Equilibrium, Kinetic and thermodynamic study of adsorption of Safranine O dye from aqueous solution by Bael tree(Aegle marmelos)bark powder

D. Bala[a], T. Jaison Jose[a], Ramavath JanrajNaik[b],Sudip Mandal[c], Y. Subbareddy[a]*

[a]Department of Chemistry, Andhra Loyola College(Autonomous), Vijayawada-520008,

[b]Department of Chemistry, Sri Venkateswara College, University of Delhi, Delhi 110021,

[c]Department of Chemistry, School of Applied Sciences and Humanities, Vignan's

Foundation for Science, Technology and Research (Deemed to be University), Vadlamudi,

Guntur- 522213

*Corresponding Author, e-mail: ysrdpalc@gmail.com

Abstract

Bael tree bark powder is used as an adsorbent to remove Safranine O (SO) dye from aqueous solutionsThe percentage of Safranine O dye removal, the effects of initial dye concentration, various temperatures, contact time, pH influence, and adsorbent dose were examined. An increase in contact time, adsorbent dose, and temperature the betterremoval of SO dye is observed. To examine the equilibrium data, Langmuir and Freundlich adsorption isotherms were applied. The Langmuir adsorption isotherm was used to validate the homogeneous adsorption of SO onto Bael tree bark. The mono layer adsorption capacity of Bael tree bark was found to be 4.88×10^{-4}mol/g. Using fictitious first order and second order equations, the kinetic data was examined. The kinetic analyses revealed that chemisorption of the SO dye over the bark of the bael tree powder follows the pseudo-second order ($R^2 = 0.999$). The use of bael tree bark powder for removal of the SO dye can be considered to be the best approach as far as water quality and environmental safety is concerned.

Key Words: Bael Tree Bark, Safranine O, Adsorption Isotherms, Kinetics and Thermodynamic parameters

1.0. INTRODUCTION

Dyes are commonly used to colour products such as paper, textiles, plastics, leather, cosmetics, and food. Every year, massive amounts of various dyes and pigments are produced. Over 100,000 dyes are commonly produced, with over 8×10^5 tone of dyestuff produced annually [1]. In the textile industry, many different types of dyes are used, including direct, reactive, acid, and basic dyes. The majority of these dyes are toxic and has negative health effects, making the water toxic to aquatic life, posing serious problems for the ecological system.Dyes, due to their chemical structure, have a high resistance to fading when exposed to light and water. The washing and bleaching of natural fibers, as well as the dyeing and finishing steps, are the primary sources of wastewater generated by the textile industry.

Because of the wide range of fibers, dyes, and process aids used, these processes generate wastewater with high chemical complexity and diversity, which is insufficiently treated in conventional wastewater treatment plants. Water dye contamination is a major issue in all of these processes. Dye decolorization is difficult in aquatic environments because dyes are stable in water and are usually resistant to light and many chemicals. These coloured compounds are not only unsightly, but they also block sunlight from entering the stream, harming the aquatic ecosystem. Dyes have complex aromatic molecular structures, making them more stable and difficult to biodegrade. Furthermore, many dyes are toxic to certain microorganisms, causing direct destruction or inhibition of their catalytic abilities.

Chemical coagulation [2], ozonization [3], membrane filtration [4], electrolysis [5], oxidation [6], and bio-degradation [7] are all common methods for removing dyes from water and wastewater. Researchers are looking for more effective and cost-effective treatment methods because established technologies are frequently unable to adequately reduce contaminant concentrations to desired levels [8]. These methods, however, are not widely used due to their high cost and economic disadvantage. Adsorption, on the other hand, is by far the most versatile and widely used technique. Alumina, silica, metal hydroxides, and activated carbon are the most common adsorbent materials. Many researchers have demonstrated that removing dyes with activated carbon is both economically and technically advantageous. Because of its high adsorption capacity, large surface area, microporous structure, and high degree of surface, activated carbon is widely used as an adsorbent.

Adsorption is a well-known equilibrium separation process that is also an effective method for water decontamination. Adsorption has been shown to outperform other techniques in terms of initial cost, design flexibility and simplicity, ease of operation, and sensitivity to toxic pollutants. Adsorption does not also result in the formation of hazardous substances. A common adsorbent, activated carbon, has a high capacity for pollutant removal. However, its main disadvantages are high treatment costs and difficult regeneration, both of which raise the cost of wastewater treatment. As a result, there is a demand for other adsorbents made of low-cost materials that do not necessitate any costly additional pretreatment steps. As a result, the adsorption process will be profitable. A successful adsorption process is dependent not only on the dye adsorption performance of the adsorbents, but also on a steady supply of the process materials. As a result, it is preferable to use low-cost adsorbents such as industrial waste, natural ores and agricultural byproducts.

The goal of this study is to find out how well BTB can remove SO from aqueous solutions through adsorption. A batch investigation using commercial SO dye as a model pollutant was

carried out on a lab scale. Many factors were examined for SO removal, including adsorbent dose, pH effect, starting dye concentration, contact time, and temperature effect. Adsorption, kinetic, and thermodynamic parameter isotherms were investigated. The kinetic parameters were used to calculate rate constants. The experimental data from the equilibrium were fitted into the Langmuir and Freundlich equations to see which isotherm gives the best correlation.

