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# Isothermal Evaluation of Chemical Modification of *Ricinus communis* Stem Used for Adsorptive Removal of Brilliant Blue FCF Dye from Water

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Agricultural solid waste namely *Ricinus communis* stem was used for removing an anionic dye namely Brilliant blue FCF from synthetic waste-water. In order to enhance adsorption capacity of *Ricinus communis* stem, it was treated with acid and base separately and comparative adsorption studies were carried out for determining effectiveness of chemical modification in terms of sorption capacity on batch scale. Chemisorption occurred during removal of dye by adsorption as indicated by Langmuir model applicability and maximum sorption capacities were 52.4 μg/g, which is increased after acid treatment to 2445 μg/g and decreased by base treatment to 31.4 μg/g. The values of thermodynamic parameter free energy of adsorption (ΔG°) for these adsorbents were -1.24, -3.46 and -0.63 KJ/mol, indicating exothermic nature. Results showed that acid modification of *Ricinus communis* stem is more suitable for adsorptive removal of Brilliant blue FCF dye.

**Key Words: Brilliant blue FCF, *Ricinus communis* stem, Adsorption, Chemical modification.**

## INTRODUCTION

Adequate supply of clean water is necessary for sustainability of any community and industries. Dyes are extensively used in many industries for colouring and/or camouflage original materials like fabrics, clothes, foods, leather, furnitures *etc*. Mostly synthetic dyes are employed now because of enormous variety in colour shades. About 10-15 % of these dyes are wasted during industrial processings[1-4]. Although their discharge is not as much of as compared to other pollutants but they are noticeable in small quantities due to their colour intensity, which in turns pose hazards during photosynthesis in aquatic plants and lead to death of phytoplanktons and zooplanktons[5-8]. So their removal from industrial effluents is necessary and of vital importance. Adsorption methodology is one of the commonly employed waste-water treatment ways. Researchers are trying to find new adsorbents from their indigenous sources, especially from agro-waste origin, because of their low cost and ease in handling during processing[9-11].

In this study, anionic food stuff, *i.e.*, brilliant blue FCF dye (Fig. 1) was used. Its characteristics, synonyms, applications and hazardous effects are tabulated in Table-1. Dyes are usually categorized in cationic or anionic dyes on the presence of ionizable functional groups. Brilliant blue FCF is an anionic dye due to the presence of two sulfonic groups.

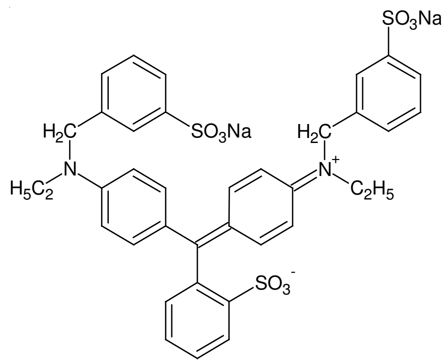


Fig. 1. Molecular structure of Brilliant blue FCF dye

Scientists have tried to remove it by electrochemical, photochemical and adsorption processes[12-15].

During past few decades, adsorption methodologies were focused more for detoxification of dyes from effluents and new adsorbents were tried to replace activated charcoal. Cost, availability and handling are important parameters for selection of adsorbent. Agro-waste materials fulfill these criteria, but generally their adsorption capacities are lowered as compared to synthetic adsorbents. So, different types of physical and chemical modifications are investigated by researchers for improving adsorption capacity of agro-waste materials depending on the nature of pollutant removed[16-19].

