperature. The adsorbed amount of RR120 and RB5 increased with increasing dye concentration, pH and temperature. Moreover, presence of SE and SC increases the adsorbed amount. The adsorption of RR120 and RB5 onto cotton fiber in presence of SE and SC was successively achieved, and these results are also promising for the use SE and SC to increase adsorption capacity and offer the potential as an exhausting and fixing agent for reactive dyeing of cotton.

The data obtained from adsorption isotherms are well fitted to Langmuir model. The applicability of the Langmuir isotherm suggests monolayer coverage of the two reactive dyes on surfaces of cotton fiber. The results obtained in batch adsorption of RR120 and RB5 onto cotton fiber showed that the adsorption kinetics can be explained by a second order equation better than Lagergren's first order.

Kinetic studies showed that adsorption profiles of all materials followed pseudo-second order model with multi-step diffusion process. The values of k_2, $q_{e,exp}$ and $q_{e,cal}$ all increased with the temperature, suggesting that increasing the temperature increased the adsorption capacity and the adsorption rate. The regression results of the intraparticle diffusion model suggested that intraparticle diffusion is not the only rate-controlling step. The activation energies (E_a) for the pseudo second-order kinetics and intraparticle diffusion kinetics for RR120 and RB5 are energetically favorable with different salts at different dye concentrations and the adsorption process is a combination of chemical and diffusion processes.

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Table 1: Langmuir and Freundlich isotherm constants of adsorption of RR120 and RB5 onto cotton fabric at different temperatures, and different salts.

Salt add	Temp °C	RR120							RB5						
		Langmuir isotherm				**Freundlich isotherm**			**Langmuir isotherm**				**Freundlich isotherm**		
		Q (mg/g)	b (l/mg)	R_L	r	Q_f (mg/g)	n	r	Q (mg/g)	b (l/mg)	R_L	r	Q_f (mg/g)	n	r
Aqueous and pH 10.02	40	11.363	1.258	0.0069	0.995	9.207	1.069	0.999	6.221	1.977	0.0046	0.996	8.068	1.062	0.996
	50	11.627	1.387	0.0063	0.996	10.708	1.058	0.999	7.751	1.914	0.0047	0.999	9.825	1.081	0.999
	60	12.987	1.327	0.0066	0.996	11.279	1.072	0.999	8.064	1.992	0.0045	0.995	11.100	1.102	0.999
	70	16.129	1.247	0.0070	0.996	12.705	1.081	0.999	11.764	1.990	0.0046	0.998	12.974	1.074	0.998
	80	25.440	1.611	0.0054	0.997	15.471	1.075	0.999	12.870	1.710	0.0053	0.999	15.104	1.076	0.998
	90	19.960	1.302	0.0067	0.996	13.971	1.097	0.999	6.335	1.569	0.0058	0.997	8.068	1.063	0.998
[SS] = 50g/l, [Na_2CO_3] = 20g/l and pH 10.02(RR120) and 11.01 (RB5)	40	15.625	2.560	0.0034	0.995	27.632	1.061	0.999	19.607	2.200	0.0041	0.999	34.109	1.092	0.999
	50	19.230	2.481	0.0035	0.996	31.249	1.091	0.999	21.739	2.550	0.0036	0.996	38.628	1.10٩	0.999
	60	22.222	2.703	0.0032	0.998	43.206	1.097	0.999	25.710	2.555	0.0036	0.999	46.525	1.362	0.999
	70	31.250	2.722	0.0032	0.996	57.569	1.126	0.999	30.300	3.076	0.0029	0.996	48.715	1.089	0.999
	80	42.372	2.971	0.0029	0.996	65.039	1.233	0.999	38.181	4.708	0.0019	0.999	53.037	1.084	0.999
	90	36.496	2.882	0.0030	0.995	60.805	1.171	0.999	15.625	2.501	0.0036	0.997	34.709	1.090	0.999
[SE] = 40g/l and pH 9.52	40	18.867	2.663	0.0033	0.995	33.148	1.076	0.999	18.841	1.306	0.0069	0.999	42.140	1.117	0.999
	50	21.786	2.508	0.0035	0.999	36.855	1.118	0.999	20.727	1.901	0.0047	0.998	42.948	1.200	0.999
	60	25.974	2.683	0.0032	0.996	49.205	1.111	0.999	22.727	2.528	0.0035	0.999	44.701	1.323	0.999
	70	33.337	2.800	0.0031	0.997	60.880	1.223	0.999	28.169	4.333	0.0020	0.999	50.856	1.063	0.999
	80	47.600	2.887	0.0030	0.997	67.897	1.477	0.999	35.250	5.600	0.0016	0.998	57.340	1.066	0.999
	90	40.650	2.827	0.0031	0.996	65.235	1.332	0.999	20.833	1.783	0.0050	0.999	38.321	1.069	0.999
[SC] = 25g/l and pH 8.31	40	22.220	2.743	0.0032	0.998	39.251	1.086	0.999	18.214	2.818	0.0032	0.998	57.454	1.091	0.999
	50	25.640	2.789	0.0031	0.996	42.034	1.119	0.999	21.739	3.771	0.0024	0.999	70.456	1.435	0.999
	60	37.735	2.366	0.0037	0.997	55.146	1.123	0.999	22.720	5.500	0.0016	0.996	73.699	1.556	0.999
	70	43.470	2.785	0.0031	0.996	70.809	1.411	0.999	29.411	6.571	0.0013	0.999	82.096	1.084	0.999
	80	51.282	3.251	0.0027	0.997	91.740	1.656	0.999	35.714	10.981	0.0008	0.997	92.210	1.086	0.999
	90	48.780	2.697	0.0032	0.996	82.105	1.519	0.999	32.758	2.153	0.0042	0.998	49.849	1.071	0.999

Table 2: Kinetic parameters for RR120 (113.366mg/l) and RB55 (110.011mg/l) at different temperatures and L.R. 1:30 by using different salts.

