A study of the kinetics and equilibrium of decolorization for dyes using sorbent

J. Anitha[1] and Dr. CH. A. I. Raju[2]

[1]Research Scholar, [2]Assistant Professor

Department of Chemical Engineering, Andhra University,

Visakhapatnam – 530 003, AP, INDIA

Abstract:

Ricinus Communis, an inexpensive and environmentally acceptable sorbent, has been effectively used to decolorize textile colours from aqueous solutions. Originally, aniline blue was employed as a model textile dye. We looked at the impacts of contact time, pH, initial dye concentration, sorbent dose, and temperature. The following were discovered to be the best decolorization conditions: contact period 30 minutes, pH 5.0, beginning dye concentration 20 mg/L, sorbent dose 1.75 g, and temperature 30°C. The findings show that dye decolorization on the Ricinus Communis was aided by an acidic pH. This dye had a decolorization capability of 26.88 mg/g. Using experimental data, the Langmuir and Freundlich models were tested, and the experimental results revealed that the Langmuir equation fit better than the Freundlich equation. Various thermodynamic parameters, e.g.Changes in standard free energy, enthalpy, and entropy were also measured, and the reaction was discovered to be spontaneous and exothermic.

Keywords: Ricinus Communis, isotherms, kinetics and thermodynamic.

1.Introduction

Water is the greatest gift from nature because it is essential for the existence of many biotas on our planet [1] and because it is one of the finite natural resources, preserving its quality is a global demand that is rapidly increasing. Moreover, several water pollutants are linked to numerous human activities that are emitted into water bodies at the same time, creating serious declination in water requirements [2].Clean water scarcity will affect the agricultural, commercial, domestic, and industrial sectors. As a result of an intense contradiction between limited resources and economic progress, the current and future generations will pay a high price. Water contamination is caused by a variety of businesses, including machinery production, printing, textile [3], chemicals, electronics, and pharmaceuticals. They are responsible for the seepage of various contaminants into the aquatic environment as by-products, including dyes, heavy metals, phenols, pesticides, insecticides, and pharmaceuticals.

The presence of pollutants in water bodies over the World Health Organization's (WHO) and Environmental Agencies' allowed levels can have devastating consequences [4]. Human and animal health may be harmed as a result of these impacts (neural toxicity, carcinogenicity, and reproduction capabilities) Dyes and heavy metals are thought to be among the most harmful contaminants in water systems because they are mutagenic, immunogenic,

carcinogenic, and teratogenic [5].Discharging wastewater into bodies of water without first purifying it produces a slew of environmental and health issues for aquatic flora and wildlife, as well as human health. Purification of aqueous effluents polluted with harmful compounds has become a significant environmental burden in recent years [6]. Water purification from dyes and heavy metals becomes a critical requirement.It's a significant concern for the economy, the environment, and human health. To remove it from water systems, physical, chemical, and biological methods are used. Coagulation/flocculation [7], precipitation, and adsorption are examples of physical and chemical processes. It's past time to develop a more efficient, greener, and less expensive system for removing various impurities from water. Biosorption is a potential and cost-effective alternative to traditional methods. It is dependent on the use of bio-waste for the removal of various water pollutants [8].

2. Experimental procedure:

2.1 Chemicals

Analytical grade chemicals were used.

2.2 Stock solution of Rose Bengal

By dissolving a requisite amount of A.R. grade Rose Bengal dye in double distilled water, 1000 ppm of Rose Bengal solution was prepared. The solution was suitably diluted based on the requirement.

2.3 Preparation of Adsorbent

During the study of plant materials for their decolourization abilities apropos the Rose Bengal, it was perceived that the sorbent derived from leaves of Ricinus Communis have shown kinship towards the Rose Bengal.

2.4 Batch Experiments for Dye adsorption

The amount of dye decolourized and percentage removal of dye were calculated by using equation

Dye Removal % = $(C_o - C_e)/C_o \times 100$

Dye uptake $q_e = (C_o - C_e) \times V/W$

Where qe is the amount of dye decolourized at equilibrium, where Co (mg/L) is the RB initial concentration while Ce (mg/L) is the equilibrium concentration of RB. V (L) is the volume of RB solution, and W (g) is the weight of powder.

2.5 EquilibriumStudies

This was carried out in batch process by adding a pre-weighed amount of Ceiba pentandra and Ricinus Communis plant leaves, leaves to known volume of aqueous solution for a predetermined time interval in a magnetic stirrer. The procedures are adopted to evaluate the various parameters like agitation time, pH, initial concentration of Aniline blue and Rose Bengal in aqueous solution, dosage and temperature were explained below.