TABLE-1
CHARACTERISTICS OF BRILLIANT BLUE FCF DYE[12-14]

| Properties | Specifications |
|---|---|
| CI Number | 42090 |
| Molecular formula | $C_{37}H_{34}N_2O_9S_3$ $Na_2$ |
| CAS number | 3844-45-9 |
| IUPAC name | Benzenemethanaminium, N-ethyl-N-[4-[[4-[ethyl[(3-sulfophenyl)methyl]amino]phenyl](2-sulfophenyl)methylene]-2,5-cyclohexadien-1-ylidene]-3-sulfo-, inner salt, disodium salt |
| Molecular weight | 792.86 (g/mol) |
| Water solubility | 200 g/L at 2-60 ºC |
| Synonyms | Acid Blue 9, Alzen Food Blue No. 1, Atracid Blue FG, Erioglaucine, Eriosky blue, Patent Blue AR, Xylene Blue VSG |
| Applications | As food color in: ice creams, processed vegetables, soups, dairy products and drinks. In cosmetics employed in: beauty soaps, shampoos, conditioners, mouthwash and other hygiene products. In soil science, used as tracer for monitoring water penetration in soil. |
| Hazards for human beings | Allergic for asthmatic patients, dermatitis, carcinogenic, reproductive and CNS disorders |

In this study, *Ricinus communis* (Local name: Castor, Arund) stem is used for adsorption of Brilliant blue FCF dye. It belongs to Euphorbiaceae family. Its seeds are used in Ayurvedic medicines[20]. Castor oil is also used for treating gastrointestinal problems, hair conditioning, skin infections, constipation and arthritis. It is used in various industries like plastic, synthetic resins (*e.g.*: polyurethane), food, cosmetics, paints, varnishes and lubricants. Its adsorption capacity was further enhanced by chemical treatment[21-24]. Here different adsorption parameters were investigated after chemically modifying *Ricinus communis* stem with acid and base separately and then isothermal studies were carried out for investigating mechanism of adsorption and feasibility of this process.

## EXPERIMENTAL

Brilliant Blue FCF dye (Fluka), HCl and NaOH (Merck) were used as received without further processing. The adsorbent *Ricinus communis* stems were collected from local fields, washed and dried in sunlight for a week and chopped into small pieces. Spectro UV-visible Double Beam (UVD-3500, Labomed) spectrophotometer, FT-IR (Perkin Elmer-RXI) and S.E.M (JEOL, JSM-5910) were used in this work.

**Preparation of biomass:** The chopped dried *Ricinus communis* stems were dried in an oven at 70 ºC for 8 h and crushed into powder by grinding. Then it was sieved and preserved in the plastic air tight bottles for use[25]. It was labeled as untreated adsorbent.

**Chemical treatment of biomass:** For this purpose, chopped dried *Ricinus communis* stems were treated with acid and base separately by soaking them into 0.01 M HCl and 0.01 M NaOH for 6 h. Then after filtering and washing, they were dried in air for two days, followed by oven drying at 70 ºC for 7 h and crushed into powder by grinding in Electric grinder (Ken-Wood). They were labeled as acid treated adsorbent and base treated adsorbent. For finding structural changes and characterizing functional groups in untreated and chemical treated *Ricinus communis* stem powder, they were analyzed by recording their FT-IR spectra and S.E.M. graphs before and after chemical treatment[26].

**Preparation of synthetic waste-water:** Brilliant blue FCF stock solution (0.1 g/100 mL) was prepared within distilled water and further dilutions were done as required during experiments.

**Adsorption studies:** Optimization of various process parameters like particle size of adsorbent, pH of dye solution, agitation speed, contact time and temperature for enhanced removal of Brilliant blue FCF dye was done by adopting developed methodology for dye adsorption using 25 mL of synthetic waste-water[27]. At the end, dye solutions were separated from adsorbent by centrifugation and remaining dye concentration was determined spectrometrically at $\lambda_{max}$ 637 nm. The amount of adsorbed dye 'q'(mg/g) was calculated by eqn. 1:

$$q = \frac{(C_0 - C_e)V}{m} \quad (1)$$

Here V is the volume of dye solution (mL) and m is adsorbent dose (g). The % adsorption was measured by eqn. 2:

$$\text{Adsorption } (\%) = \frac{C_0 - C_e}{C_0} \times 100 \quad (2)$$

These set of experiments were done in triplicate and average values were used for plotting graphs.