Salt add	**Temp. °C**	RR120										RB5									
			Pseudo first-order model			**Pseudo second-order model**				**Intraparticle diffusion mode**			**Pseudo first-order model**			**Pseudo second-order model**				**Intraparticle diffusion mode**	
		q_e,exp mg/g cotton	**q_{e1}, cal mg/g cotton**	**k_1 x10^2 min^{-1}**	r_1	**q_{e2}, cal mg/g cotton**	**k_2 x10^2g cotton/ mg min**	**h x10 mg/g cotton min**	r_2	**k_i x10 g/m min^{-1}**	r_i	**q_e,exp mg/g cotton**	**q_{e1}, cal mg/g cotton**	**k_1 x10^2 min^{-1}**	**r_1**	**q_{e2}, cal mg/g cotton**	**k_2 x10^2g cotton/ mg min**	**h x10 mg/g cotton min**	**r_2**	**k_i x10 g/m min^{-1}**	**r_i**
Aqueous and pH 10.02	40	1.192	1.367	2.471	0.944	1.256	0.0123	0.0194	0.942	0.178	0.996	1.627	1.085	2.581	0.999	1.507	1.790	0.4065	0.966	1.710	0.991
	50	1.272	1.271	2.523	0.904	1.308	0.0125	0.0214	0.905	0.188	0.992	1.868	1.507	3.762	0.999	1.611	1.891	0.4905	0.985	1.801	0.991
	60	1.266	1.351	2.669	0.971	1.385	0.013	0.0249	0.975	0.201	0.991	2.122	1.117	3.641	0.999	2.111	2.001	0.8913	0.990	1.911	0.992
	70	1.353	1.450	2.831	0.976	1.476	0.014	0.0305	0.976	0.215	0.987	1.709	0.668	2.191	0.999	1.425	1.591	0.3229	0.984	1.412	0.991
	80	1.553	1.174	2.842	0.963	1.553	0.015	0.0361	0.988	0.222	0.990	1.516	0.569	1.953	0.999	1.355	1.140	0.2093	0.965	1.161	0.997
	90	1.457	1.206	2.632	0.906	1.469	0.0145	0.0313	0.987	0.219	0.992	1.180	0.774	2.998	0.999	1.175	1.015	1.1401	0.961	1.002	0.998
[SS] = 50g/l, [Na_2CO_3] = 20g/l and pH 10.02(RR120) and 11.01(RB5)	40	2.125	1.599	2.415	0.959	2.309	0.0139	0.0742	0.998	0.179	0.990	1.997	2.161	3.852	0.999	1.982	3.203	1.58	0.993	2.011	0.996
	50	2.486	1.723	2.238	0.958	2.562	0.0171	0.1123	0.998	0.274	0.990	2.295	1.942	3.731	0.999	2.049	3.872	1.625	0.994	3.272	0.995
	60	2.833	2.413	2.471	0.980	2.849	0.0211	0.1713	0.997	0.355	0.987	2.795	1.827	3.922	0.999	2.451	4.803	2.885	0.996	4.531	0.995
	70	3.385	3.319	3.772	0.972	3.024	0.0230	0.2109	0.997	0.496	0.996	1.908	2.087	3.951	0.999	1.913	3.112	1.141	0.995	2.881	0.989
	80	3.905	3.765	4.366	0.961	3.445	0.0289	0.3431	0.999	0.653	0.992	1.652	0.602	3.182	0.999	1.601	3.009	0.792	0.994	2.431	0.997
	90	3.202	2.849	3.491	0.974	3.344	0.027	0.3020	0.998	0.526	0.991	1.424	0.493	3.623	0.999	1.505	2.815	0.6376	0.999	2.012	0.986
[SE] = 40g/l and pH 9.52	40	2.557	3.455	4.192	0.992	2.793	0.0121	0.0944	0.997	0.197	0.999	2.048	2.591	4.339	0.999	2.066	3.003	1.280	0.995	2.212	0.994
	50	2.689	3.589	4.821	0.991	2.732	0.0164	0.1226	0.998	0.269	0.996	2.507	3.126	5.692	0.999	2.151	3.811	1.762	0.998	3.422	0.996
	60	3.004	5.054	5.211	0.990	3.125	0.0195	0.1912	0.997	0.413	0.991	2.903	3.346	5.366	0.999	2.672	4.732	3.377	0.997	4.650	0.993
	70	3.422	6.855	6.330	0.981	3.215	0.0235	0.2429	0.996	0.525	0.991	1.938	2.721	5.106	0.999	1.993	2.951	1.171	0.998	3.522	0.995
	80	4.071	7.652	6.594	0.982	3.924	0.0274	0.4220	0.995	0.677	0.990	1.893	1.121	4.428	0.999	1.801	2.811	0.9115	0.999	2.752	0.995
	90	3.866	6.372	5.735	0.984	3.767	0.0226	0.3207	0.995	0.584	0.992	1.802	1.717	4.668	0.999	1.708	2.631	0.7672	0.998	2.220	0.996
[SC] = 25g/l and pH 8.31	40	2.734	3.431	4.210	0.980	3.100	0.0100	0.966	0.998	0.219	0.996	2.269	4.567	6.618	0.999	2.449	2.310	1.379	0.992	3.002	0.998
	50	2.929	3.438	4.137	0.945	3.133	0.0140	0.1381	0.998	0.292	0.997	2.806	2.418	4.596	0.999	2.644	2.962	2.069	0.997	4.296	0.996
	60	3.322	4.473	4.842	0.972	3.424	0.0174	0.2040	0.997	0.442	0.992	3.223	3.455	5.291	0.999	3.025	3.881	3.550	0.995	6.091	0.993
	70	3.680	6.246	6.003	0.974	3.495	0.0219	02677	0.996	0.563	0.989	2.385	2.974	5.199	0.999	2.381	2.096	1.188	0.998	3.752	0.994
	80	4.320	7.308	6.076	0.978	4.151	0.0260	0.4488	0.997	0.178	0.993	2.072	2.247	6.072	0.999	2.188	1.948	0.9326	0.998	3.071	0.996
	90	3.875	7.344	6.089	0.977	3.923	0.021	0.3232	0.996	0.188	0.997	2.059	2.017	2.581	0.999	2.109	1.914	0.8513	0.996	2.642	0.997