SAFRANINE O:Safranin O (Basic Red 2) is a contaminant agent widely used as a food dye in flavouring and colouring candies and cookies, textile industries, leather, paper, and histology, textile, cytology, and bacteriology research [9, 10]. Safranine O or basic red 2 is used as a counterstain in some staining protocols, colouring all cell nuclei red. In a gramme stain, this is the classic counter stain. It is also useful for detecting cartilage, mucin, and mast cell granules. Safranin O is commonly used to stain Gram negative bacteria red in smears to contrast with Gram positive organisms that are blue. It is useful as a red nuclear counterstain in tissue sections and was once popular for staining cartilage metachromatically yellow against red nuclei on a pink background.
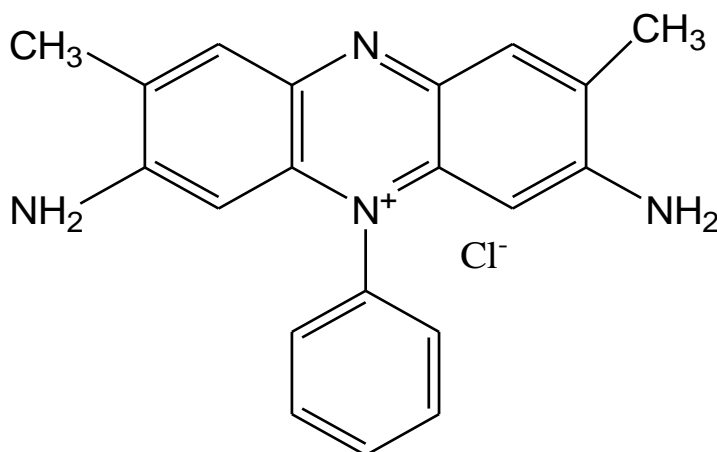

Fig.1. Structure of Safranine O

2.0. Experimental analysis

2.1. Preparation of Adsorbent

The bark of the bael tree was gathered from Andhra Loyola College in India's NTR District. They were collected from twigs and placed in pristine plastic bags. Put flat on a clean surface to dry after being washed with triple-distilled water. A grinder was used to grind dry bark. After being pulverized, the bark fragments were sieved, kept in plastic bags according to size, and made ready for usage. For this research, BT bark particles with a 40 mesh size were utilized as an adsorbent.

2.2. Preparation of artificial wastewater

A stock solution of 5 x 10^{-3}M was prepared in 250 ml of distilled water by dissolving the appropriate amount of SO (99% purity; molecular formula is $C_{20}H_{19}N_4Cl$, C.I.No.50240; M.Wt = 350.85, obtained from Himedia). Figure 1 depicts the chemical structure of SO. To create the standard curve, concentrations ranging from 0.2 x10^{-5}M to 5.0x10^{-5}M were prepared from the stock solution.All of the chemicals used in the study were analytical-grade reagents. All solutions and reagents were made with double-distilled water, and the pH was adjusted with 0.1 N HCl or 0.1 N NaOH. All adsorption experiments were conducted at room temperature (30°C).

2.2. Batch equilibrium adsorption experiment

The effects of concentration, adsorbent dose, contact time, pH, and temperature on SO removal over the surface of BTB were studied using batch adsorption experiments. Batch experiments were carried out in temperature-controlled shakers in 100ml conical flasks with 50ml SO working solution for 120 minutes (time required for equilibrium to be reached between SO adsorbed and SO in solution).To adjust the pH of the dye solution, a few drops of 0.1N HCl or 0.1N NaOH were added. After centrifuging the solutions at 5000 rpm for 15 minutes, the absorbance of the supernatant solution was measured with a UV-visible spectrophotometer to determine the residual concentration at λ_{max} of 520 nm. The amount of dye adsorbed and removed were calculated by using Eq. (1) and (2), respectively.

$$\text{Amount Adsorbed}(q_e) = (C_0 - C_e) \times \frac{V}{w} \qquad (1)$$

$$\text{Percentage removal (\%)} = \frac{C_0 - C_e}{C_0} \times 100 \qquad (2)$$

Where C_0 and Ce (mol/l) are the initial and equilibrium concentrations of the dye solution respectively, V(l) is the volume of dye solution and w(g) is the weight of adsorbent used.

2.3. Adsorption Kinetics studies

For adsorption kinetics, 0.1g of BTB was mixed with 50 ml of SO solution of different concentrations ($4x10^{-4}$, $5x10^{-4}$, and $6x10^{-4}$M) at room temperature. The initial pH of SO solution is found to be 6.33The mixture was agitated using a temperature-controlled shaker. The samples were removed from the shaker at predetermined time intervals and centrifuged at 5000 rpm. The slandered calibration curve was used to calculate the final concentrations of the samples. Using the equation below, the amount of dye adsorbed at time t was calculated.

$$\text{Amount Adsorbed (q}_t) = (C_0 - C_t) \times \frac{V}{w} \qquad\qquad (3)$$

3. Characterization of Adsorbent

3.1. FTIR of BTB

The potential interactions between BTB and SO were investigated using FT-IR spectroscopy. The FT-IR spectra were recorded before and after SO sorption to determine the vibrational frequency changes for the adsorbent's functional groups.The stretching vibration of hydroxyl functionalgroups was assigned to the broad band around $3430 cm^{-1}$. The bands at 2923, 1436, and 1315 $cm^{-1}$are mostly assigned to –CH$_3$ units in BTB. The absorbance at 1622 and 1061 $cm^{-1}$is due to C- O of carboxylic acids (Fig.2).The differences in peak frequency and intensity in the FT-IR spectra of native and SO-loaded BTB indicate that carboxylic acid and hydroxyl groups are involved in the adsorption process.
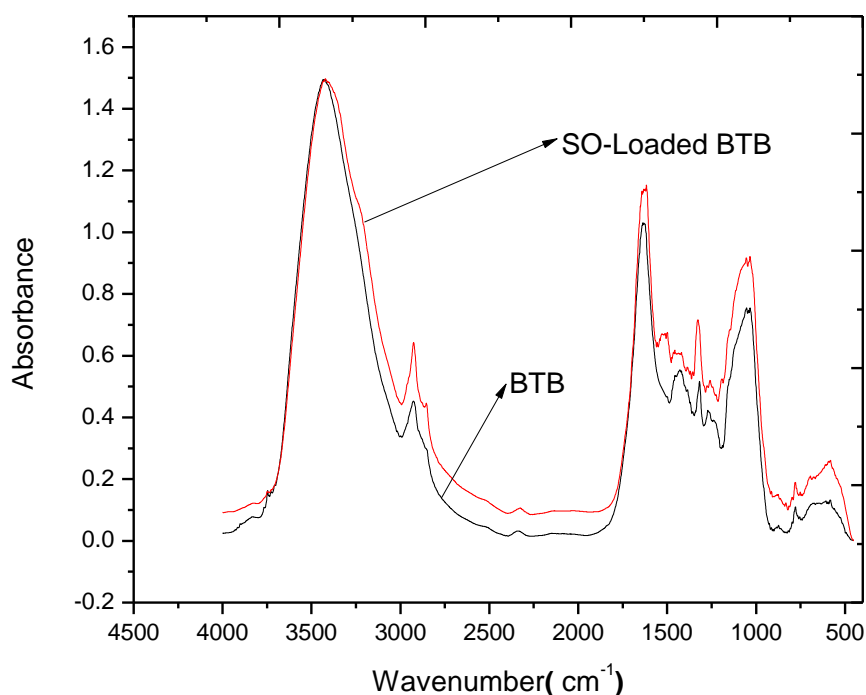