**Isothermal evaluation:** Langmuir and Freundlich models are used to explain the adsorption mechanisms. The applicability of Langmuir model on equilibrium data shows the homogenous distribution of active binding sites on adsorbent and chemisorptive removal of pollutant. It was plotted by using eqn. 3:

$$\frac{C_e}{q} = \frac{1}{bq_m} + \frac{C_e}{q_m} \quad (3)$$

Here '$q_m$' and 'b' are Langmuir isotherm parameters. The applicability of Freundlich model on equilibrium data pointed towards multilayer physiosorption of pollutant on adsorbent. It was plotted by using eqn. 4[28]

$$\log q = \log K_F + \frac{1}{n}\log C_e \quad (4)$$

Here '$K_F$' and 'n' are Freundlich constants. For studying adsorption isotherm, the optimized conditions of all influencing parameters were used accordingly for 100 mL solutions with varying concentration range 10-35 mg/L.

**Thermodynamical studies[27,28]:** ΔGº (Gibbs free energy change in KJ/mol) value was calculated by eqn. 5:

$$\Delta G^\circ = -RT \ln K \quad (5)$$

T is temperature in Kelvin, R is gas constant and K is the reciprocal of Langmuir constant b.

## RESULTS AND DISCUSSION

**Characterization of adsorbent:** Fourier transform infrared spectroscopy (FT-IR) was used to determine the functional groups on the adsorbents surface. The FT-IR spectra of untreated, acid treated and base treated *Ricinus communis* stem powder are shown in Figs. 2-4 and corresponding vibrational assignments of specific peaks are given in Table-2 As can be inferred from the FT-IR analysis, the functional groups present on adsorbent surface were: aldehyde, ester, ether, aromatic ring, carboxylic acid, ketone, alcohol and amide groups reflecting the complex nature of binding sites. After acid and base treatments, some of these peaks moved to lower wave number values indicating the chemical changes. These changes observed in the spectra indicated the contribution of these functional groups on *Ricinus communis* stem surface in adsorption process.

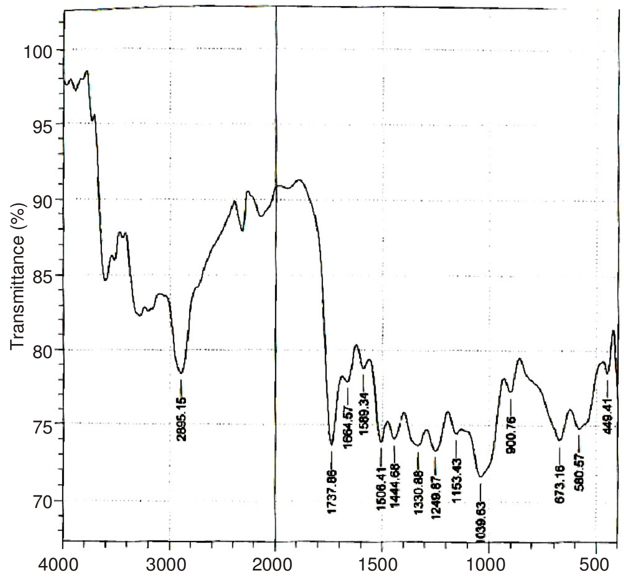


Fig. 2. FT-IR spectrum of *Ricinus communis* stem

Scanning electron micrographs of untreated and chemically treated *Ricinus communis* stem powder was shown in Fig. 5, which is indicating its complex rough surface in untreated form (Fig. 5(a)). Its roughness increased a lot after

