EQUILIBRIUM AND THERMODYNAMIC STUDIES FOR DYE REMOVAL USING PLANT LEAVES (CEIBA PENTANDRA) AS SORBEBNT

Dr. CH. A. I. Raju¹ and J. Anitha²

¹Assistant Professor, ²Research Scholar

Department of Chemical Engineering, Andhra University,

Visakhapatnam – 530 003, AP, INDIA

Abstract: The efficacy of Ceiba Pentandra (CP) prepared from plant waste materials was investigated in this study as a novel sorbent for the elimination of dye molecules. The influence of variables including pH, concentration of the dye and amount of sorbent, particle size, contact time and temperature on the dye removal has been investigated. The kinetic models were used to describe the decolorization process. Three isotherm models were applied to evaluate the decolorization equilibrium, and its thermodynamic parameters were calculated. More than 40% removal efficiency was obtained within 30 min at adsorbent dose of 1.5 g per 50 mL for initial dye concentration of 100 mg L-1. The maximum decolorization capacity was found to be at pH 5 and at 303 K. The decolorization kinetic data were found to be in accordance with pseudo-first order kinetics. Calculations of various thermodynamic parameters indicate the endothermic and spontaneous nature of the decolorization process.

Keywords: Ceiba Pentandra, Rose Bengal, kinetics, Thermodynamics and Isotherms

1. INTRODUCTION

Textile knit industry uses large amount of organic and inorganic chemicals as dyes that are directly or indirectly responsible for producing wastewater. The rate of wastewater disposals from the textile industries is reaching a warning level nowadays, sorption techniques employing solid sorbents are widely used to remove certain classes of chemical pollutants from waters, especially those that are hardly destroyed in conventional wastewater treatment plants [1,2]. Dyes and pigments represent one of the problematic groups; they are emitted into wastewaters from various industrial branches, mainly from the dye manufacturing and textile finishing [3]. The sorption process provides an attractive alternative for the treatment of contaminated waters, especially if the sorbent is inexpensive and does not require an additional pre-treatment step before its application. Currently, the most commonly used adsorption agent in industry is activated carbon, which has been extensively studied also for the dye removal [4] Nanotechnology is one of the most active research fields in modern material science and technology [5]. Textile industries produce a huge amount of toxic and non-toxic biodegradable dye effluents. Which cause severe environmental pollution problems [6], searching an environmentally friendly chemical process for removal of dyes from aqueous system has been an active topic.

2. Experimental procedure

2.1 Stock solution of Rose Bengal

By dissolving an essential measure of A.R. grade Rose Bengal color in double distilled water, 1000 ppm of Rose Bengal arrangement was arranged. The arrangement was reasonably weakened dependent on the prerequisite.

2.2 Preparation of Adsorbents

During the investigation of plant materials for their sorption capacities relevant the Rose Bengal, it was seen that the sorbent got from leaves of Ceiba pentandra have shown connection towards the Rose Bengal.

2.3 Batch Experiments for Dye decolorization

The batch dye decolorization experiments were carried out in Erlenmeyer flasks in a temperature-controlled water bath shaker at 100 rpm. The effects of control variables, such as the pH (2–8) of the dye solution, temperature (10-50 °C), sorbent dose (0.5–4 g/L), and contact time (1–180 min) were studied and the dye concentrations in water streams were approximately 20–200 mg/L. The percentage dye removal was calculated according to the following equation and used in the ensuing decolorization experiments:

Dye removal (%) = $C0 - Ce/C0 \times 100\%$ decolorization capacity (qe) = $C0 - Ce/W \times V$

3. RESULTS AND DISCUSSIONS

3.1 Time:

The group decolorization learns at different stretches of time (1–180 min) were accomplished for Rose Bengal tone. Various limits were consistent for instance early on obsession 20 ppm, pH 7.0, divide 0.5 g/L and temperature 30 °C. The outcomes of this effect are showed up in Fig. 3.1. It was seen that the decolorization extended from 1.0 to 30.0 min and got predictable at 30 min percentage 42% and dye uptake is 0.84mg/g. There might have been no further addition of take-up of shading by growing the contact time 30 min. Therefore, 30 min contact time was considered as the ideal one [7-8].