Table 3: Kinetic parameters for RR120 and RB5 with different initial dye concentrations at temperature 80^{o}C and 60^{o}C and L.R. 1:30 by using different salts.

Salt add	[Dye] mg/l	RR120										[Dye] mg/l	RB5									
		q_e,exp mg/g cotton	Pseudo first-order model			Pseudo second-order model				Intraparticle diffusion mode			q_e,exp mg/g cotton	Pseudo first-order model			Pseudo second-order model				Intraparticle diffusion mode	
			q_{e1}, cal mg/g cotton	k_1 x10^2 min^{-1}	r_1	q_{e2}, cal mg/g cotton	k_2 x10^2 g cotton/ mg min	h x10 mg/g cotton min	r_2	k_i x10 g/m min^{-1}	r_i			q_{e1}, cal mg/g cotton	k_1 x10^2 min^{-1}	r_1	q_{e2}, cal mg/g cotton	k_2 x10^{2}g cotton/ mg min	h x10 mg/g cotton min	r_2	k_i x10 g/m min^{-1}	r_i
Aqueous and pH 10.02	24.166	0.364	0.338	3.138	0.965	0.393	9.600	0.148	0.995	0.543	0.995	20.081	0.270	0.204	3.033	0.984	0.290	21.266	0.178	0.998	0.320	0.990
	51.366	0.863	0.860	3.162	0.966	0.905	7.511	0.614	0.993	1.303	0.994	50.216	0.656	0.448	2.930	0.950	0.684	11.469	0.532	0.998	0.921	0.998
	73.500	1.199	1.250	3.571	0.940	1.402	5.315	0.104	0.990	1.939	0.991	70.296	0.915	0.766	2.974	0.975	1.003	10.721	1.078	0.997	1.301	0.992
	113.366	1.553	1.854	3.915	0.931	1.553	1.50	0.368	0.988	2.531	0.990	110.011	1.833	1.117	3.642	0.975	1.591	9.028	2.285	0.991	2.561	0.992
	592.700	7.819	12.603	5.017	0.981	8.808	0.752	0.5834	0.982	14.241	0.992	502.227	5.996	4.567	3.211	0.942	5.476	1.727	5.178	0.994	8.432	0.998
	1183.40	14.582	21.242	4.343	0.961	14.230	0.522	1.057	0.960	27.091	0.998	1004.67	11.761	10.527	3.136	0.979	11.534	0.596	7.927	0.995	16.615	0.996
[SS] = 50g/l, [Na_2CO_3] = 20g/l and pH 10.02 (RR120) and 11.01 (RB5)	24.166	0.680	0..576	3.376	0.937	0.711	8.041	0.406	0.998	0.855	0.992	20.081	0.442	0.327	3.081	0.964	0.458	13.120	0.275	0.998	0.627	0.994
	51.366	1.705	1.336	3.132	0.944	1.805	3.211	1.042	0.997	2.116	0.993	50.216	1.084	0.682	3.119	0.947	1.062	7.402	0.834	0.998	1.321	0.997
	73.500	2.282	2.459	4.371	0.976	2.406	2.974	1.719	0.996	2.983	0.993	70.296	1.793	1.179	3.381	0.960	1.687	6.469	1.841	0.996	2.452	0.989
	113.366	3.905	3.766	4.366	0.961	3.448	2.824	3.352	0.999	6.468	0.992	110.011	2.295	1.827	3.921	0.977	2.451	4.542	2.727	0.996	3.411	0.995
	592.700	15.831	14.097	3.711	0.950	16.543	0.312	8.483	0.996	21.471	0.994	502.227	12.281	7.078	3.542	0.943	11.111	1.141	14.070	0.996	19.123	0.994
	1183.40	31.155	66.420	5.692	0.983	32.714	0.132	14.211	0.994	40.194	0.997	1004.67	20.930	18.878	3.907	0.970	21.039	0.400	17.723	0.997	32.682	0.997
[SE] = 40g/l and pH 9.52	24.166	0.751	0.776	4.161	0.990	0.806	6.462	0.419	0.996	0.905	0.989	20.081	0.462	0.515	4.922	0.981	0.482	12.671	0.294	0.996	0.679	0.993
	51.366	1.865	2.556	4.868	0.986	1.927	3.051	1.132	0.996	2.268	0.993	50.216	1.222	0.821	3.912	0.973	1.215	6.983	1.030	0.998	1.572	0.997
	73.500	2.502	4.185	5.377	0.980	2.590	2.880	1.932	0.998	3.081	0.994	70.296	1.947	1.754	5.162	0.987	1.796	5.997	1.932	0.998	2.774	0.992
	113.366	4.071	7.085	5.884	0.966	3.924	2.651	4.080	0.995	6.714	0.994	110.011	2.993	3.028	5.366	0.979	2.672	4.172	2.977	0.997	4.463	0.993
	592.700	17.130	29.606	5.551	0.981	18.801	0.249	8.832	0.995	22.321	0.997	502.227	12.176	15.752	5.932	0.978	11.906	0.851	12.048	0.996	19.776	0.997
	1183.40	33.198	90.919	7.074	0.951	34.611	0.124	14.861	0.995	42.801	0.998	1004.67	21.762	33.852	6.318	0.991	22.022	0.382	18.535	0.996	33.562	0.999
[SC] = 25g/l and pH 8.31	24.166	0.770	0.624	3.228	0.968	0.844	6.161	0.438	0.996	0.933	0.993	20.081	0.523	0.509	4.819	0.995	0.557	10.612	0.329	0.999	0.839	0.997
	51.366	1.927	2.321	5.020	0.990	2.136	2.541	1.158	0.997	2.321	0.991	50.216	1.296	1.881	6.023	0.991	1.334	6.111	1.087	0.997	1.623	0.998
	73.500	2.602	3.223	5.391	0.989	2.791	2.712	2.111	0.997	3.112	0.994	70.296	2.188	2.011	5.283	0.992	2.137	4.974	2.269	0.996	2.862	0.998
	113.366	4.320	4.645	4.996	0.992	4.150	2.581	4.443	0.997	7.094	0.992	110.011	3.423	3.129	5.291	0.993	3.025	3.711	3.404	0.995	5.001	0.993
	592.700	17.741	27.357	5.741	0.993	19.261	0.244	9.051	0.996	23.421	0.998	502.227	13.394	17.707	6.432	0.995	13.196	0.721	12.551	0.998	20.563	0.998
	1183.40	34.671	80.479	5.662	0.988	36.215	0.118	15.512	0.996	43.887	0.996	1004.670	23.758	49.008	7.769	0.991	25.055	0.305	19.203	0.997	33.811	0.991