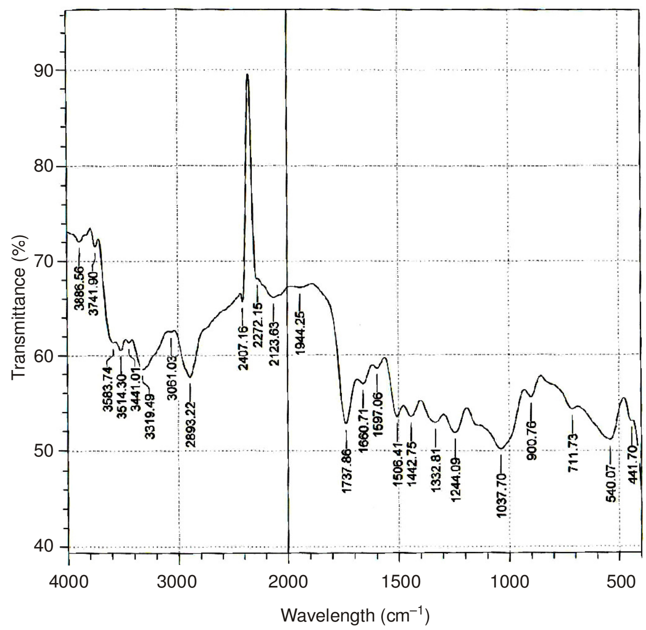


Fig. 3. FT-IR spectrum of acid treated *Ricinus communis* stem

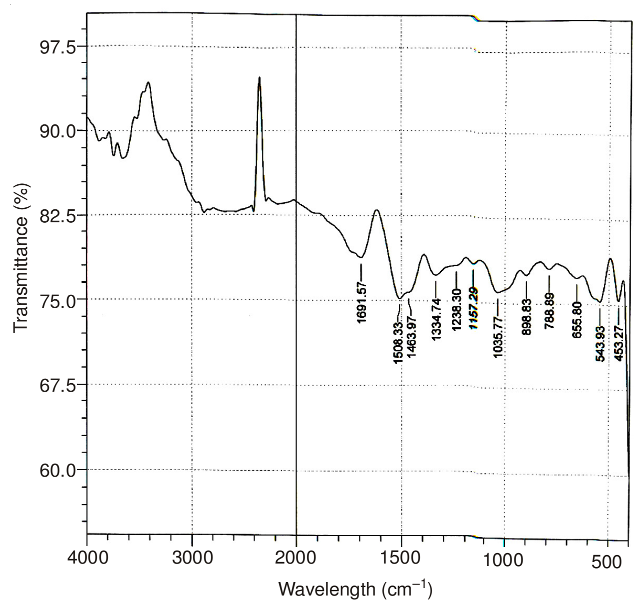


Fig. 4. FT-IR spectrum of base treated *Ricinus communis* stem before adsorption

TABLE-2
CHARACTERISTIC PEAKS IN FT-IR SPECTRUM OF *Ricinus communis* STEM

| Possible vibrational assignments | Wave number ($cm^{-1}$) | | |
|---|---|---|---|
| | Untreated adsorbent | Acid treated adsorbent | Base treated adsorbent |
| OH stretching of carboxylic acid, phenols | 3600 | 3583.74, 3514.30 | 3650-3600 |
| NH asymmetric stretching of amides | 3360 | 3319.49 | 3420-3300 |
| C=C-H asymmetric stretching of alkenes | – | 3061.03 | – |
| C-H stretching of CH and $CH_2$ | 2895.15 | 2893.22 | – |
| $NH^+$ stretching of amine | 2260 | 2407.16, 2272.15 | 2350-2200 |
| Conjugated aromatic CN stretching | 2125 | 2123.63, 1944.25 | 2140-2100 |
| C=O stretching of aldehyde, ketones | 1737.86 | 1737.86 | 1691.57 |
| C=C stretching of aromatic ring and olefins | 1664.57, 1589.34 | 1660.71, 1597.06 1506.41 | 1508.33 |
| -C $(CH_3)_3$ bending vibration | 1444.88 | 1442.75 | 1463.97 |
| C≡N stretching of aryl amines | 1330.88 | 1332.81 | 1344.74 |
| C-O-C symmetric stretching of esters, ethers and epoxides | 1249.87 | 1244.09 | 1238.30, |
| (C-O) Hydroxyl and ether groups | 1153.43 | 1037.70 | 1157.29, 1035.77 |
| (C-H) bending of aromatic groups | 900.76 | 900.76 | 898.83 |

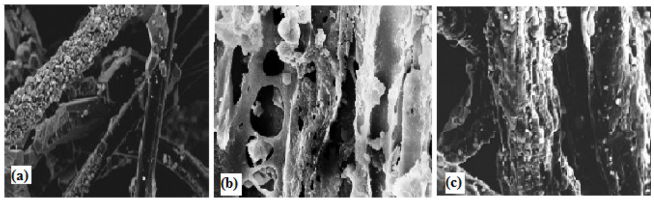


Fig. 5. Scanning electron micrographs of *Ricinus communis* stem (a) before chemical treatment (b) after acid treatment (c) after base treatment

acid treatment, which enhances adsorptive removal of dye by exposing more surface area [Fig. 5(b)]. Base treatment has increased the bulginess of adsorbent as indicated from Fig. 5(b), which did not help in more adsorption as compared to untreated form of *Ricinus communis* stem powder.