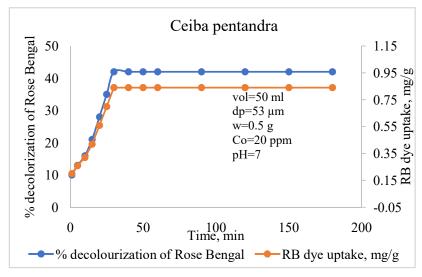


Fig 3.1. Effect of time on % decolorization of Rose Bengal dye

3.2 Size:

The assortments in % decolorization of Rose Bengal from the liquid course of action with Ceiba pen Tandra size are gotten. The results are pulled in fig.3.2 with rate decolorization of Rose Bengal as a component of Ceiba pen Tandra size. Different boundaries were consistent for instance beginning concentration 20 ppm, time 30 min, 0.5 g and temperature 30 °C The rate decolorization is reduced from 42.5 % to 31 % (0.85 to 0.62 mg/g) as the Ceiba pen Tandra size lessens from 53 to 152 μ m. This marvel is ordinary, as the size of the particle lessens, surface space of the Ceiba pen Tandra increases; likewise, the number of dynamic objections on the Ceiba pen Tandra moreover augments [9-10].

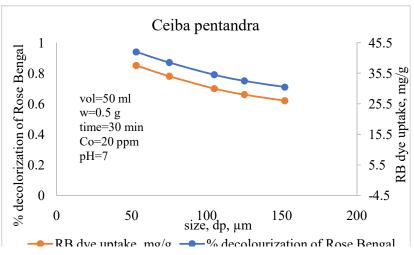


Fig 3.2. Effect of size on % decolorization of Rose Bengal dye

3.3 pH:

The cluster decolorization peruses for nuclear take-up of Rose Bengal tone was finished with changing pHs going from 2.0 to 8.0. Different boundaries were consistent for instance beginning concentration 20 ppm, time 30 min, 0.5 g and temperature 30 °C. The results of this effect are plotted in Fig. 3.3. It is clear from this figure that from the start the sub-atomic take-up was 0.756 mg/g which extended to 1.076 mg/g at pH 5.0. Moreover, the decolorization was extended at low assessments of pH for instance 6.0 (0.972 mg/g) 7 and 8 (0.858 and 0.756 mg/g). It might be a result of the truth this tone contains two carboxylic social event and at high pH these carboxylic get-together exits as anions, provoking high decolorization. However, we considered 6.0 as the best pH for additional examines due to the way that most of the water bodies has pH in the extent of 6.5 to 7.5 [11-12].

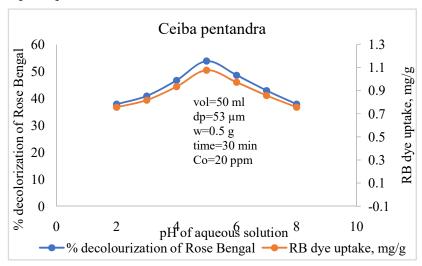


Fig 3.3. Effect of pH on % decolorization of Rose Bengal dye

3.4 Concentration:

The effect of the emphasis on the departure of Rose Bengal tone was finished at the unmistakable starting obsessions going from 20 to 200 ppm keeping the other preliminary limits consistent (time 30 min, pH 5.0, partition 0.5 g and temperature 30 °C). The percentage expulsion of Rose Bengal color was 54.4% (1.088 mg/g), 51.56%

(2.578mg/g), 47.78% (4.778 mg/g), 44.37% (6.656 mg/g), 39.78 % (7.956 mg/g) removals were occurred at 20, 50, 100, 150 and 200 ppm concentrations (Fig. 3.4). It got consistent at higher intermingling of the shading. It doubtlessly exhibited that the decolorization was dependent upon the hidden groupings of Rose Bengal tone. It very well might be a result of the free available genuine surface domain on the Ceiba pen Tandra at low obsession, which reduced as the gathering of the shading extended. Notice that total at balance (qe) extended as the rate decreased. It is a result of the route that, at high concentration, enormous number of the shading particles included the Ceiba pen Tandra surface, occurring into decolorization of high number of the shading iotas. Hence, the best sub-nuclear take-up of Rose Bengal tone was gotten at 20 ppm concentration under the nitty gritty exploratory conditions [13-14].

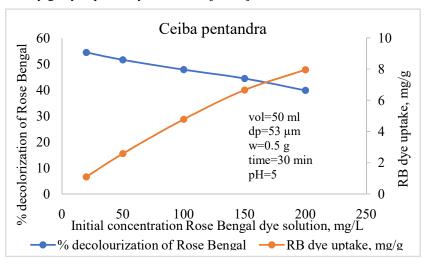


Fig 3.4. Effect of Concentration on % decolorization of Rose Bengal dye

3.5 Dosagee:

The gathering decolorization peruses for Rose Bengal tone were finished with fluctuating measurements going from 0.5 to 4 g/L. Various limits were reliable for instance starting Concentration 20ppm, time 30 min, pH 5.0 and temperature 30 °C. The eventual outcomes of this effect are plotted in Fig. 3.5. The rate ejection of shading extended from 69 % (1.38 mg/g) to 84 % (0.56 mg/g) at 0.5 what's more, 1.5 g/L. This is a consequence of greater receptiveness of the Ceiba pen Tandra objections (surface area) at high segment of the Ceiba pen Tandra. Further development in the bit of 1.5 and 4 g/L couldn't give more decolorization. It was relied upon to the way that the surface space of 1.5 g/L part was satisfactory for the ejection of Rose Bengal shade of 20ppm core interest [15-16].