2.6 UV-Visible Spectroscopy

According to this technique various molecules hold splendid or clear light. The degree of transport light radiation concludes when light of explicit repeat is gone through the models. This spectrophotometer examination records the force of ingestion (A) or optical thickness (O.D) as a part of recurrence. Absorbance is clearly comparative with the way length, L, and the concentration, c, of the engaging species.

3. Results and discussions

3.1 Effect of Time:

The effect of contact time for the decolorization of RB dye by Ricinus Communis was considered for a period of 5-180 min for starting shading centralizations of 20 ppm at 303 K with pH 7 and measurement 0.5 g. As such, after 180 min of contact, a consistent state suppose was acknowledged and a semi equilibrium situation was recognized (Fig. 3.1). The contact time twist shows that the shading departure was fast in the underlying 30 min and the shading take-up of RB is 1.2 mg/g with 60%. The curves of contact time are single, smooth and relentless inciting submersion. These curves show the possible monolayer incorporation of shading outside of Ricinus Communis[9].
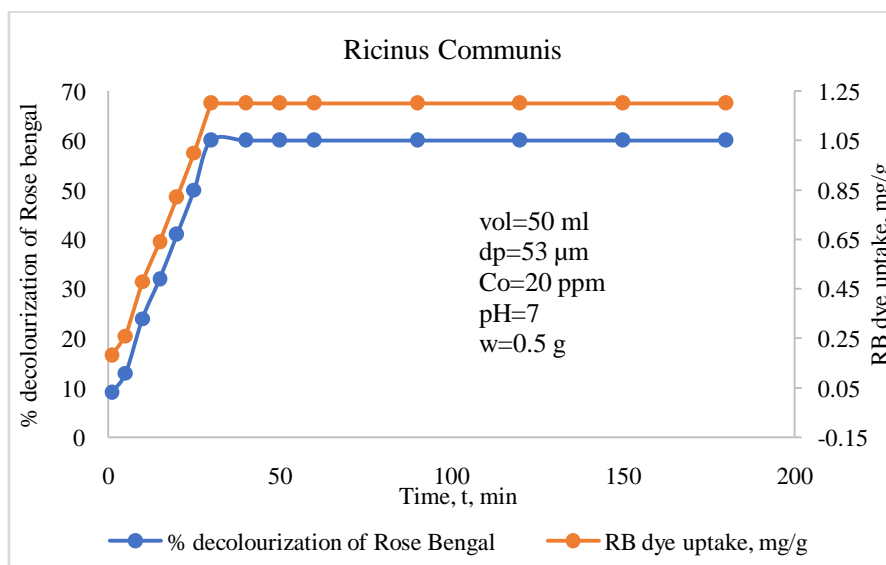

Fig. 3.1. Effect of time on % decolourization of Rose Bengal dye

3.2 Effect of Size:

Clearing is directly related with surface space of sorbent. Therefore, decolorization of RB tone was learned at five assorted particle sizes of RS (53, 75, 105,125 and 152 μm) keeping various limits as consistent. The consequences of variety of these particle sizes on decolorization rate are showed up in Fig. 3.2. It will in general be considered that to be the particle size lessens 53 to 152 μm, the decolorization of the shading augmentations 60 % to 40.5 % (1.18 to 0.81 mg/g). This is a result of a greater surface area that is connected with more modest particles. For bigger particles, the scattering security from mass vehicle is

higher and an enormous bit of the inner surface of the particles may not be utilized for decolorization and subsequently, the proportion of shading decolorized is pretty much nothing. According to the got results, the following examinations were finished using particle sizes under 53 μm[10].
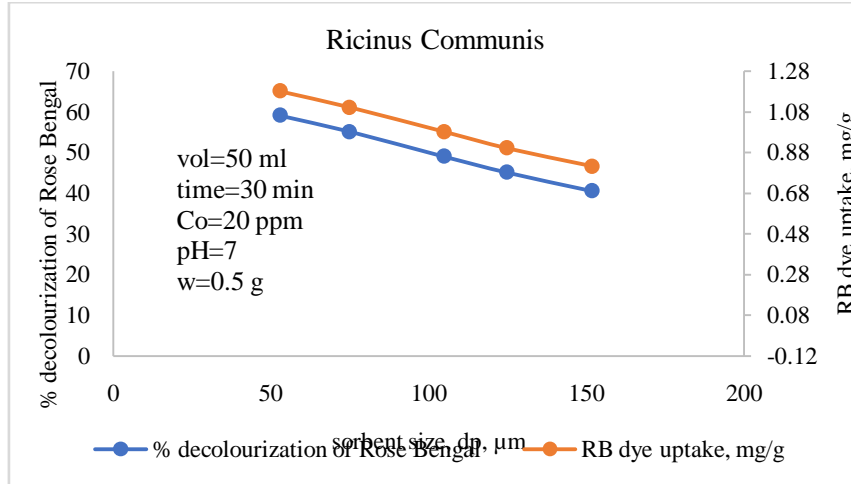