**Optimization of operational conditions:** Various operational parameters were optimized one after the other keeping other conditions constant. Particle size is related with the adsorbent exposed surface area. Different mesh sized *Ricinus communis* stem particles were utilized for adsorption of dye and results are given in Fig. 6. As mesh size increases, adsorbent particle size decreases producing more fine powder which can interact with dye solution more effectively[21]. Maximum adsorption of Brilliant Blue FCF dye was observed at 20, 80 and 60 mesh size (ASTM) using untreated adsorbent, acid treated adsorbent and for base treated adsorbent, respectively. If particle size decreased further, it results in coagulation of *Ricinus communis* stem particles which hindered adsorption.

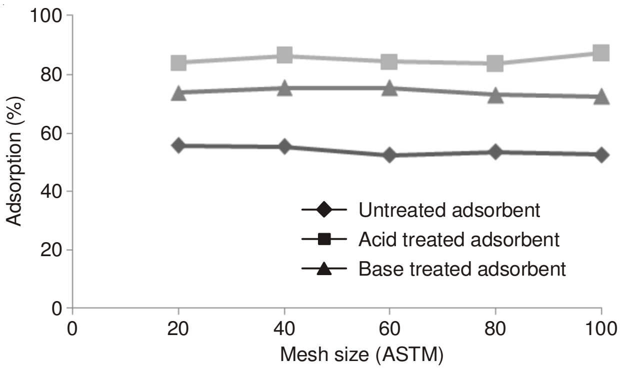


Fig. 6. Comparitive graph showing effect of particle size on adsorption of Brilliant blue FCF dye by *Ricinus communis* stem

The adsorption of Brilliant blue FCF dye on acid treated, base treated and untreated *Ricinus communis* stem particles were studied by changing adsorbent dose in the range of 0.5-3.0 g. As shown in Fig. 7, untreated adsorbent gave adsorption maxima 64.72 % at 0.5 g of adsorbent which decreases for higher adsorbent doses, but base treated adsorbent adsorbed maximum dye 85.84 % at 3.0 g dose, while acid treated adsorbent progressed in the same way giving adsorption maxima 98.04 % at 3.0 g dose. Enhanced adsorption capacity with increased adsorbent dose in case of chemically treated *Ricinus communis* stem particles indicate that its binding sites are enhanced.

The relationship of percentage dye removal by adsorbent with contact time was plotted in Fig. 8. Untreated adsorbent, acid treated adsorbent and base treated adsorbent showed 67.10, 93.83 and 79.13 % within 40, 80 and 100 min, respectively. As after chemical treatmet, adsorption sites are increased,

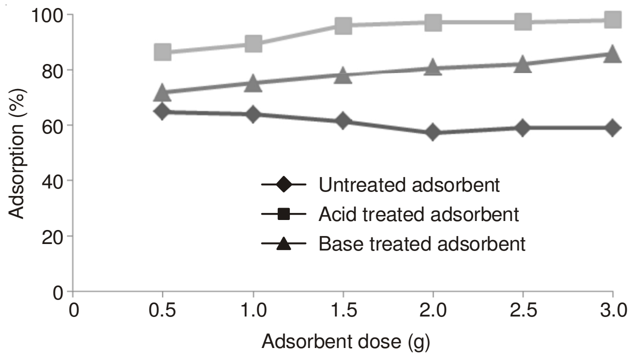


Fig. 7. Comparitive graph showing effect of adsorbent dose on adsorption of Brilliant blue FCF dye by *Ricinus communis* stem