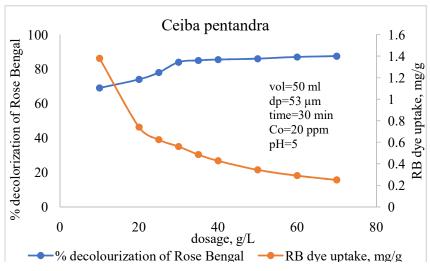


Fig 3.5. Effect of dosage on % decolorization of Rose Bengal dye

3.6 Temperature:

The bunch decolorization peruses for Rose Bengal tone were finished with fluctuating temperature (10, 20, 30, 40 and 50 °C). Various limits were steady for instance initial concentration 20ppm, time 30 min, pH 5.0 and divide 1.5 g. The results of this effect are plotted in Fig. 3.6. An assessment of this figure clearly exhibits that the decolorization 93.2%, 93.8%, 94.4%, 94.7% and 94.9% was same up to 20ppm obsession for all of the temperatures for instance 10, 20, 30, 40 and 50 °C. In any case, it was low and high at 10 and 30 °C. In this way, the solicitation for the decolorization was 30 °C. This lead of the nuclear take-up showed exothermic nature of the decolorization system. It might be a direct result of the augmentation in the speed of scattering of shading particles crossways the outer edges layer [17-18].

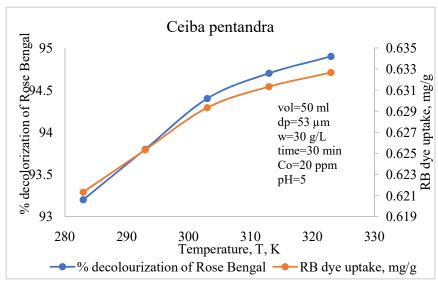


Fig 3.6. Effect of dosage on % decolorization of Rose Bengal dye

3.7 Isotherms:

3.7.1 Langmuir Isotherms:

The essential characteristics of Langmuir isotherm can be expressed in terms of dimensionless constant separation factor for equilibrium parameter, RL, which is defined as:

$$RL = 1/1 + KLC0 \tag{1}$$

The value of RL indicates the type of Langmuir isotherm to be irreversible (RL = 0), favourable (0 < RL < 1), linear (RL = 1) or un favourable (RL > 1).

Langmuir isotherm is drawn for the present data and shown in Fig.3.7. The equation obtained 'n' Ce/qe = 0.0592 Ce + 7.8484 with a good linearity (correlation coefficient, $R2\sim0.9964$) indicating strong binding of Rose Bengal ions to the surface of Ceiba pen Tandra.

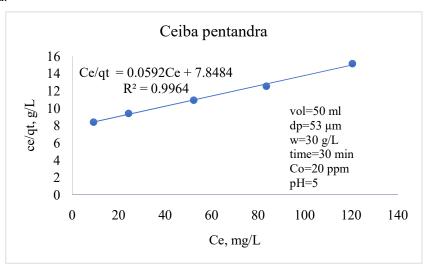


Fig 3.7. Langmuir isotherm for % decolorization of Rose Bengal dye

3.7.2 Freundlich Isotherms:

The Freundlich isotherm model proposes a monolayer decolorization with a heterogeneous energetic distribution of active sites, accompanied by interactions between decolorization molecules. The Freundlich model can be expressed as:

$$qe = KFCe1/n$$
 (2)

where Kf is a constant relating the decolorization capacity and 1/n is an empirical parameter relating the decolorization intensity, which varies with the heterogeneity of the material.

Freundlich isotherm is drawn between $\log qe = 0.7825 \log Ce -1.5928$; $\log Ce$ and $\log qe$ in Fig.3.8 for the present data. The resulting equation has a correlation coefficient of 0.9938.