Table 4: Activation parameters for pseudo second-order model of RR120 and RB5 with initial dye concentration 110.366mg/l and 110.011mg/l and L.R. 1:30 by using different salts.

Salt add	Temp. ^{o}C	RR120						RB5					
		$\Delta G^{\#}_2$ (kj/mol)	$\Delta H^{\#}_2$ (kj/mol)	$\Delta S^{\#}_2$ (j/mol K)	r_2	Ea_2 (kj/mol)	r_2	$\Delta G^{\#}_2$ (kj/mol)	$\Delta H^{\#}_2$ (kj/mol)	$\Delta S^{\#}_2$ (j/mol K)	r_2	Ea_2 (kj/mol)	r_2
Aqueous medium and pH 10.02	313	88.387	0.846	-279.682	0.971	3.607	0.998	87.253	2.120	-271.992	0.998	4.797	0.999
	323	91.183						89.973					
	333	93.980						92.693					
	343	96.777						95.413					
	353	99.574						98.132					
	363	102.371						100.853					
[S.S.] = 50g/l, [Na_2CO_3] = 20g/l and pH 10.02 (RR120) and 11.01 (RB5)	313	87.894	14.010	-236.059	0.988	16.771	0.991	85.746	14.848	-226.514	0.998	17.537	0.998
	323	90.254						88.012					
	333	92.615						90.277					
	343	94.975						92.542					
	353	97.326						94.807					
	363	99.696						97.072					
[S.E.] = 40g/l and pH 9.52	313	159.347	15.600	-231.819	0.991	18.361	0.994	85.896	17.043	-219.980	0.999	19.731	0.999
	323	90.477						88.96					
	333	92.795						90.296					
	343	95.113						92.496					
	353	97.432						94.695					
	363	99.750						96.895					
[S.C.] = 25g/l and pH 8.31	313	88.675	18.732	-223.463	0.988	21.493	0.991	86.612	19.958	-212.954	0.999	22.641	0.992
	323	90.910						88.742					
	333	93.154						90.871					
	343	95.379						93.001					
	353	97.614						95.130					
	363	99.849						97.260					

Table 5: Activation parameters for intraparticle diffusion model of RR120 and RB5 with initial dye concentration 113.366mg/l and 110.011mg/l and L.R. 1:30 by using different salts.

Salt add	Temp. ^{o}C	RR120						RB5					
		$\Delta G^{\#}_i$ (kj/mol)	$\Delta H^{\#}_i$ (kj/mol)	$\Delta S^{\#}_i$ (j/mol K)	r_i	Ea_i (kj/mol)	r_i	$\Delta G^{\#}_i$ (kj/mol)	$\Delta H^{\#}_i$ (kj/mol)	$\Delta S^{\#}_i$ (j/mol K)	r_i	Ea_i (kj/mol)	r_i
Aqueous medium and pH 10.02	313	81274	2.537	-251.556	0.981	5.211	0.995	81.381	2.103	-253.286	0.992	4.787	0.998
	323	83.789						83.914					
	333	86.305						86.447					
	343	88.820						88.980					
	353	91.336						91.512					
	363	93.851						94.045					