Fig. 3.2. Effect of size on % decolourization of Rose Bengal dye

3.3 Effect of pH

The adjustment of arrangement pH impacts the surface charge by protonation and deprotonation of the sorbent material. In present assessments, the effect of pH on the decolorization of Rose Bengal was concentrated over a pH extent of 2.0–8.0 for beginning shading obsession 20ppm at 303 K. The pH impact on the decolorization of RC on Rose Bengal were concentrated from 2 to 5 and saw that the decolorization increments from 54 to 75%, take-up is 1.08 to 1.5 mg/g shown in Fig. 3.3. This demonstrate that the RB surface become more negative to draw in the cationic RC molecule when expands the pH of the arrangement. Thus, decolorization expanded with increment of pH of the dye arrangement. This is the proof for the solid RC decolorization on fundamental surface of RB dye[11].
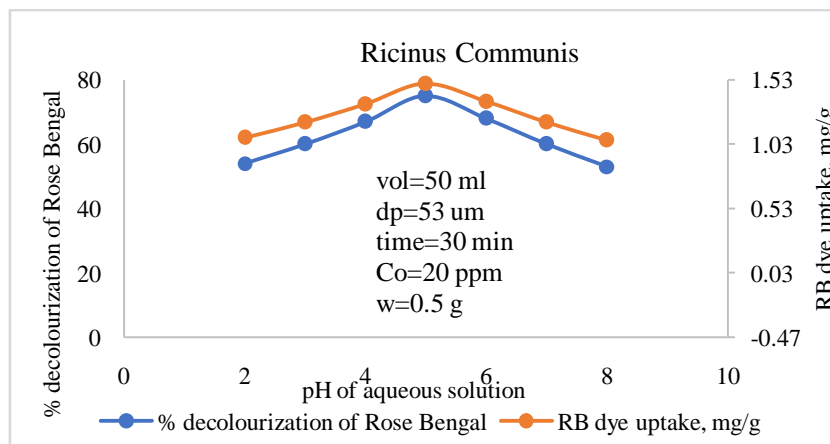

Fig. 3.3. Effect of pH on % decolourization of Rose Bengal dye

3.4 Effect of initial Concentration:

The impact of concentration of RC for most extreme take-up was concentrated between the focus ranges 20 to 200ppm. The examinations were completed at room temperature. The decolorization limit of the dye was discovered to be diminishes from 75% to 62.5 % with expanding the RC fixation (Fig. 3.4). The level of take-up diminishes with increment of RC focus might be because of the saturation of active sites with RC molecule. Consequently, decolorization diminishes with increment of RC concentrations. The initial dye concentration of an effluent is important since a given mass of sorbent material can only adsorb a fixed amount of dye. The effect of the initial of dye concentration factor depends on the immediate relation between the concentration of the dye and the available binding sites on a sorbent surface. The higher the concentration of the dye, the smaller the volume it can remove[12].
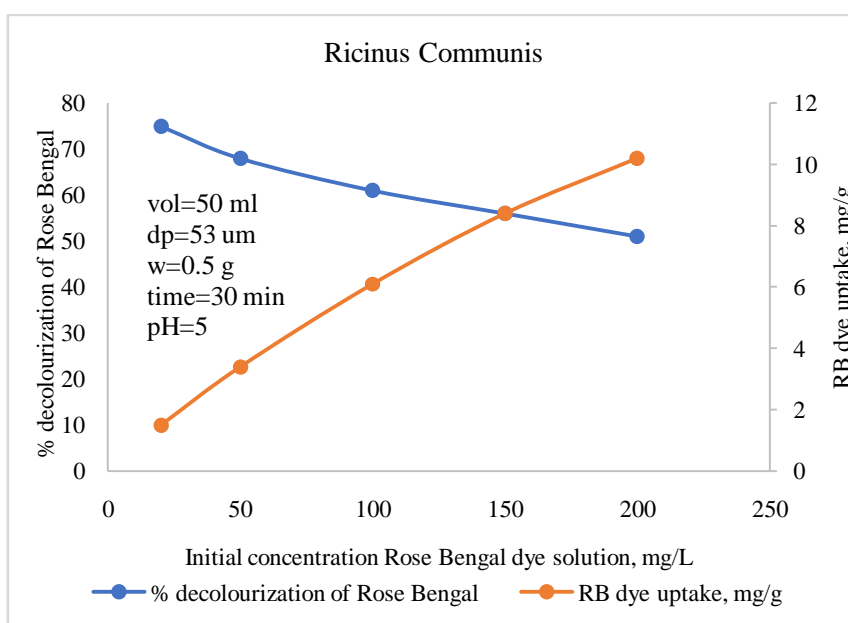