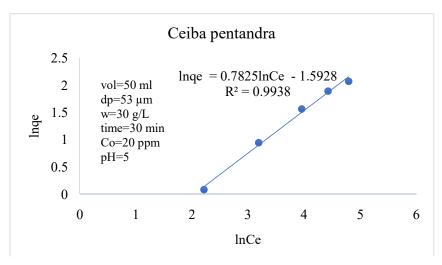


Fig 3.8. Freundlich isotherm for % decolorization of Rose Bengal dye

3.7.3 Temkin Isotherm:

Temkin isotherm takes into consideration the indirect interaction between adsorbate molecules and assumes that the heat of decolorization of all molecules in the layer decreases linearly with coverage due to adsorbent–adsorbate interactions and that the decolorization 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.

$$qe = B \ln A + B \ln Ce$$

where B = RT/b, b is the Temkin constant associated to heat of decolorization (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) [19-20].

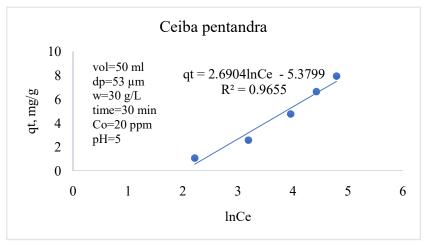


Fig 3.9. Temkin isotherm for % decolorization of Rose Bengal dye

3.8 Kinetics:

The kinetic constants of dye photodegradation are usually estimated by applying a pseudo-first-order and second-order reaction rate Eqs. (3) and (4).

$$lg (qe - qt) = lg qe - (K1t/2.303)$$

$$t/qt = 1/K2 qe 2 + t/qe$$
(4)

where qe and qt are the amounts decolorization at t, min and equilibrium time and Kad is the rate constant of the pseudo first order biodecolorization and 'K' is the second order rate constant represents the first order and second-order reaction rate constant. 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) [21-22].

Applying the initial condition qt = 0 at t = 0, we get

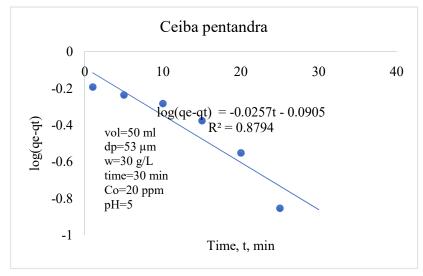
$$\log (qe - qt) = \log qe - (Kad/2.303) t$$

$$log (qe - qt) = -0.0257 t + 0.0905, R^2 = 0.8794$$

Rearranging the terms, we get the linear form as:

$$(t/qt) = (1/Kqe2) + (1/qe)t.$$

$$(t/qt) = 1.2015 t + 11.885, R^2 = 0.7551$$



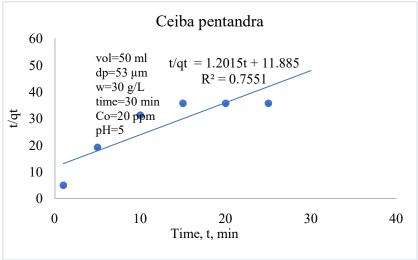


Fig 3.10. (a, b). first order and second order kinetics for Rose Bengal dye

3.9 Thermodynamics:

decolorization is temperature dependent. All in all, the temperature reliance is related with three thermodynamic boundaries to be specific change in enthalpy of decolorization ((ΔH) , change in entropy of decolorization (ΔS) and change in Gibbs free energy (ΔG).

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

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

where KD 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 decolorization, ΔH , and the entropy change of decolorization, 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 decolorization process and the spontaneous nature of decolorization. The positive values of ΔH confirm the endothermic nature of the process and the positive values of entropy, ΔS , indicate the affinity of the Ceiba pen Tandra for Rose Bengal [23-24].

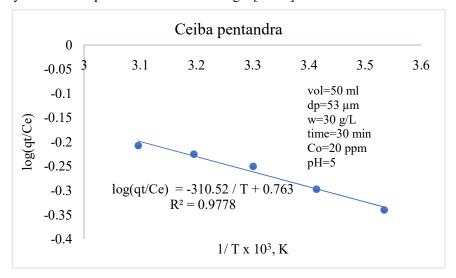


Fig 3.11. Effect of thermodynamic study on % decolorization of Rose Bengal dye

4. Conclusions

The current examination has shown that the Rose Bengal dye can be effectively utilized for the expulsion of shading from mash and textile industry. The material displays great expulsion limit and most extreme evacuation of 42% can be accomplished in 30 min, Concentration is 20ppm and Temperature is 303 K. The rate removal increments with expanding sorbent dosages, what's more, as such evacuation increments with diminishing size of the sorbent material. The harmony information depicts both the Langmuir and the Freundlich isotherm models sufficiently. The thermodynamic boundaries and trial information uncovered that the decolorization was, unconstrained, exothermic and plausible.

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