Fig.2.FT-IR of BTB and SO-loaded BTB.

3.2. Scanning Electron Microscope

The Scanning Electron Microscope (SEM)images are used to study the morphologies of BTB adsorbent material before (Fig. 3a) and after (Fig. 3b) SO adsorptionas shown in the Fig. 3. The porous, irregular shapes and sizes of BTB adsorbent enables the effective dye adsorption. Furthermore, availability of the large number of active sites over the BTB surface additionally enhances the SO dye adsorption. The uniform distribution of SO dye over the BTB adsorbent surface is shown in Fig.3b.
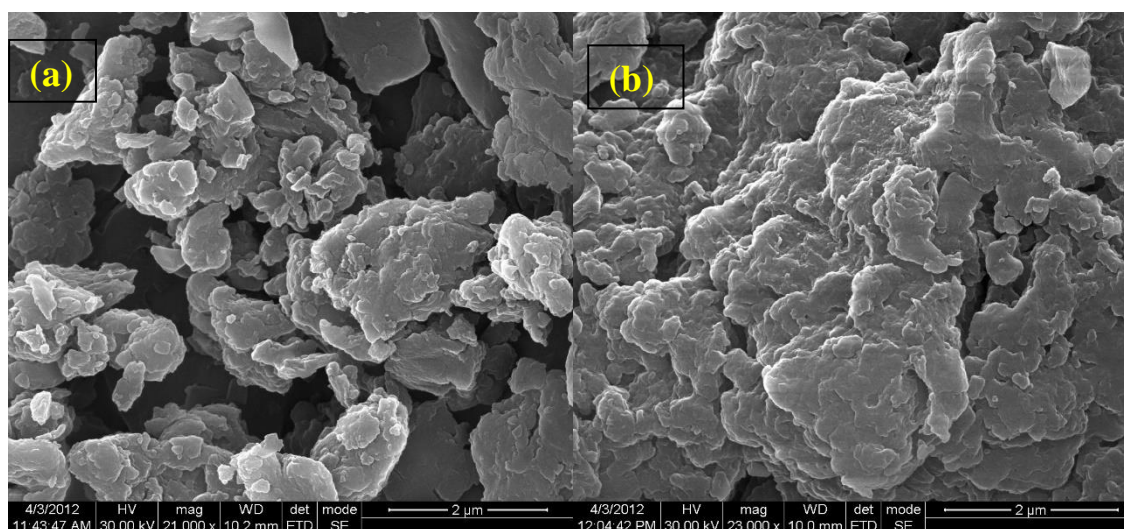

Fig.3a. SEM image of BTB before adsorption

Fig.3b. SEM image of BTB after adsorption

4.0. Results and Discussion

4.1. Effect of Contact time

Contact time studies can help you understand how much dye is adsorbed by a fixed amount of adsorbent over time. The effect of contact time on SO removal was investigated during the removal process and discovered to be an important parameter. Figure 4depicts the effect of contact time on SO removal by BTB for initial dye concentrations of 4×10^{-4}, 5×10^{-4}, and 6×10^{-4} M.Adsorption was rapid in the first 40 minutes and gradually increased after that. Contact time curves revealed that the equilibrium time for all dye concentrations was 120 minutes. This is why the optimum contact time in the above batch equilibrium experiments was 120 minutes.The curves are single, smooth, and continuous, indicating the possibility of dye monolayer coverage on the adsorbent's surface[11]. The adsorption capacity of SO dye, on the other hand, increases with increasing concentration and contact time (Fig.4). As a result, BTB could be used to remove SO from aqueous solutions.
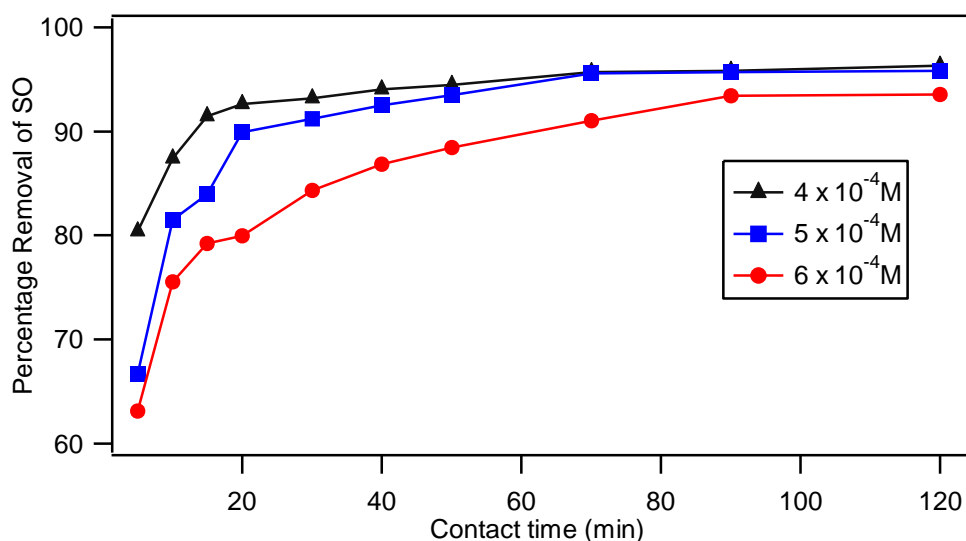
Fig.4. Effect of contact time: Concentration of SO (4-6) x10^{-4} M, Time from 5 min to 120min, dose 0.1g and at Room temperature.