Fig. 3.4. Effect of concentration on % decolourization of Rose Bengal dye

3.5 Effect of Dosage

The effect of variety of sorbent entirety on the ejection of RB dye by RC is showed up in Fig. 3.5. Proportion of sorbent was varied from 0.5 to 4 g at 303 K RB dye concentration of 20 mg L^{-1} and shaken together until equilibrium time. It is apparent that the RB shading obsession in arrangement decreases with growing sorbent summarize to 35 g/L the decolorization limit of RC was 0.525 mg/g for a given beginning RB obsession. For the most part, the level of dye expulsion increments with expanding adsorbent dose. At first the pace of expansion in the percent dye expulsion has been discovered to be fast which eased back down as the portion expanded. Thusly, the bit of sorbent was fixed to 35 g/L for the subsequent examinations[13].
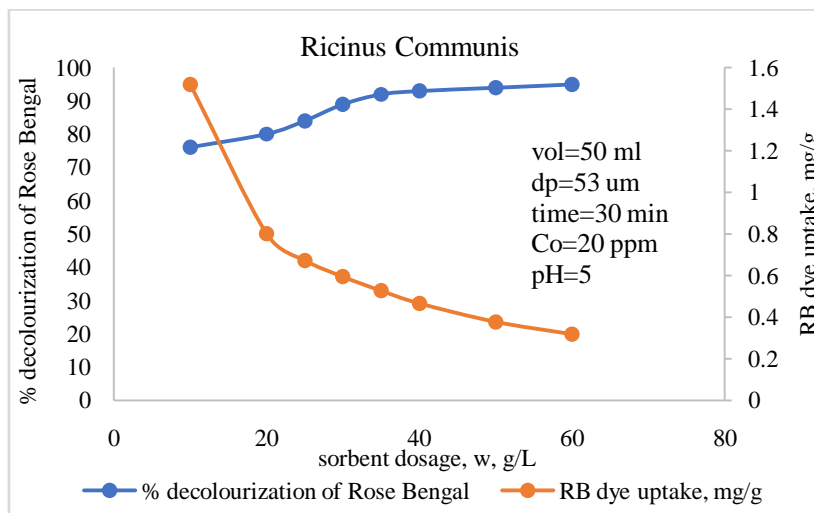
Fig. 3.5. Effect of dosage on % decolourization of Rose Bengal dye

3.6 Temperature:

The effect of temperature for the removal of RB on RC was studied for the concentration of RB dye solution 20 ppm in the range of 283 to 323 K (Fig. 3.6). The study of the temperature dependence of decolorization reactions gives valuable knowledge about the enthalpy and entropy changes during decolorization Temperature is an indicator for the decolorization nature whether it is an exothermic or endothermic process. If the decolorization capacity increases with increasing temperature, then the decolorization is an endothermic process. The adsorption increased 88 to 93% and uptake 0.586 to 0.62 mg/g when the temperature increases from 283 to 323 K. This indicate that the decolorization is endothermic[14].
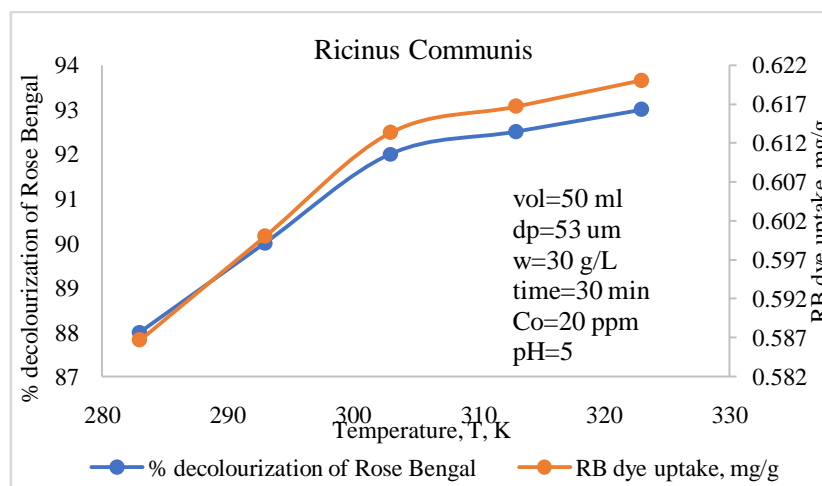