[S.S.] = 50g/l, [Na$_2$CO$_3$] = 20g/l and pH 10.02 (RR120) and 11.01 (RB5)	313	81.223	26.937	-173.438	0.996	29.698	0.997	80.898	32.582	-154.366	0.994	35.267	0.995
	323	82.957						82.442					
	333	84.691						83.985					
	343	86.426						85.529					
	353	88.160						87.073					
	363	89.894						88.616					
[S.E.] = 40g/l and pH 9.52	313	80.993	26.122	-175.309	0.995	28.884	0.996	80.666	29.594	-163.170	0.995	32.278	0.996
	323	82.746						82.297					
	333	84.449						83.929					
	343	86.252						85.561					
	353	88.006						87.193					
	363	89.759						88.824					
[S.C.] = 25g/l and pH 8.31	313	80.483	22.312	-185.851	0.979	25.073	0.983	79.887	27.264	-168.125	0.999	29.947	0.999
	323	82.341						81.568					
	333	84.200						83.249					
	343	86.058						84.930					
	353	87.917						86.612					
	363	89.775						88.293					

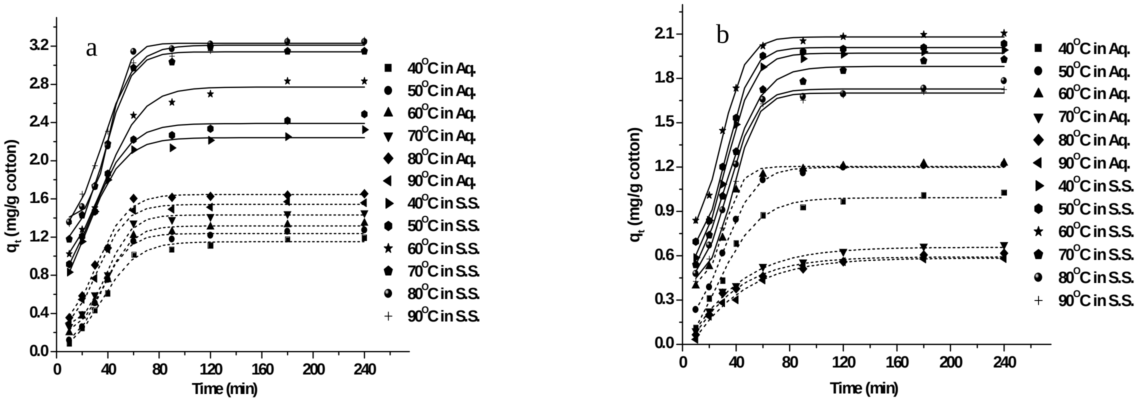

Figure 1: The effect of contact time and temperature of RR120 (a) and RB5 (b) on cotton fabric with initial dye concentration 113.366mg/l, 110.011mg/l and L.R. 1:30 at pH 10.02 and 11.01 in aqueous medium (…) and in presence of 50g/l salt concentration (SS) and 20g/l sodium carbonate concentration used for fixation (—).

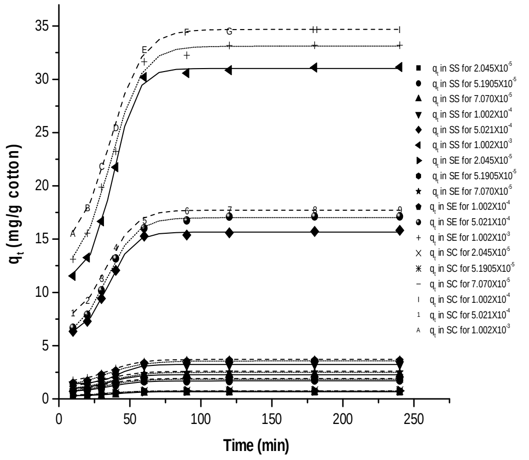

Figure 2: Effect of different RR120 concentrations on *q_t* at L.R.1:30 for 2 hours dyeing time in presence of 50g/l SS in presence of 20 g/l sodium carbonate used in fixation at pH 10.02, 40 g/l SE at pH 9.52 and 25 g/l SC at pH 8.31.

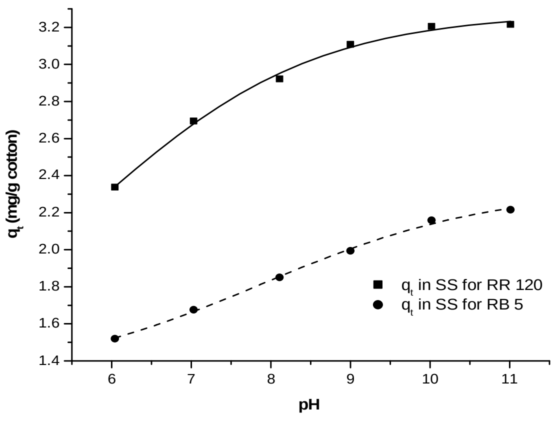

Figure 3: Effect of pH on *q_t* in presence of SS of RR120 (—) and RB5 (…..) on cotton fabric with initial dye concentration 113.366mg/l and 110.011mg/l for RR120 and RB5 respectively and L.R.1:30 for 2 hours dyeing time at temperatures 80 and 60 °C for RR120 and RB5 respectively.

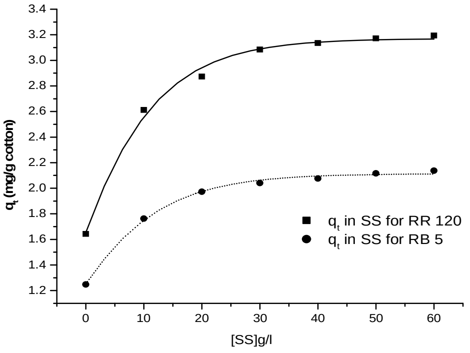

Figure 4: Effect of different SS concentrations on q_t of RR120 (—) and RB5 (…..) on cotton fabric with initial dye concentration 113.366mg/l and 110.011mg/l for RR120 and RB5 respectively, L.R.1:30 and pH 7.03 for 2 hours dyeing time at temperatures 80 and 60 ^oC for RR120 and RB5 respectively.