4.2. Effect of adsorbent dose

A dosage study is an important parameter in adsorption studies because it determines the capacity of the adsorbent for a given initial concentration of SO dye solution. The effect of adsorbent dose was investigated at room temperature by varying the sorbent amounts from 0.02 to 0.24g/L. Figure 5 shows the effect of adsorbent dose on SO removal percentage at an initial concentration of 6X 10^{-4}M. The graph shows that increasing the adsorbent dose increased the percentage removal of SO from 45.14% to 99.82%. Because increasing the adsorbent dose provides more surface area or adsorption sites for a fixed initial adsorbate concentration, increasing the adsorbent dose increased the removal efficiency for a given initial SO concentration[13].However, as the BTB dose was increased, the adsorption capacity (the amount of adsorbent adsorbed per unit mass of adsorbent) decreased (Fig.5). Because of an increase in free adsorption sites in the adsorption reaction, adsorption capacity decreases with increasing adsorbent dose. Any additional adsorbent addition had no discernible effect on adsorption. This could be due to overlapping adsorption sites caused by adsorbent particle overcrowding.
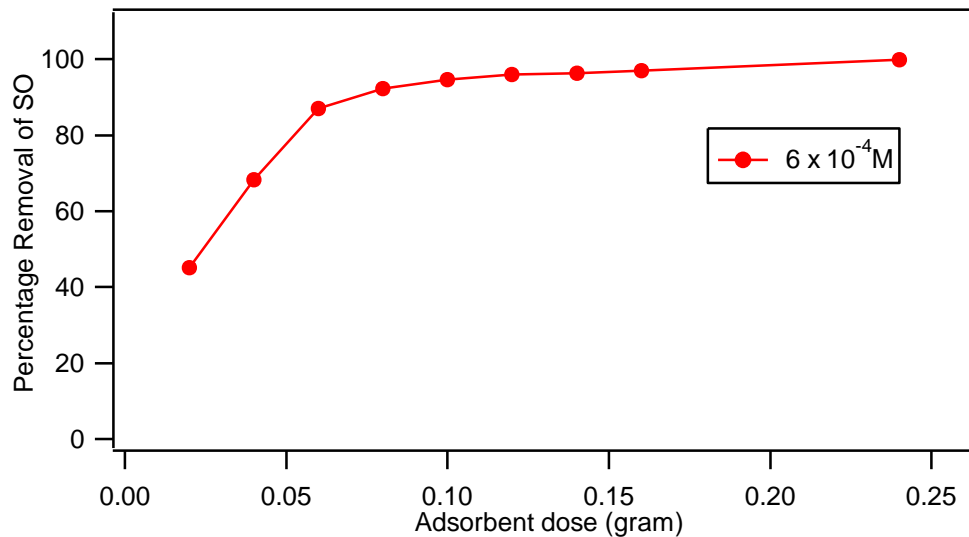
Fig.5. Effect of adsorbent dose SO dye concentration 6 x10^{-4}M, Time 2hrs, dose from 0.02g to 0.24g and at Room temperature.

4. 3. Effect of concentration at different temperature

The initial SO dye concentration is varied from (2 to 16) x10^{-4} M at different temperatures, while the BTB dosage remains constant at 0.1 g/L. The adsorption of SO dye by BTB by Fig. 6 also increases with temperature, indicating that the process is endothermic in nature. The initial removal of dye is also observed to be rapid, and as concentration increases, the percentage uptake gradually decreases (Fig.6).
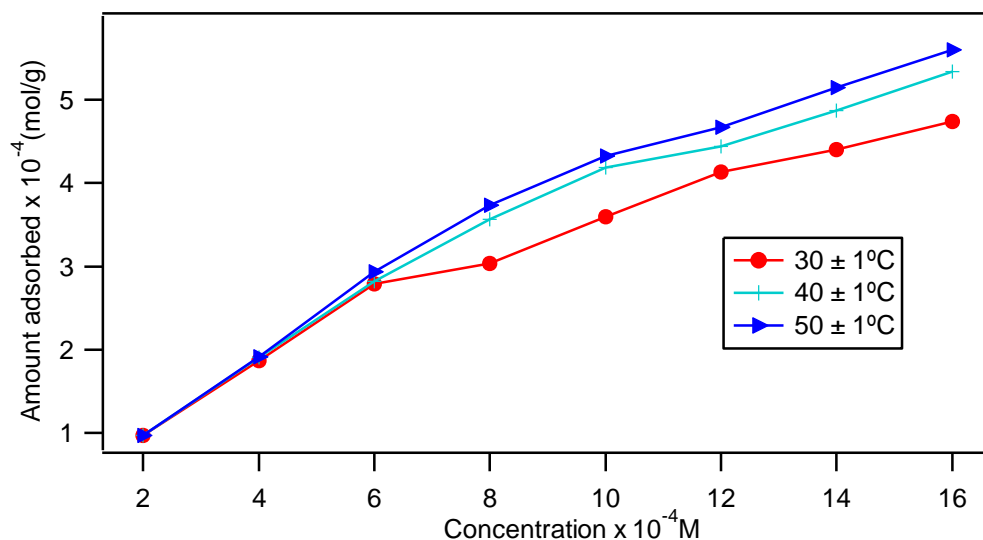

Fig.6. Effect of concentration on the removal of Safranine O by BTB at different temperatures.