Fig. 3.6. Effect of temperature on % decolourization of Rose Bengal dye

3.7 Isotherms study:
3.7.1 Langmuir isotherm:
The Langmuir isotherm postulates monolayer decolourization on a uniform surface with a limited number of decolourization sites. Once a site is filled, no additional decolourization can occur at that site. The linear equation of the Langmuir isotherm model is described by Eq.

$q_e/c_e = 1/q_m\, b + c_e/q_m$

where qm is the maximum decolourization capacity (mg/g) and b is the Langmuir constant which related to decolourization rate. Values of qm and b are shown in Table 3.1. The attraction between sorbent and sorbate can be deduced by using separation factor, b, as shown in Eq.

$RL = 1\,/1 + b\, Co$

Langmuir isotherm is drawn for the present data and shown in Fig. 3.7. The equation obtained 'n' Ce/qe = 0.065 Ce + 3.4661 with a good linearity (correlation coefficient, $R^2 \sim 0.9811$) indicating strong binding of RoseBengalto the surface of Ricinus communis[15].
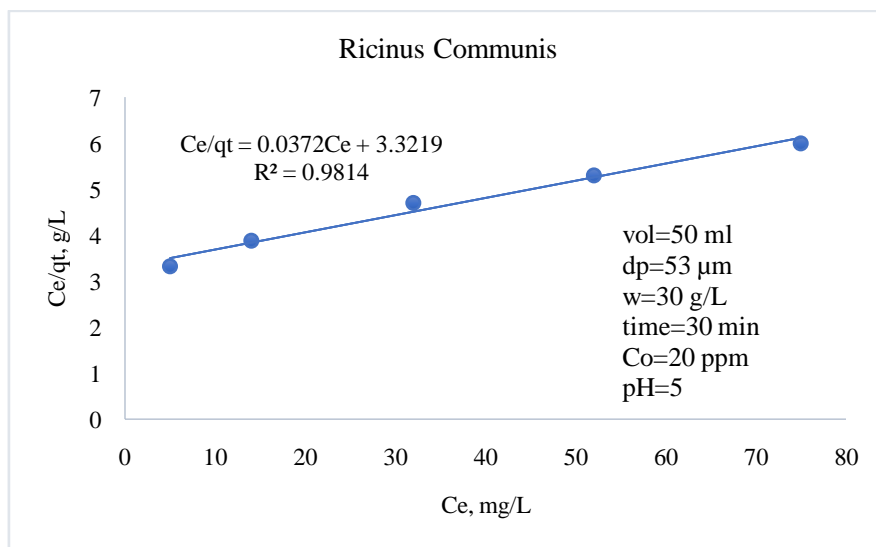

Fig. 3.7. Langmuir isotherm for % decolourization of Rose Bengal dye

3.7.2 Freundlich isotherm

This model is applied to decolourization on heterogeneous surfaces with the interaction between decolourized molecules. Application of the Freundlich equation suggests that decolourization energy exponentially decreases on completion of the decolourization concentration of Ricinus communis. This isotherm is an empirical equation and can be employed to describe heterogeneous systems as shown in Eq. (2).

$\ln qe = \ln Kf + 1/n \ln Ce$

where Kf is the decolourization capacity of sorbent, n value determines the degree of non-linearity between solution concentration and decolourization in this manner: if n = 1, then decolourization is linear; if n > 1, then decolourization is a chemical process; if n <1, then decolourization is a physical process.