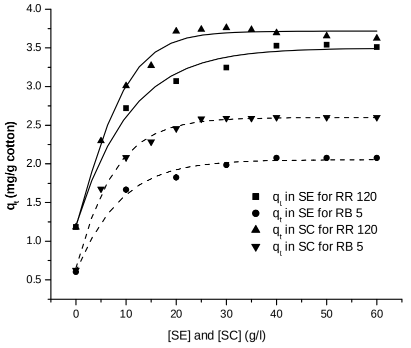

Figure 5: Effect of different SE and SC concentrations on q_t of RR120 (—) and RB5 (…..) on cotton fabric with initial dye concentration 113.366mg/l and 110.011mg/l for RR120 and RB5 respectively, L.R.1:30 and pH 7.03 for 2 hours dyeing time at temperatures 80 and 60 ^oC for RR120 and RB5 respectively.

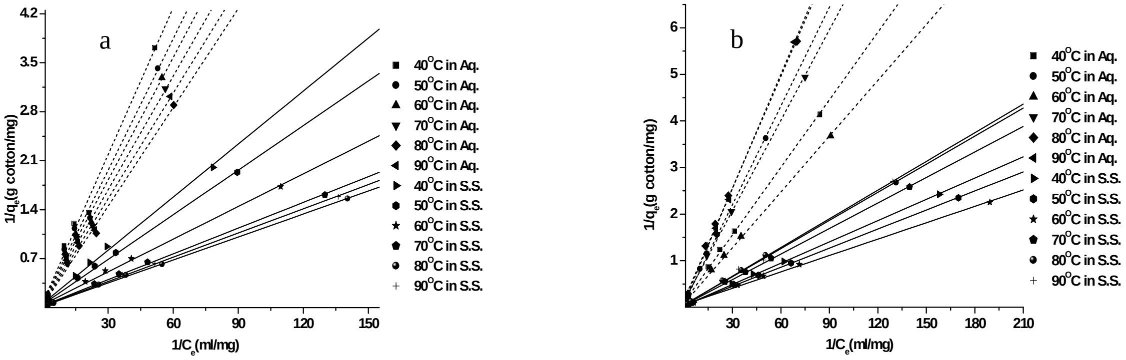

Figure 6: Langmuir adsorption isotherm of RR120 (a) and RB5 (b) onto cotton fabric at different temperatures with L.R.1:30 and pH 10.02 and 11.01 in aqueous medium (…) and in presence of 50g/l salt concentration (SS) and 20g/l sodium carbonate used for fixation (—).

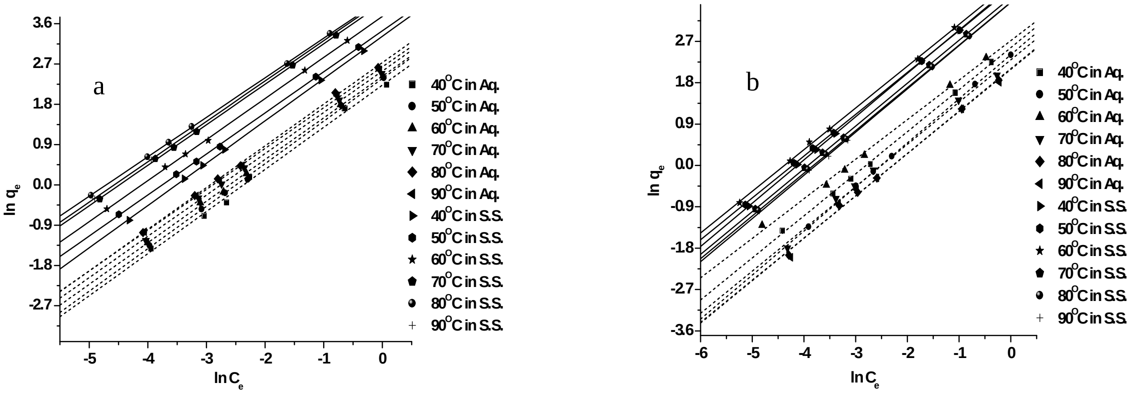

Figure 7: Freundlich adsorption isotherm of RR120 (a) and RB5 (b) onto cotton fabric at different temperatures with L.R.1:30 and pH 10.02 and 11.01 in aqueous medium (…) and in presence of 50g/l salt concentration (SS) and 20g/l sodium carbonate used for fixation (—).

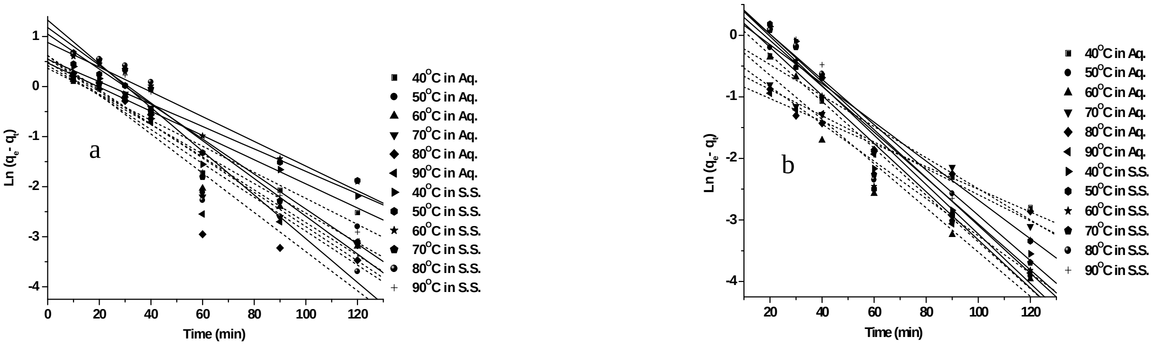

Figure 8: The pseudo first-order plot of RR120 (a) and RB5 (b) on cotton fabric at different temperatures with initial dye concentration 113.366mg/l and 110.011mg/l, L.R. 1:30 and pH 10.02 and 11.01 used in aqueous medium (…) and in presence of 50g/l salt concentration (SS) and 20g/l sodium carbonate concentration used for fixation (—).