4.4. Effect of pH

The pH of the system has a significant impact on the adsorptive uptake of adsorbate molecules, owing to its influence on adsorbent surface properties and ionization/dissociation of the adsorbate molecule. The lowest adsorption occurred at pH 2.0, and the constant removal of SO began at pH 4. The absorbance becomes constant after pH 4 (Fig.7).
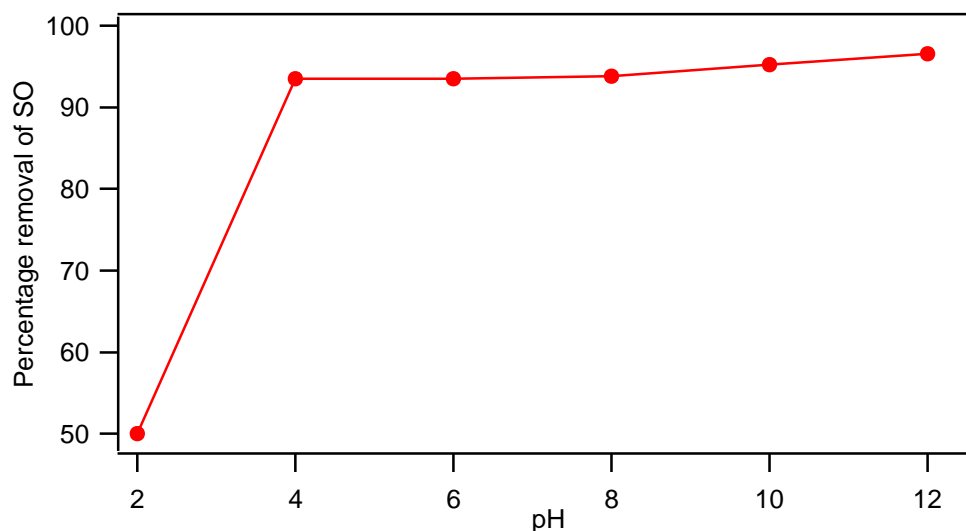

Fig.7. Effect of pH: Concentration of SO 6 x10^{-4} M, Time 2hrs, dose 0.1g and at Room temperature

4.5. Adsorption isotherms

The equilibrium adsorption isotherms are one of the most important data to understand the adsorption mechanism, the surface properties and affinities of the adsorbent. The most widely accepted surface adsorption models for single-solute systems are the Langmuir and Freundlich models. The Langmuir and Freundlich equations are commonly used to describe adsorption isotherms at a constant temperature for water and wastewater treatment applications.

4.6. Langmuir adsorption isotherm

The theoretical Langmuir sorption isotherm [13] is most widely used for the adsorption of a pollutant from a solution. It is valid for adsorption of a solute from a solution as monolayer adsorption at specific homogeneous sites within the adsorbent surface, which are energetically equivalent. The non linear equation of the Langmuir isotherm model can be written as follows:

$$q_e = (Q_m K_a C_e)/(1+K_a C_e) \qquad (4)$$

where q_e is equilibrium dye concentration on adsorbent (mol/ g), Q_m is monolayer capacity of the adsorbent (mol/g), K_L is adsorption constant (L/ mol) and Ce is equilibrium dye concentration in solution (mol /L). The Langmuir isotherm Eq. (4) can be linearized into the following form:

$$\frac{C_e}{q_e} = \frac{1}{Q_m K_L} + \frac{1}{Q_m} C_e \qquad (5)$$

A plot of C_e /q_e versus C_e(Fig.8) should indicate a straight line of slope $1/Q_m$ and an intercept of 1/ ($K_L Q_m$). The Langmuir constant K_L and Q_m evaluated, and the values of these at the three different temperatures studied (30, 40 and 50 °C) are reported in Table. The Langmuir constant K_L and Q_m increased with increasing temperature, which indicates the endothermic nature of adsorption process (Table.1). The essential characteristics of the Langmuir isotherm can be expressed by means of 'R_L', a dimensionless constant referred to as a separation factor or equilibrium parameter R_L is defined by

$$R_L = 1/ (1+K_L C_o) \qquad (6)$$

Where C_0 is the highest initial dye concentration. The parameter indicates the type of isotherm to be irreversible ($R_L=0$), favorable ($0<R_L<1$), linear ($R_L=1$) or unfavorable ($R_L>1$). The separation factor R_L was found to be < 1 for this system, which confirms the favorable adsorption found in this study (Table.5.).
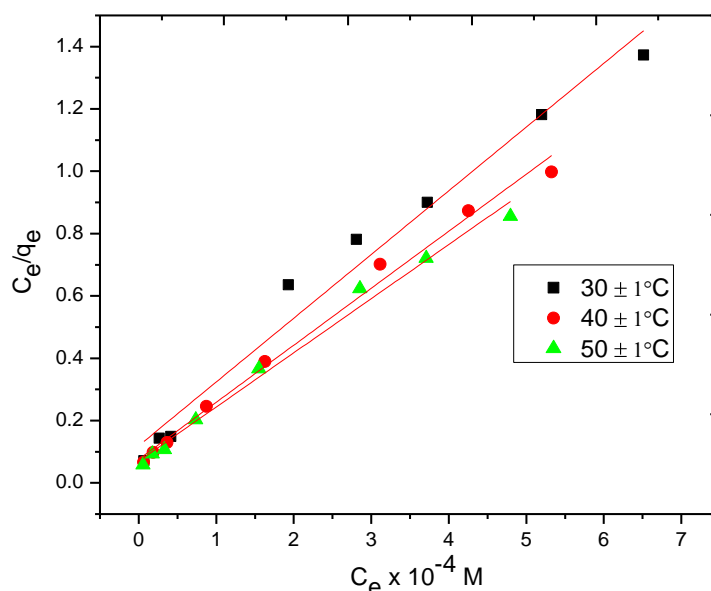