Freundlich isotherm is drawn between log qe = 0.65 log Ce - 0.6091; log Ce and log qe in Fig. 3.8 for the present data. The resulting equation has a correlation coefficient of 0.9976.
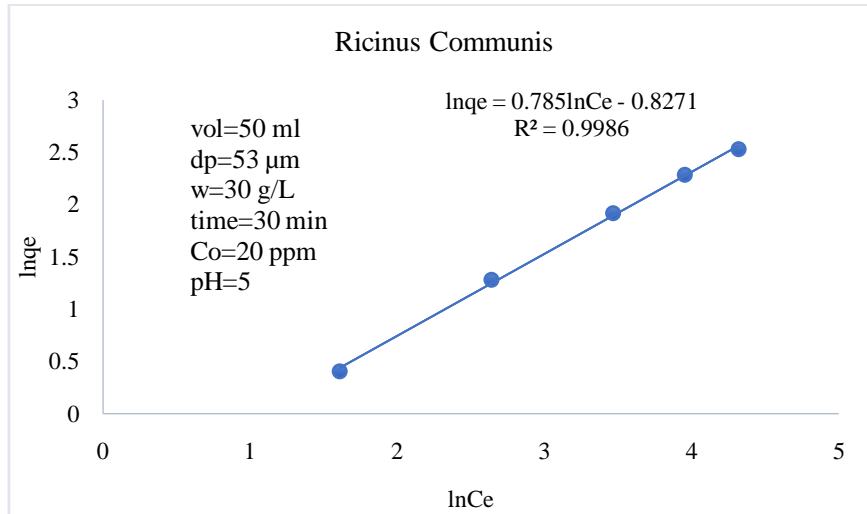
Fig. 8. Freundlich isotherm for % decolourization of Rose Bengal dye

3.7.3 Temkin Isotherm:

Temkin isotherm takes into consideration the indirect interaction between adsorbate molecules and assumes that the heat of decolourization of all molecules in the layer decreases linearly with coverage due to adsorbent–adsorbate interactions and that the decolourization is characterized by a uniform distribution of the binding energies up to a maximum binding energy. The Temkin isotherm model has been used in the linear form as shown in Eq.

$q_e = B \ln A + B \ln C_e$

where $B = RT/b$, b is the Temkin constant associated to heat of decolourization(J/mol), A is the Temkin isotherm constant (L/g), R is the universal gas constant (8.314) J/mol. K, and T is the absolute temperature (K).
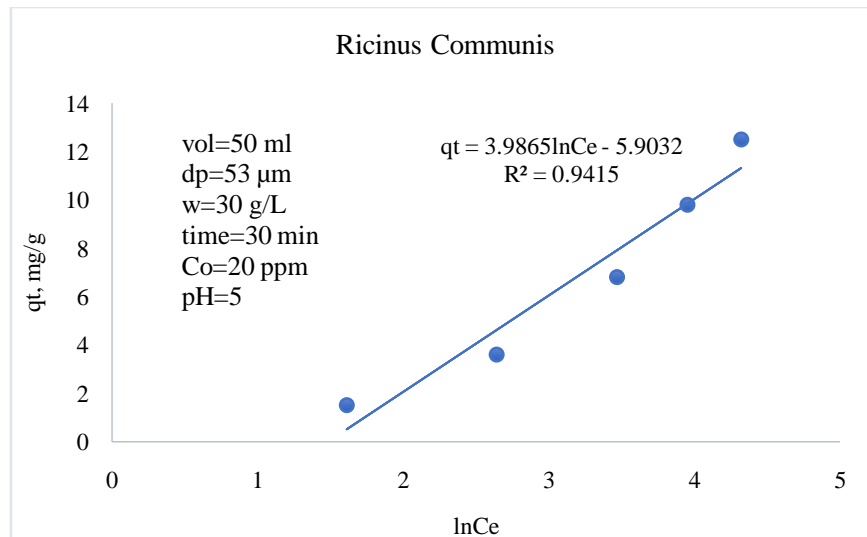

Fig. 3.9. Temkin isotherm for % decolourization of Rose Bengal dye

Table – 3.1 Isotherm constants (linear method)

Langmuir isotherm	Freundlich isotherm	Temkin isotherm
$q_m = 26.8817$mg/g	$K_f = 0.43732$mg/g	$A_T = 0.22746$ L/mg
$K_L = 0.0112$	$n = 0.705$	$b_T = 631.918$
$R^2 = 0.9814$	$R^2 = 0.9986$	$R^2 = 0.9415$