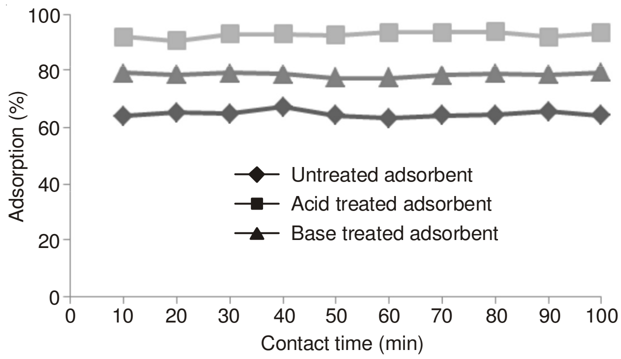


Fig. 8. Comparitive graph showing effect of contact time on adsorption of Brilliant blue FCF dye by *Ricinus communis* stem

so more time is required to attain equlibrium and enhanced adsorption.

Fig. 9 shows the effect of pH variation on adsorption of Brilliant blue FCF dye on *Ricinus communis* stem. Acid treated adsorbent adsorb maximum 98.65 % at pH 7.0, untreated adsorb maximum 94.62 % at pH 2 and base treated adsorb maximum 91.29 % at pH 10. At lower pH, a strong electrostatic contact developed between positively charged *Ricinus communis* stem surface and negatively charged Brilliant Blue FCF molecules using untreated form. Using acid treated *Ricinus communis* stem, the concentration of $H^+$ ions increased on its surface, which helps in more adsorption of anionic dye in neutral conditions. Whereas using base treated *Ricinus communis* stem, more adsorption occurred in basic conditions because that helps in hydrolysis of lignin and cellulosic components of biomass, exposing more adsorption sites for binding of anionic dye[29].

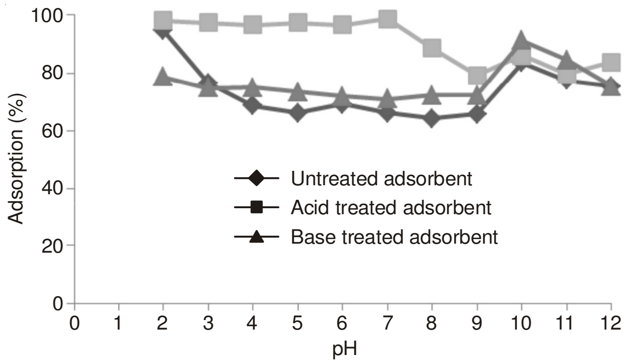


Fig. 9. Comparitive graph showing effect of pH on adsorption of Brilliant blue FCF dye by *Ricinus communis* stem

TABLE-3
LANGMUIR MODEL AND THERMODYNAMICAL PARAMETERS FOR ADSORPTIVE REMOVAL OF BRILLIANT BLUE FCF DYE BY *Ricinus communis* STEM

| Adsorbent | Slope | Intercept | $R^2$ | $q_m$ (µg/ g) | b (L/g) | Thermo dynamical parameter ΔG° (KJ/mol) |
|---|---|---|---|---|---|---|
| Untreated adsorbent | -11.57 | 19.08 | 0.887 | 52.4 | -1.649 | -1.24 |
| Acid treated adsorbent | 1.655 | 0.409 | 0.987 | 2445 | 0.247 | -3.46 |
| Base treated adsorbent | -24.78 | 31.89 | 0.973 | 31.4 | -0.777 | -0.63 |

Agitation of dye solution during adsorption helps in better interaction between the binding sites of adsorbent and dye molecules. Fig. 10 showed that maximum adsorption 67.36 % was observed at 300 rpm using untreated *Ricinus communis* stem, 73.68 % at 100 rpm for base treated and 92.62 % at 250 rpm for acid treated adsorbent. Again acid treated adsorbent showed better efficiency in removing anionic dye, because acid helps in protonation of biomass surface, which can interact more with negatively charged species.