Fig. 8. Langmuir plots for SO adsorption on BTB

4.7. Freundlich adsorption isotherm:

The Freundlich equation is widely used in the environmental engineering practice to model adsorption of pollutants from an aqueous medium [14]. The expression for Freundlich equation is given as,

$$q_e = k_f C_e^{1/n} \qquad (7)$$

The linear form of Freundlich equation is given by the following expression.

$$Log(q_e) = log(K_f) + 1/n \, log(C_e) \qquad (8)$$

Where C_e is the equilibrium concentration of the dye in solution (mol/lit), K_f and n are the constants incorporating factors affecting the adsorption process such as adsorption capacity and intensity of adsorption respectively. Linear plot of $log(q_e)$ vs. $log(C_e)$ show that the adsorption follows Freundlich isotherm (Fig.9). The value of $1 < n < 10$ represents beneficial adsorption. The isotherm constant, K_f, and n calculated from the equation are shown in Table.1
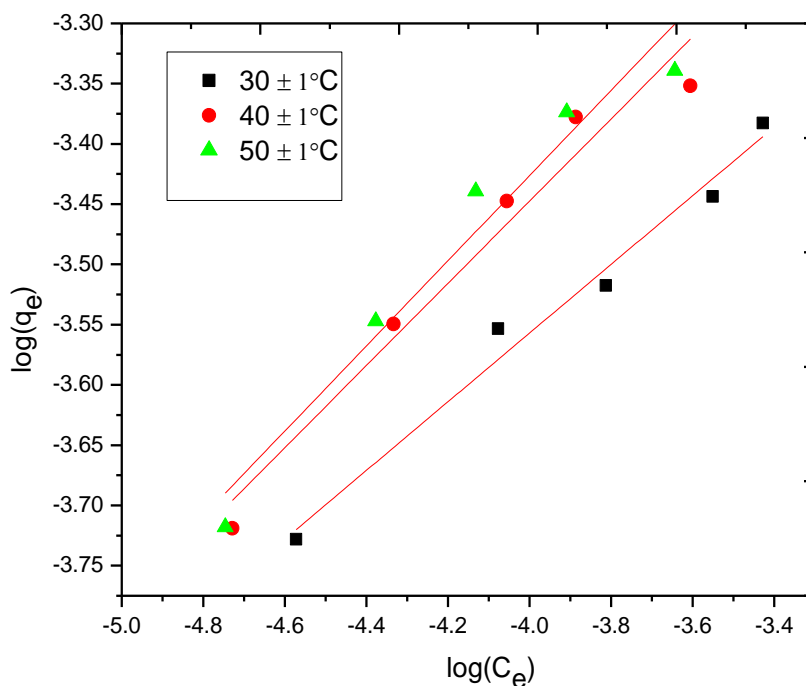

Fig. 9. Freundlich plots for SO adsorption on BTB

Table .1. Freundlich Isotherm and Langmuir Isotherm Constants for SO adsorption on BTB

Adsorption isotherm	Temperature(°C)		
	30	40	50
Langmuir adsorption isotherm			
Q_m(mol/g)	4.88×10^{-4}	5.46×10^{-4}	5.75×10^{-4}
K_L(l/mol)	1.71×10^{4}	2.22×10^{4}	2.49×10^{4}
R^2	0.975	0.991	0.987
Freundlich adsorption isotherm			
N	3.5	2.9	2.8
K_f(mol/g)	3.82×10^{-3}	8.25×10^{-3}	9.70×10^{-3}
R^2	0.975	0.947	0.943

4.8. Adsorption kinetics

To test the experimental data, pseudo-first order and pseudo-second order kinetic equations were used to examine the controlling mechanism of adsorption processes such as mass transfer and chemical reaction. The correlation coefficients expressed the degree of agreement between experimental data and model-predicted values `(R^2, values close or equal to 1).

4.9. Pseudo-first-order equation

The adsorption kinetic data were described by the Lagergren pseudo-first-order model [13], which is the earliest known equation describing the adsorption rate based on the adsorption capacity. The pseudo first order equation is as follows**:**

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \qquad (7)$$

From the linear plots of log (q_e-q_t) versus t (Fig. 10), the rate constant, k_1, and correlation coefficients of SO at various concentrations were calculated and are shown in table 2. Even though the plot has a high correlation coefficient (0.963 to 0.993) with the experimental data, if the calculated q_e differs from the experimental q_e, the reaction is not likely to be a first-order reaction. The data do not fit the Lagergren model because the calculated $q_e$values are too low when compared to the experimental q_e values for all adsorption data, indicating that SO adsorption onto BTB is not a first-order reaction (Fig.10.).
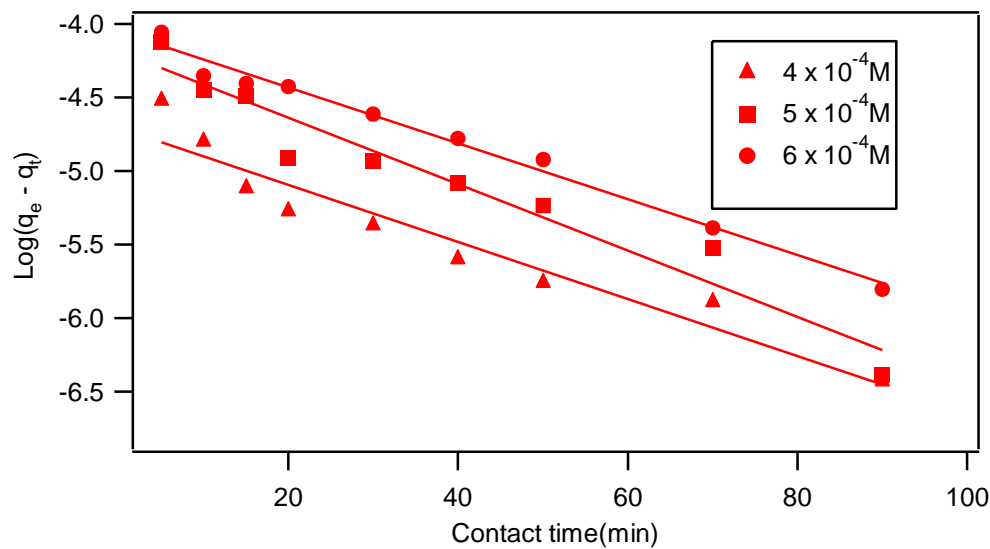
Fig.10.Pseudo first order plots for SO adsorption on BTB