3.8 Kinetics study:

The kinetic constants of dye photodegradation are usually estimated by applying a pseudo-first-order and second-order reaction rate Eqs. (1) and (2).

$$\lg (q_e - q_t) = \lg q_e - (K_1 t / 2.303) \qquad (1)$$

$$t/q_t = 1/K_2 q_e^2 + t/q_e \qquad (2)$$

where q_e and q_t are the amounts decolourization at t, min and equilibrium time and Kad is the rate constant of the pseudo first order bio decolourization and 'K' is the second order rate constant represents the first order and second-order reaction rate constant[16]. The rate constant (k) of first-order reaction was obtained by plotting ln (t/qt) against the reaction time t and 1/Ct- 1/Co against time (t) for second-order reaction as shown in Figure 3.10(a-b). Applying the initial condition $q_t = 0$ at $t = 0$, we get
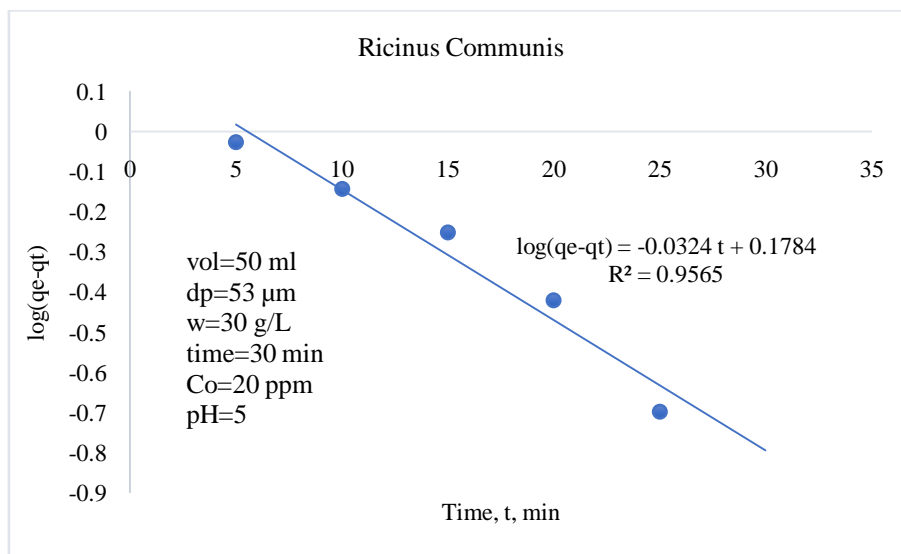
$$\log (q_e - q_t) = \log q_e - (K_{ad}/2.303) t$$

$$\log (q_e - q_t) = -0.0324 t + 0.1784, R^2 = 0.9565$$

Rearranging the terms, we get the linear form as:

$$(t/q_t) = (1/ K q_e^2) + (1/q_e) t.$$

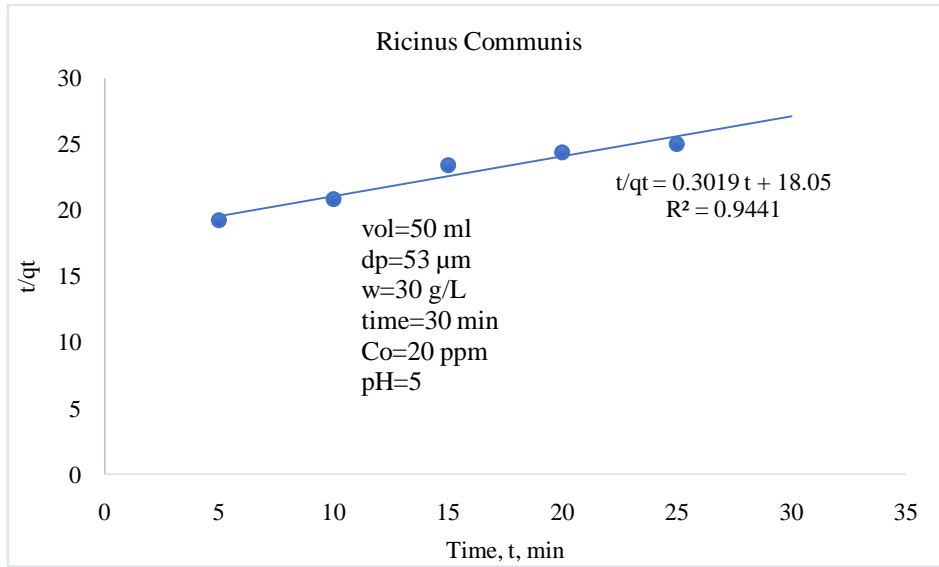$$(t/q_t) = 0.3019 t + 18.05, R^2 = 0.9441$$