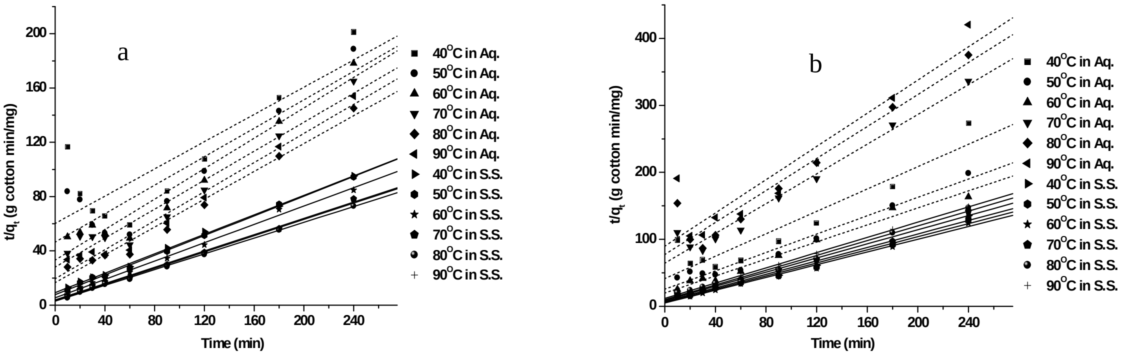

Figure 9: The pseudo second-order plot of RR120 (a) and RB5 (b) on cotton fabric at different temperatures with initial dye concentration 113.366mg/l and 110.011mg/l L.R. 1:30 and pH 10.02 and 11.01 used in aqueous medium (…) and in presence of 50g/l salt concentration (SS) and 20g/l sodium carbonate concentration used for fixation (—).

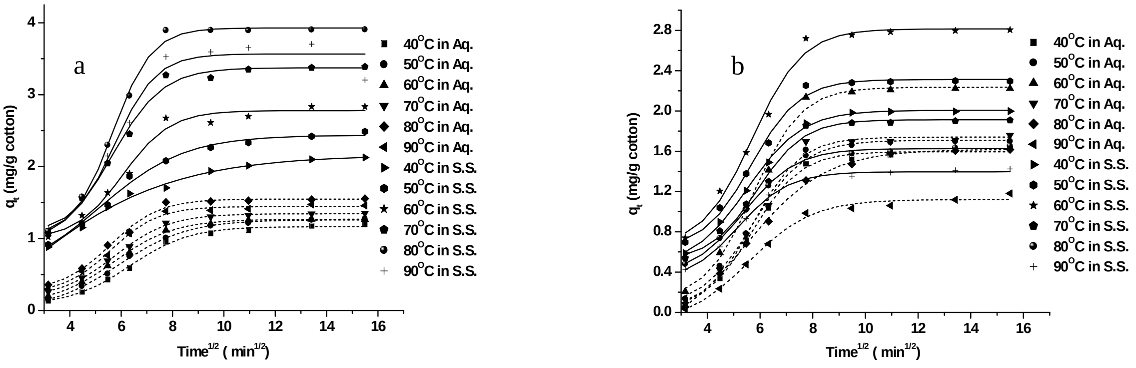

Figure 10: The intraparticle diffusion kinetics plot of RR120 (a) and RB5 (b) on cotton fabric at different temperatures with initial dye concentration 113.366mg/l and 110.011mg/l, L.R. 1:30 and pH 10.02 and 11.01 used in aqueous medium (…) and in presence of 50g/l salt concentration (SS) and 20g/l sodium carbonate concentration used for fixation (—).

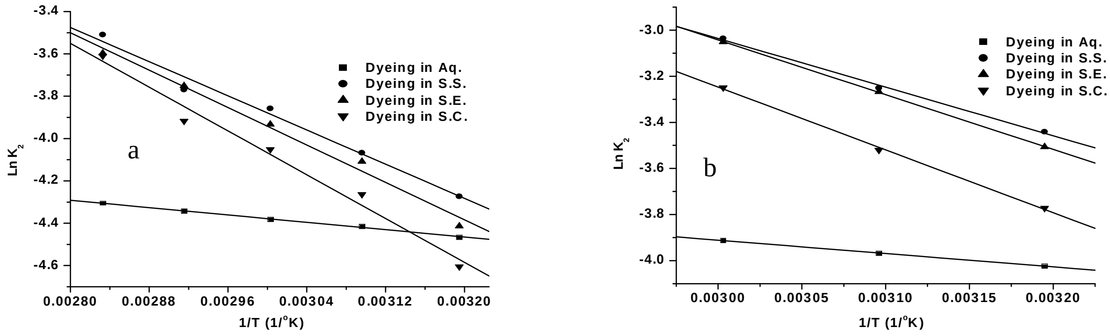

Figure 11: Arrhenius plot for pseudo second-order model of RR120 (a) and RB5 (b) with initial dye concentration 113.366mg/l and 110.011mg/l and L.R 1:30 in aqueous medium, in presence of 50g/l salt concentration (SS) and 20g/l sodium carbonate concentration used for fixation at pH 10.02 and 11.01 and in presence of 40g/l add at pH 9.52 and 25g/l add at pH 8.31 from SE and SC, respectively.

