SEM, FTIR and EDAX Studies for the Removal of Safranin Dye from Water Bodies using Modified Biomaterial - *Bambusa Tulda*

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**Abstract:** In the present study, removal of safranin dye from water bodies was investigated using modified biomaterial - *Bambusa Tulda*. Initial experiments were conducted with NaOH, HCI and distilled washed bambusa tulda, out of which NaOH treated bambusa tulda (NHBT) showed best results. FTIR, SEM and EDAX were done to identify the functional characterization, surface morphology and elemental composition of adsorbent. Presence of hydroxyl groups and carboxyl group at the surface of NHBT results in the adsorption of safranin dye from water bodies. The operation parameters such as pH (3-10), contact time (0 – 90 mins) and dose (1 to 10) gm/l were taken for investigation. The best removal takes place at pH 7, 200 rpm, dose at 10 gm/l, initial concentration 50 mg/l, at equilibrium time 60 minutes and at 298 K temperature with maximum adsorption capacity of 32.26 mg/gm. Langmuir isotherm model found to be best suited with experimental data out of 4 isotherm i.e Langmuir, Freundlich, Temkin and D-R isotherm. The adsorption process followed pseudo second order model. Taking above results into consideration, it is concluded that NHBT is a promising and efficient bioadsorbent for the removal of safranin dye from water bodies.

**Keywords:** Adsorption isotherm, Bambusa tulda, Bioadsorbent, Safranin dye.

**1. INTRODUCTION**

Water is the most important natural resource for survival of all living beings. However, present condition is that the fresh natural water is polluted with several pollutants and it is a major issue to address by all countries of the world. Industrial dye effluents are one of the major cause of pollution of fresh water. Dyes are used by industries like textile, leather, cosmetic, plastic, rubber, food etc as a colouring agent. The untreated discharge from such industries enters into the water bodies and makes it polluted. Such polluted water is toxic and it is carcinogenic and mutagenic in nature. Because of change in colour, photosynthesis process gets disturbed and as a result, aquatic life gets disturbed completely. Removal of such dyes from water bodies is a major challenge for humankind [1].

Safranin is a cationic dye mostly used as a colouring agent by the industries. The Safranin dye has much worst impact on human as well as aquatic animals and plants life. It effects directly on lungs, throat, kidney, liver, skin infection and irritation of eyes causing redness. It is structurally more stable and so very difficult to biodegrade [2]. Traditional technologies are expensive and
not very effective, so new technologies with cost effectiveness is necessary to meet the need for treatment of dye pollution in our water bodies. Among all the advanced techniques like photo catalysis, oxidation process, ion exchange, electrolysis, adsorption techniques is best among all due to its high efficiency, simple design, easy maintenance operation, resistance and insensitivity towards toxin dyes [3].

Activated carbon is commonly used as adsorbent, however activated carbon is expensive and hence modern researcher are in search of other low cost adsorbent mainly bioadsorbent because of its greater availability, low cost as compared to activated carbon and eco-friendly. Many low cost bioadsorbent such as jackfruit peel, garlic peel, hazelnut shell, tea leaves etc. have been studied in literature for dye removal [4]. *Bambusa Tulda* (a variety of bamboo) is a well-known high growth rate plant with high tensile strength; it is available in abundance, inexpensive, bio-degradable and insoluble in water. It consists mainly of cellulose, hemicelluloses and lignin. Other constituents are resins, waxes, starch, silica and inorganic salts with density of 0.96 gm/cc of *bambusa tulda* [5, 6]. But like all lingo cellulosic materials, bamboo too got low resistance towards biological degrading agents so, an effort was made to enhance the resistance and increase the removal rate of dyes by chemically modifying the *bambusa tulda*. However, literature survey also reveals that till now no significant work has been done on chemically modified *Bambusa Tulda* by NaOH for the removal of Safranin dye from water bodies.

The objective of the study is to find out the potential efficiency of low cost chemically modified bioadsorbent NHBT (NaOH treated *Bambusa Tulda*) for the removal of safranin dye from water bodies. In this study, the comparisons of *bambusa tulda* treated with NaOH, HCl and raw distilled washed were evaluated along with the effect of pH, dose and contact time for safranin dye removal. SEM, FTIR, EDAX, adsorption isotherm, kinetic models was also investigated.

2. MATERIAL AND METHODS

2.1 Characterization and preparation of Bio-material.

Bamboo was collected from local market and cut into small pieces. Particle size between 425 to 600 microns sieve size (Geometric mean size 539 microns) were selected for present study. It was than washed with distilled water and dried at 60 °C for 24 hours. It was than treated with 0.1 M sodium hydroxide (NaOH) at 27 °C temperature for 4 hours at 200 rpm in rotary shaker. Similarly it was also treated with 0.1 M hydrochloric acid (HCl). Than excess of NaOH or HCl was removed after washing it several times with distilled water and pH was maintained between 7 ± 0.5 and dried again in oven, it was later kept in air tight container for the study. The distilled washed, NaOH and HCl treated *bambusa tulda* were named as DWBT, NHBT and HBT respectively. Scanning electron microscope (SEM) was done to study the surface morphology of the *bambusa tulda*. Functional group analysis was studied by the Fourier transform infrared radiation (FTIR) spectra. The elemental composition of materials was done by EDAX.