4.11. Pseudo-second-order equation

The pseudo-second order kinetics model [16-17] was used to further analyse the kinetic data. In general, the linearized equation looks like this:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_t}t \qquad (8)$$

If second-order kinetics is correct, the plot of t/q_t versus time should be linear. The values of k_2, q_e, and initial adsorption rate were calculated using the intercept and slope of the t/q_t versus t plots (Fig.11). The calculated q_e values are consistent with the experimental data (Table.2), indicating that the SO adsorption system adheres to the pseudo-second-order kinetic model throughout the sorption period.
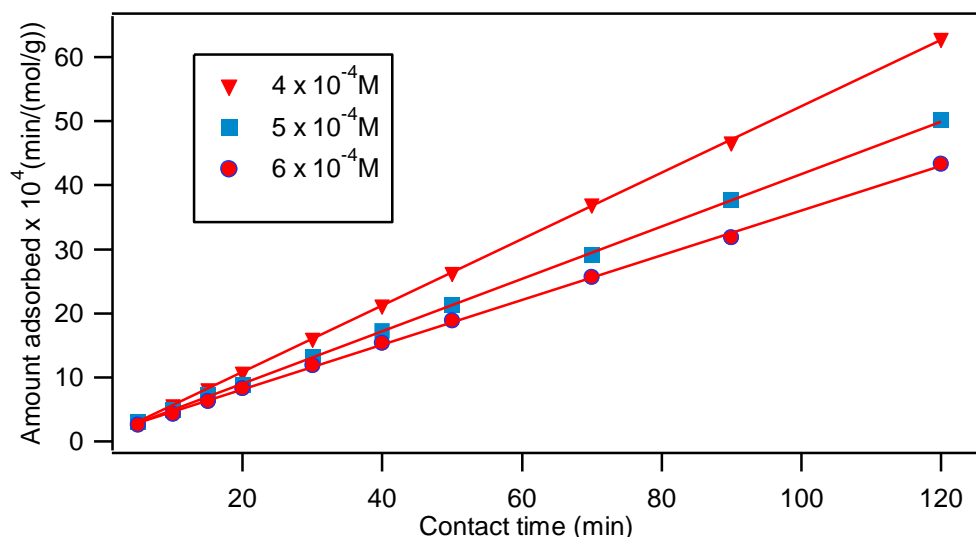
Fig.11.Pseudo second order plots for SO adsorption on BTB

Table.2.Kinetic parameters for the adsorption of SO on BTB

Adsorbate conc. (M)	Pseudo-first-order				Pseudo-second-order			
	q_e(exp) (mol/g)	k_1 (1/min)	q_e(calc) (mol/g)	R^2	k_2 (g / mol min)	q_e(calc) (mol/g)		R^2
4.0×10^{-4}	1.837×10^{-4}	0.044	1.958×10^{-5}	0.963	0.560×10^4	1.927×10^{-4}	0.999	
5.0×10^{-4}	2.221×10^{-4}	0.052	6.519×10^{-5}	0.970	0.189×10^4	2.448×10^{-4}		0.999
6.0×10^{-4}	2.504×10^{-4}	0.043	8.840×10^{-5}	0.993	0.108×10^4	2.863×10^{-4}		0.999

5. Thermodynamic parameters

The following relationships [15] were used to calculate thermodynamic parameters such as Gibb's free energy change (ΔG), enthalpy changes (ΔH), and entropy change (ΔS).

$$\Delta G = -RT\, lnK \qquad (9)$$

According to Van't Hoff equation, we have

$$lnK = -\frac{\Delta G}{RT} = \frac{\Delta S}{R} - \frac{\Delta H}{R}\left(\frac{1}{T}\right) \qquad (10)$$

where K (l/mol) is the Langmuir equilibrium constant calculated from the C_e/q_e versus C_e plot, R (8.314J/mol/K) is the universal gas constant, and T is the temperature. The slope and intercepts of lnK_L versus 1/T (Fig.12) were used to calculate ΔH and ΔS.Even if positive

ΔH values signify an endothermic process, positive ΔS values cause the process to become spontaneous with negative ΔG values.
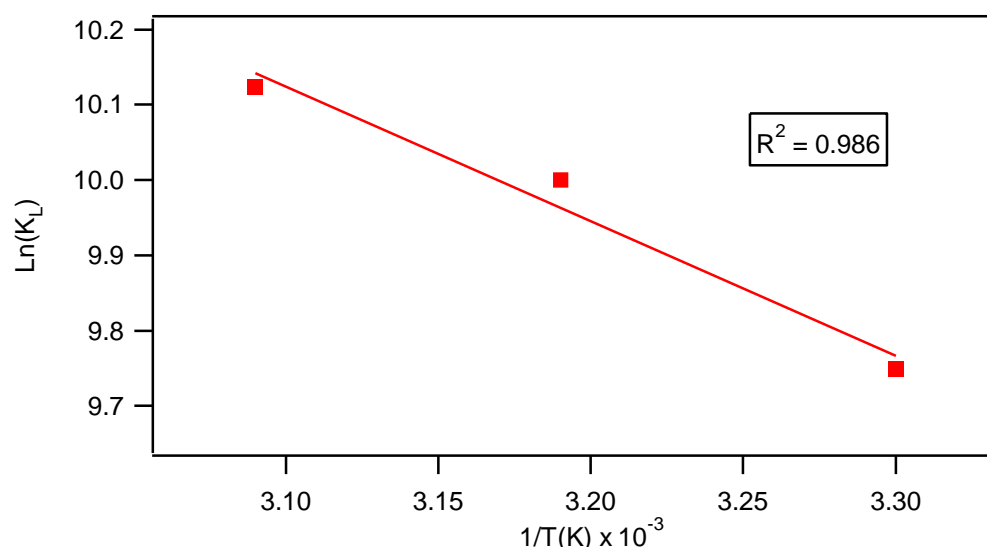