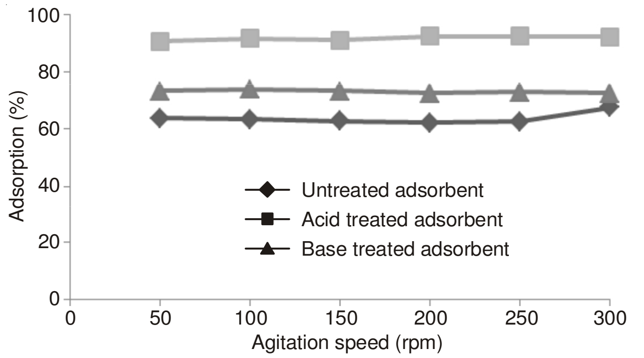


Fig. 10. Comparitive graph showing effect of agitation speed on adsorption of Brilliant blue FCF dye by *Ricinus communis* stem

The temperature effect was investigated in 10-60 °C range and results are given in Fig. 11. The maximum adsorption 67.29 % was found at 60 °C by untreated adsorbent, 96.65 % at 20 °C by acid treated adsorbent and 78.75 % at 20 °C by base treated adsorbent Due to exothermic nature of this process, increase in temperature decreased adsorption capacity[30].

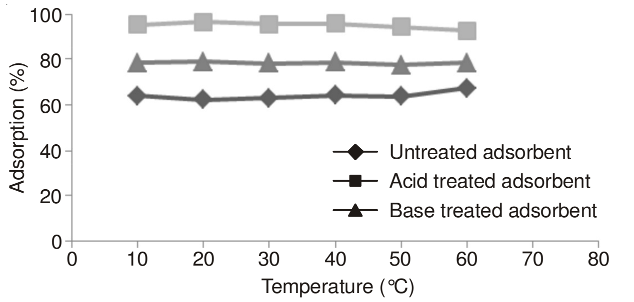


Fig. 11. Comparitive graph showing effect of temprature on adsorption of Brilliant blue FCF dye by *Ricinus communis* stem

**Mechanistic and thermodynamical studies:** Figs. 12 and 13 showing Langmuir and Freundlich curves for Brilliant blue FCF dye adsorption by *Ricinus communis* stem and corresponding parameters are summarized in Tables 3 and 4. The correlation coefficient $R^2$ values indicated the Langmuir model fitted more as compared to Freundlich model in case of acid treated adsorbent suggesting that chemisorptive removal of Brilliant Blue FCF dye occurred more as compared to physio-

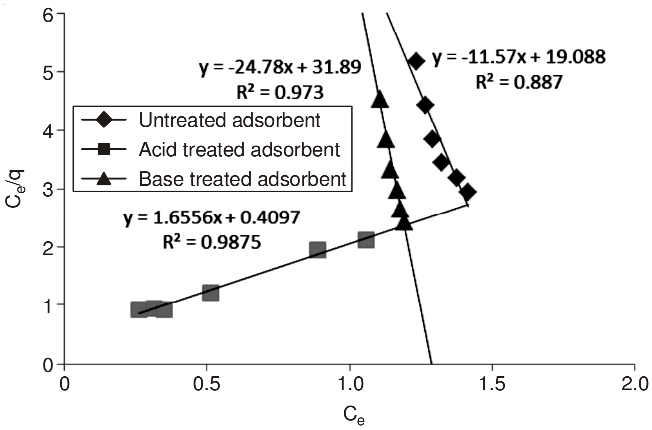


Fig. 12. Langmuir model linear plots showing comparison of untreated and chemically treated *Ricinus communis* stem for removal of Brilliant blue FCF dye