Fig. 3.10. (a, b). first order and second order kinetics for Rose Bengal dye

Table – 3.2 Equations and rate constants

Order	Equation	Rate constant	R^2
Lagergren first order	$\log(q_e-q_t) = -0.0324\,t+0.1784$	0.07462 min^{-1}	0.9565
Pseudo Second order	$t/q_t = 0.3019\,t + 18.05$	0.00505 g/(mg-min)	0.9441

3.9 Thermodynamics study:

decolourisation is temperature dependant. All in all, the temperature reliance is related with three thermodynamic boundaries to be specific change in enthalpy of decolourization ((ΔH), change in entropy of decolourization (ΔS) and change in Gibbs free energy (ΔG)**[17]**.

The thermodynamic parameters obtained for the decolourization process are calculated by using the following equation:

$\ln K_D = \Delta S/R - \Delta H/RT$

where K_D is the distribution coefficient (mL/g), ΔH is the enthalpy change (kJ/mol), ΔS is the entropy change (J/mol K), T is the temperature (K), and R is the universal gas constant (8.314 J/ mol K). The Gibbs free energy change (ΔG) values (kJ/mol) are calculated from the following equation:

$\Delta G = \Delta H - T\,\Delta S$

The enthalpy changes of decolourization, ΔH, and the entropy change of decolourization, ΔS, can be obtained the slopes and intercepts of linear regression of ln qt/ce vs. 1/T (Fig. 3.11). The negative ΔG values confirm the feasibility of the decolourization process and the spontaneous nature of decolourization. The positive values of ΔH confirm the endothermic nature of the process and the positive values of entropy, ΔS, indicate the affinity of the Ricinus communis for RoseBengal.
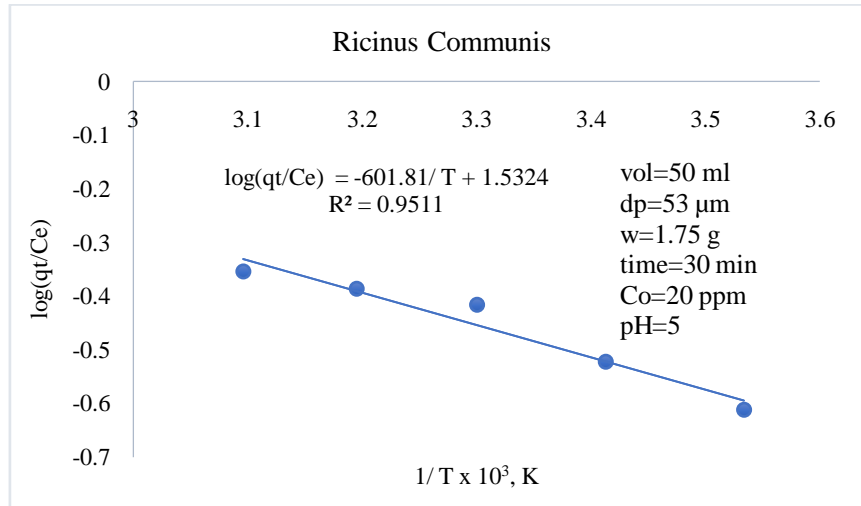
Fig. 3.11. Effect of thermodynamic study on % decolourization of Rose Bengal dye

Conclusions

The equilibrium agitation time for decolorization of RB dye is 30 min (60%).The optimum dosage is 35 g/L (0.525 mg/g). % Dyedecolorization is increased up to pH = 5 (75%).The maximum uptake capacity of 0.61 mg/g is obtained at 303 K.With an increase in the initial concentration of RB dye (20 to 200 mg/L) in the aqueous solution, the percentage decolorization of RB dye from the aqueous solution is decreased (75 to 62.5 %). The kinetic studies show that the decolorization of RB dye is described by both Lagergren first order (R^2 = 0.9565) and pseudo second order kinetics (R^2 = 0.9441). The experimental data are well represented by Langmuir (R^2 = 0.9814), Freundlich (R^2 = 0.9988) and Temkin(R^2 = 0.9366) isotherms.

Acknowledgements

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