Fig.12.Van't Hoff plot for SO adsorption

Table.3. Thermodynamic Parameters

T (K)	Thermodynamic parameters		
	ΔG(KJ/mol)	ΔH(KJ/mol)	ΔS(J/mol/K)
303	-24.55	14.86	130.25
313	-26.04		
323	-27.18		

6. Summary and conclusions

Bael tree bark is an effective adsorbent for removing Safranine O dye from aqueous solutions.The percentage removal of Safranine O dye varied with adsorbent dose, initial dye concentration, pH, contact time, and temperature.FT-IR and SEM were used to characterize the adsorbent. Because of the increased surface area and availability of active sites, the percentage removal increased with increasing adsorbent dose.Equilibrium data best fit to the Langmuir adsorption isotherm equation, confirming Safranine O monolayer coverage onto Bael tree bark with a monolayer adsorption capacity of 4.88 x 10$^-$ ^{4}mol/g.Adsorption isotherms obeyed the Langmuir isotherm confirming that monolayer – adsorption of Safranine Oon Bael tree bark is possible.The calculated and experimental q_e

values (equilibrium sorption capacity) were not close to each other, the adsorption kinetics of Safranine O with Bael tree bark did not follow pseudo first order kinetics. The adsorption kinetics of Safranine O with Bael tree bark followed pseudo second order because the calculated and experimental q_e values agreed well. This demonstrated that the system used pseudo second order kinetics.A temperature increases from 30°C to 50°C significantly increases the adsorption capacity of SO dye on Bael tree bark powder, indicating that adsorption is endothermic or chemisorption in nature.Despite the fact that positive ΔH values indicate an endothermic process, the process becomes spontaneous with negative ΔG values due to positive ΔS values. Bael tree bark could be used to remove Safranine O dye from an aqueous system at a low cost.

References

1. D. Asma, S. Kahraman, S. Cing, O. Yesilada, "Adsorptive removal of textile dyes from aqueous solutions by dead fungal biomass", J.Basic Microbial, 46[1] 3-9 (2006).

2. Choi J H, Shin W S, Lee W S, Joo D J, Lee J D and Choi S J, "Studies on the Removal of rhodamine B and Malachite Green from aqueous Solution by Activated carbon", Environ Technol., 2001, 22, 1025-1033.

3. Wu J and Wang T, "Ozonation of aqueous azo dye in a semi-batch reactor", Water Res.,2001, 35, 1093-1099.

4. C. A. Buckley "Membrane technology for the treatment of dye house effluents", Water Sci Technol., 1992, 22, 265-274.

5. S.H. Lin, C.F. Peng, "Continuous treatment of textile wastewater by combined coagulation", Water Res., 1996, 30, 587-592.

6. R. Aplin, T. D. Wait. "Comparison of three advanced oxidation processes for degradation of textile dyes", Water Sci Technol., 2000, 42, 345-354.

7. A.L. Henderson, T. C. Schmitt, T.M. Heinze, C. E. Cerniglia, "Reduction of malachite green to leucomalachite green by intestinal bacteria", Appl Environ Microbiol, 1997, 63, 4099-4101.

8. Lambert S D, "Evaluation inorganic adsorbent for the removal of problematic textile dye and pesticides", Water Technol., 1997, 36, 173-180.

9. Sh. Shariati, M. Faraji, Y. Yamini, A. A. Rajab, Fe_3O_4 magnetic nanoparticles modified with sodium dodecyl sulfate for removal of safranin O dye from aqueous solutions. Desalination 270 (2011) 160–165.

10. M. R. Malekbala, S. Hosseini, S. K. Yazdi, S. M. Soltani, M. R. Malekbala, The study of the potential capability of sugar beet pulp on the removal efficiency of two cationic dyes. Chemical engineering Research and design (2011), doi:10.1016/j.cherd.2011.09.010.

11. Yasemin Bulut, HalukAydın, A kinetics and thermodynamics study of methylene blue adsorption on wheat shells, Desalination 194 (2006) 259–267

12. C. Namasivayam, N. Kanchana, Waste banana pith as adsorbent for color removal from wastewaters, Chemosphere 25, (1992), 1691-1706

13. Y. S. Ho, Review of second order models for adsorption systems, Journal of Hazardous Materials B 136 (2006), 681-689.

14. EmrahBulut, MahmutOzacar, I.Ayhansengil, Adsorption of malachite green onto bentonite: Equilibrium and Kinetic and process design, Microporous and mesoporous Materials 115, (2008), 234-246.

15. Y.S.Ho, G. Mckay, A comparison of chemisorption kinetic models applied to pollutant removal on various sorbents, Process.Saf.Environ, 76, (1998), 332-340.

16. Yu Liu, Some consideration on the Langmuir isotherm equation, Colloids and Surfaces A: Physicochem. Eng. Aspects 274 (2006) 34–36.

17. Y.S. G. McKay, D.A.J. Wase and C.F. Foster, "Kinetics And Isotherm studies on cationic Dyes adsorption onto annonasqumosa seed activated carbon", Adsorb. Sci. Techno, 2000, 18, 639– 650.