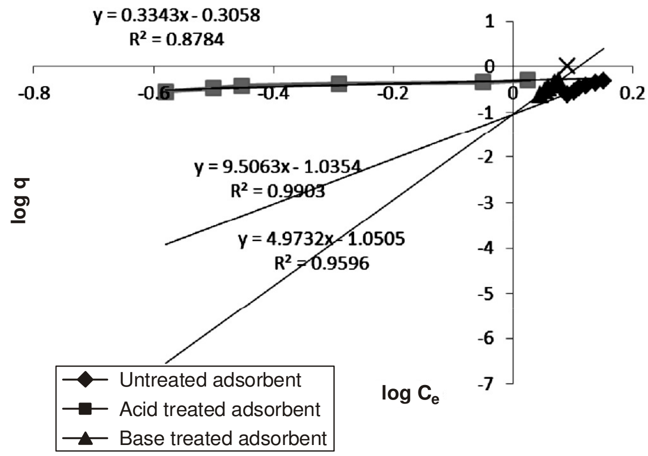


Fig. 13. Freundlich model linear plots showing comparison of untreated and chemically treated *Ricinus communis* stem for removal of Brilliant blue FCF dye

TABLE-4
FREUNDLICH MODEL PARAMETERS FOR ADSORPTIVE REMOVAL OF BRILLIANT BLUE FCF DYE BY *Ricinus communis* STEM

| Adsorbents | Freundlich isotherm parameters | | | | |
|---|---|---|---|---|---|
| | Slope | Intercept | $R^2$ | $K_F$ | n |
| Untreated adsorbent | 4.973 | -1.050 | 0.959 | 0.089 | 0.201 |
| Acid treated adsorbent | 0.334 | -0.305 | 0.878 | 0.495 | 2.994 |
| Base treated adsorbent | 9.506 | -1.035 | 0.990 | 0.092 | 0.105 |

sorption. While Freundlich model is applicable more in case of untreated adsorbent and base treated adsorbent suggesting that heterogeneity of adsorbent is enhanced by base treatment. Maximum adsorption capacity of *Ricinus communis* stem for removing Brilliant blue FCF dye was 52.4 µg/g using its untreated form. Its adsorption capacity enhanced almost 40 times after acid treatment, *i.e.*, 2445 µg/g, but base treatment decreased its adsorption capacity to 31.4 μg/g. *Ricinus communis* stem is composed of lignin, cellulose, hemi-cellulose and a mixture of functional groups like carboxyl, carbonyl, amino and hydroxyl groups with which the dye molecules interact leading to adsorption[20-22]. By acid treatment, surface area and porosity of adsorbent is improved due to hydrolysis of lingo-cellulosic components and protonation of oxygen and nitrogen containing functional groups. '$K_F$' values also indicated that acid treated *Ricinus communis* stem adsorb more by physiosorption as compared to untreated and base treated adsorbent. Same trend is also predicted form S.E.M. graphs of Fig. 5.

Thermodynamical studies showed that this process is feasible more when acid treated *Ricinus communis* stem powder was used, because ΔGº values are negative, *i.e.*, -1.24, -3.46 and -0.63 KJ/mol for untreated, acid treated and base treated *Ricinus communis* stem powder. Feasibility of process decreased after base treatment of *Ricinus communis* stem, as indicated from lower ΔGº value. These values also indicate that adsorption of Brilliant blue FCF dye by *Ricinus communis* stem is exothermic in nature, because of negative values of ΔGº, which in turns correlate to negative values of ΔHº, (as entropy changes are negligible as compared to enthalpy changes at constant temperature, so $\Delta G^o = \Delta H^o - T\Delta S^o$ becomes $\Delta G^o \approx \Delta H^o$).

## Conclusion

Adsorption of Brilliant blue FCF dye on untreated and chemically treated *Ricinus communis* stem was investigated and found that acid treatment enhanced adsorption capacity of *Ricinus communis* stem for removing anionic dye in neutral dye solution conditions, using 3 g adsorbent dose, within 80 min at 250 rpm in room temperature conditions, *i.e.*, 20 ºC and 1 atm. The adsorption of dye by the adsorbent is explained well by isothermal models. Langmuir model applicability indicates the formation of Brilliant Blue FCF dye monolayer on the outer surface of the adsorbent during chemisorption. Physiosorption also increased after acid treatment, which is indicated by Freundlich constant '$K_F$'. Spontaneity and exothermic nature of this process is indicated by ΔGº negative values. These results therefore demonstrated that *Ricinus communis* stem could be a potential source to remove anionic dyes from industrial effluents after acid treatment.

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