2.2 Adsorbate

Cationic dye Safranin (C.I. 50240, 350.85 gmo1⁻¹, C₂₉H₁₉N₄Cl, λ_max= 516 nm) was used in the experiment as a pollutant in water bodies [2]. Stock solution of 1000 mg/l was prepared by dissolving the adequate quantity of dye in distilled water. All the experimental dye solution was prepared by diluting the prepared stock solution with distilled water to get required concentration level. The pH was maintained in solution by adding 0.1 M HCl and 0.1 M NaOH solution if required.
2.3 Batch adsorption studies

The batch adsorption studies were conducted in 250 ml Erlenmeyer flasks with 50 ml of total dye solution with initial concentration of 50 mg/l. adequate dose of 1 gm/l was added into the solution and agitated at 200 rpm for 90 minutes in rotary shaker. The effect of pH (3, 5, 6, 7, 8, 10), adsorbent dose (1- 10 ) gm/l, contact time (5, 10, 15, 20, 30, 45, 60, 90 minutes) were studied. At regular interval, samples were collected and examined in UV-VIS Spectrophotometer. The amount of dye adsorbed per unit of adsorbent in mg/gm was calculated by following equation no 1.

\[ q = \frac{(C_0 - C_e) V}{m} \]  

Where, \( q \) = amount of the adsorbate adsorbed at any time (mg/gm). \( C_0 \) = initial concentration of adsorbate (dye) in (mg/l). \( C_e \) = equilibrium concentration of the dye in (mg/l). \( V \) = total volume of the solution in (l), \( m \) = mass of adsorbent in given solution (gm). All the experiments were performed in triplicate, and average values were taken for the analysis.

3. RESULTS AND DISCUSSION

3.1 Characterization of Bambusa Tulda

Scanning electron microscope studies was done to understand the surface morphology and characterization of adsorbent, before and after chemical modification and after adsorption of dye. In Fig 1 (a) uneven, rough pores and fractured structure are seen in DWBT. The structures signifies the presence of macropores very clearly and it is responsible for high surface area of bambusa tulda. In Fig 1 (b) for NHBT it was seen that there is reduction in fractured structure with increase in surface roughness and more active pores cavity were seen. The dimensions of the pores appears to be small in DWBT as compare to NHBT. After NaOH treatment, hemicellulose and lignin present in bambusa tulda gets removed and larger surface area came to existance. In Fig 1(c) Safranin dye was adsorbed by NHBT. Its shows smooth surface as all the dye molecules are mounted over the pores cavity of adsorbent [7].

EDAX analysis helps to find all the fundamental compositional information needed to do material analysis [7]. EDAX spectra of safranin adsorbed NHBT is shown in Fig 2. From the analysis it is seen that safranin dye adsorbed NHBT consist of specific elements such as C, O, Na, Cl etc. [8].

Fourier Transform Infrared Spectroscopy (FTIR) analyses were done to identify the functional group and the molecular structure present in the bambusa tulda. The spectrum range of FTIR was within 4000 to 400 cm\(^{-1}\). FTIR of Safranin dye adsorbed NHBT is shown in Fig. 3. A strong peak observed at 3451.35 cm\(^{-1}\) indicates the hydroxyl (O-H) group, the peak at 2920.09 cm\(^{-1}\) correspond to CH\(_3\) (alkane group). Presence of carboxyl group was observed at 1735.59 cm\(^{-1}\). The peak at 1635.71 cm\(^{-1}\) signifies bond of alkenyl C=C. It was seen that presence of hydroxyl groups and carboxyl group at the surface of NHBT helps in adsorption of safranin from water bodies, similar results were found in Zhang and Bing, 2014 [9].
3.2 Effect of operational parameters

3.2.1 Effect of contact time

The effect of contact time with respect to DWBT, NHBT and HBT were studies for the removal of safranin dye. The initial concentration of Safranin dye was kept at 50 mg/l, pH 7,
time 90 minutes, rpm -200, dose 10 gm/l. In Fig. 4 it was seen that at initial stage removal was higher in all the three cases and decreases as it reaches the equilibrium time. It was observed that NaOH gives best removal of safranin (98.67 %) in compare with DWBT (97.42 %) and HBT (95.83 %) treated bambusa tulda. At initial stage there are large amount of surface area and so removal was very high but after 60 minutes there is less removal because of less binding sites on adsorbent. Similar observation was noticed by Kumar and Kumar, 2015 [10].