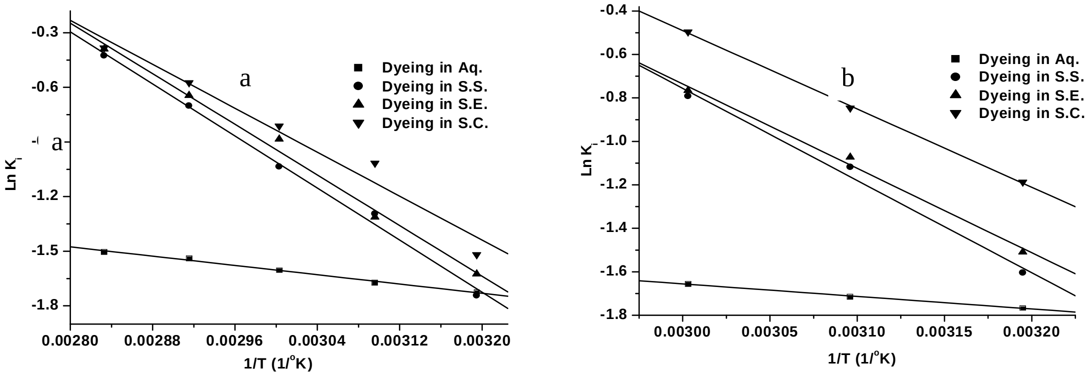

Figure 12: Arrhenius plot for intraparticle diffusion model of RR120 (a) and RB5 (b) initial dye concentration 113.366mg/l and 110.011mg/l and L.R. 1:30 in aqueous medium, in presence of 50g/l salt concentration (SS) and 20g/l sodium carbonate concentration used for fixation at pH 10.02 and 11.01 and in presence of 40g/l add at pH 9.52 and 25g/l add at pH 8.31 for SE and SC, respectively.

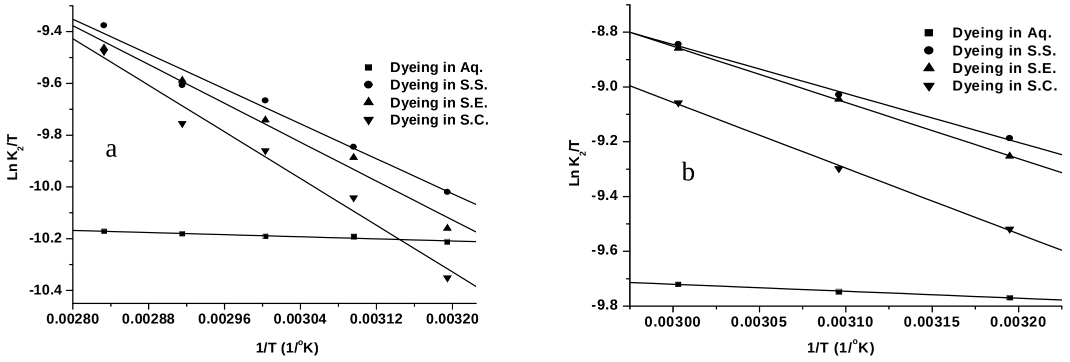

Figure 13: Eyring plot for pseudo second-order model of RR120 (a) and RB5 (b) with initial dye concentration 113.366mg/l and 110.011mg/l and L.R. 1:30 in aqueous medium, in presence of 50g/l salt concentration (SS) and 20g/l sodium carbonate concentration used for fixation at pH 10.02 and 11.01 and in presence of 40g/l add at pH 9.52 and 25g/l add at pH 8.31 for SE and SC, respectively.

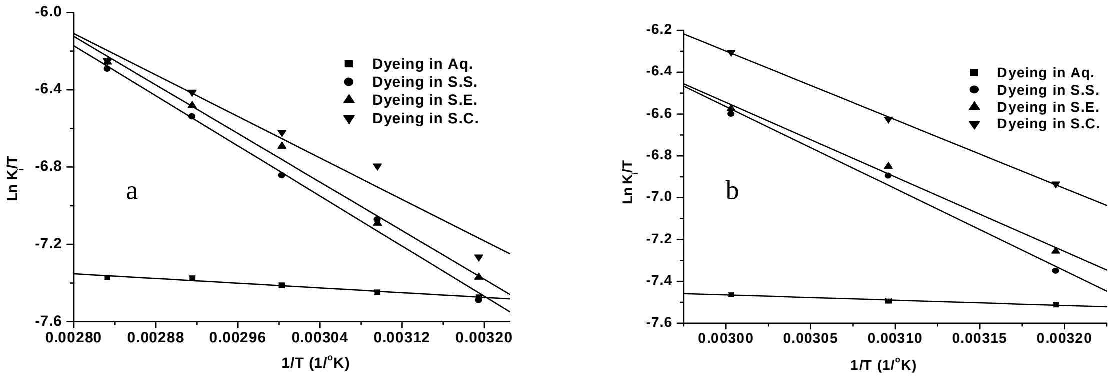

Figure 14: Eyring plot for intraparticle diffusion model of RR120 (a) and RB5 (b) with initial dye concentration 113.366mg/l and 110.011mg/l and L.R.1:30 in aqueous medium, in presence of 50g/l salt concentration (SS) and 20g/l sodium carbonate concentration used for fixation at pH 10.02 and 11.01 and in presence of 40g/l add at pH 9.52 and 25g/l add at pH 8.31 for SE and SC, respectively.

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