**Figure 4. Effect of contact time on adsorption of Safranin by DWBT, NHBT, HBT**

### 3.2.2 Effect of pH

The effect of pH is one of the important parameters in adsorption process, which affects the surface charge of the adsorbent, functional groups of adsorbate and mechanism of adsorption. The effect of pH on the removal of Safranin dye is shown in Fig 5. The removal of dye increases as the pH increases from 5 to 8 and after that there were no significant removal after pH 8. The zero point charge (pH\(_{ZPC}\)) of NHBT was found as 7.6. The adsorption sites on NHBT less than pH 7.6 is positive in nature and greater than 7.6 is negative in nature. With the increase of solution pH, negative surface charge molecules of NHBT get attracted with positive charge of safranin dye molecules under electrostatic force of attraction and it favors greater adsorption of safranin dye. It got less effect under acidic condition in compare with basic condition [11]. Similar observation was noticed by Kumar and Kumar, 2015 [10] and Hossein and Mohammadi, 2015 [12].

**Figure 5. Effect of pH on adsorption of Safranin by NHBT**
3.2.3 Effect of adsorbent dose

The effect of dose for the removal of safranin dye was studied by varying from dose from 1 gm/l to 10 gm/l. 50 ml dye solution of 100 mg/l of safranin dye were used for the experiments at temperature 25 °C, rpm 200 and pH 7. As the dose of NHBT increases the removal of dye also increases, it is because more amount of adsorbent dose NHBT results in more no of active adsorption sites for safranin dye removal.

3.3 Adsorption isotherms

Adsorption isotherm experiments were conducted at 298 K, 200 rpm, for initial dye concentration of 100 mg/l, by varying the dose of NHBT from (1 – 10) gm/l at pH 7. Isotherm studies was done to understand the interaction between of adsorbent/adsorbate and adsorption mechanism. Here four isotherm models i.e. Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich (D–R) were fitted with experimental equilibrium data for adsorption of safranin onto NHBT. By comparing the values in Table 1, it is seen that adsorption of safranin onto NHBT best fits in Langmuir isotherm with maximum adsorption capacity was $Q_{max} = 32.26$ mg/gm, which confirms the occurrence of monolayer adsorption of safranin on NHBT and adsorption taking place at specific homogenous sites. The constant $1/n$ of Freundlich was 0.303 which is less than 1 and it indicates the process is favorable. Another important concept of Langmuir isotherm is $R_L$, it signifies the shape of the isotherm models like $R_L$ value > 1 is unfavourable, $R_L$= 1 is linear, $R_L$= 0 is irreversible or 0 < $R_L$< 1 the case is favourable. Here the value of $R_L$ was 0.15 indicating the isotherm model is favorable process [13].

Table 1. Adsorption isotherm parameters of safranin onto NHBT

| Langmuir isotherms | Freundlich isotherms | Temkin isotherms | D-R isotherms |
|-------------------|----------------------|-----------------|--------------|
| $Q_{max}$ (mg/gm) = 32.26 | $K_f = 7.656$(mg/gm) | $K_T = 9.192$ (l/mg) | $q_s = -3E-06$ (mg/gm) |
| $b$ (l/mg) = 0.113 | $1/n = 0.303$ | $B_T = 0.652$ | $β = 20.73$ (m-mole$^2$ / J$^2$) |
| $R^2 = 0.923$ | $R^2 = 0.909$ | $R^2 = 0.875$ | $R^2 = 0.785$ |

3.4 Adsorption kinetics

To understand the nature of adsorption type, rate and capacity of adsorption process adsorption kinetics study was studied at temperature 298 K, pH 7, 200 rpm and optimum dose of 10 gm/l of initial safranin dye concentration of 50 mg/l. The present study is on pseudo first-order ($ln (q_e – q) = - K_p t + lnq_e$) and pseudo-second-order rate equation ($\frac{t}{q} = \frac{1}{K_sc} + \frac{1}{K_s q_e}$) in linear form. Plots of pseudo first order and pseudo second order are shown in Fig. 6 and Fig. 7 respectively. Adsorption kinetic parameters for pseudo-first order and pseudo-second order were calculated as shown in Table 2. It can be concluded that adsorption of safranin dye onto NHBT best fitted on pseudo-second order rate model, which indicates that the adsorption process is a rate limiting step which involves forces to share or exchange electrons between adsorbate and adsorbent. Similar results were reported by Kumar and Kumar, 2015 and Fayazi. et al. 2015 [10, 13].
Table 2. Adsorption kinetic parameters at initial concentration of safranin

| $C_0$ (mg/l) | $q_e$, Exp (mg/gm) | $q_e$, Cal (mg/gm) | $k_p$ | $R^2$ | $q_e$, Cal (mg/gm) | $k_p$ | $R^2$ |
|--------------|-------------------|-------------------|-------|-------|-------------------|-------|-------|
| 50           | 5.0               | 1.0764            | 0.0460 | 0.924 | 5.025             | 0.1253 | 0.998 |

4. CONCLUSION

The present study shows that NHBT (NaOH treated Bambusa Tulda) is an effective bio-adsorbent for the removal of safranin dye. All the operational parameters were found to have a great influence onto NHBT for dye removal. Optimum pH was 7, equilibrium time 60 minutes, dose 10 gm/l with maximum adsorption capacity found to be 32.26 mg/gm and kinetics property found better in pseudo-second order model. Taking above results into consideration, it is concluded that NHBT is a promising and efficient bioadsorbent for the removal of safranin dye from water bodies.

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