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# BIOSORPTION CHARACTERISTICS OF SUGARCANE BAGASSE FOR THE REMOVAL OF FORON BLUE E-BL DYE FROM AQUEOUS SOLUTIONS

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## ABSTRACT

This study presents the biosorption characteristics of sugarcane bagasse for the removal of Foron Blue E-BL (FB), a disperse dye, from aqueous solutions in a batch system. Effect of different parameters i.e., pH, biosorbent dose, contact time, initial dye concentration and temperature was studied. Effect of surfactants, salt, and heavy metal ions was also investigated. Maximum biosorption capacity of native sugarcane bagasse was found to be at pH 4 whilein pretreated and immobilized forms, the biosorbent depicted maximum dye removal at pH 7 with 0.05g biosorbent dose at 30 °C temperature. An equilibrium time of 120 min was observed for maximum removal of the dye with native and pretreated sugarcane bagasse while immobilized sugarcane bagasse required only 90 min to establish saturation point. The saturation point was obtained with 100 mg/L dye concentration. Salt caused an increase in the biosorption capacity, while heavy metal ions and surfactants decreased the biosorption capacity of the biosorbent. Kinetics of biosorption followed the pseudo 2nd order mechanism. Thermodynamics of dye biosorption showed the exothermic nature of process. The results showed that sugarcane bagasse could be used as a promising biomass for the removal of FB from aqueous solutions.

**Key words:** Biosorption; Disperse dyes; Sugarcane bagasse; Immobilization; Modeling.

## INTRODUCTION

Chemical pollution of waste water via a huge range of pollutants is an important environmentalproblem now-a-days. Synthetic dyes are extensively used in various fields of up-to-date technology, like textile,leather tanning, paper and pulp production, food products etc. (Denizand Saygidegera, 2010).Discharging large amount of dyes into water resources, accompanied by organics, bleaches and salts, can affect the physical and chemical properties of fresh water. In addition to their unwanted colors, some dyes may degrade to produce carcinogens and toxic products (Hameed *et al*., 2008).Industries employ different methods to treat wastewater such as, flocculation and coagulation (Ozer*et al.*, 2005), ozonation and oxidation (Malik and Saha, 2003), membrane separation (Ciardelli *et al.*, 2000) and sorption by activated carbon (Bhatnagar and Sillanpaa, 2010). Currently, different physical and chemical treatments are used to treat dye containing wastewater. These processes are not economical so cannot be successively used to treat wide range of dye wastewater. Conversely, biosorption is a novel and cost-effective approach for the wastewater treatment (Haq *et al*., 2011; Asgher and Bhatti, 2012). Biosorption has attracted increasing interest owing to its lower cost, its effectiveness in producing less sludge and its environmental friendliness (Park *et al*., 2003; Safa and Bhatti, 2011).Over the last few decades, there has been an increase in the use of plant waste products for dye removal by biosorption from wastewater because of their natural availability and the high degree of dye removal achieved under laboratory conditions (Ncibi*et al*., 2008; Safa and Bhatti, 2010;Bhatti *et al*., 2012).

Sugarcane bagasse is one of the primary agro-industrial wastes. Sugarcane bagasse mainly consists of cellulose (45%), hemicelluloses (28%), and lignin (18%) (Pehlivan *et al*., 2013). It contains carboxylic and hydroxyl groups, which show the capacity to adsorb the dye molecules by the ion exchange phenomena or by complexation (Dávila-Jiménez, 2005) hence it can be used as a cheap, attractive and effective adsorbent for the removal of dyes from wastewater (Vander *et al*., 2001).

Keeping in view the significance of dyes and their environmental problems, the present project is designed to explore the biosorption potential of sugarcane bagasse for the removal of FB dye from simulated aqueous solution.

## MATERIALS AND METHODS

**Preparation of biomass and dye solution:** Sugarcane bagasse was collected from local juice market and dried in an oven till constant weight. The dried biomass was pulverized in an electric ball mill made locally. Dried, powdered biosorbent was sieved to obtained uniform smallest size fraction of 0.25 mm.The commercial grade FBdye was kindly provided by Clariant Pakistan limited. A stock solution of 1000 ppm concentration was prepared and solutions of different concentrations ranging from 10-250 ppm were made by further dilutions.

Immobilization of bagasse was carried out with sodium alginate. Sodium alginate 1.0 g (1 % w/v) was dissolved in 100 ml of water by heating and then the solution was cooled down to 40 °C and then added biomass (2 g/100 ml) and mixed until to form a homogeneous mixture. Then the mixture was dropped into a solution of 50 % sodium nitrate (w/v) and 1 % $CaCl_2$ (w/v) to form uniform beads of immobilized biomass. After 1 hour, the beads were washed and stored at 4 °C in distilled water (Safa and Bhatti, 2011).

Sugarcane bagasse was treated with different chemicals like acids (nitric acid, sulphuric acid, hydrochlorioc acid, acetic acid), bases (NaOH, KOH, $NH_4OH$), surfactants (CTAB, SDS, Triton X-100), organic solvent (benzene) chelating agents (glutaraldehyde, Poly ethyleneimine, EDTA) to see the effect of treatments on its biosorption capacity following reported methods (Bhatti*et al*., 2009).

**Batch Biosorption studies:** The batch biosorption studies for FB dye was carried in 250 mL conical flasks by mixing pre-weighted amount of the powdered biosorbent in 50 mL of the aqueous dye solution of particular concentration. The conical flasks were kept at a constant temperature in orbital shaker and were shaken for a predetermined time interval at a fixed speed (120 rpm). The sorbent was separated by centrifugation and the supernatants were analyzed using spectrophotometer(Cecil, CE7200, Japan) for determining the remaining dye concentration based on Beer's law (Haq *et al*., 2011).The amount of dye sorbed by the biomass was calculated using the following equation:

$$q = (C_i - C_e) V/W \qquad 1$$

Where q (mg/g) is the amount of dye sorbed by biomass, $C_i$ and $C_e$ (mg/l) are the initial and equilibrium liquid phase concentrations of the dye, respectively, V (l), the initial volume of dye solution, and W (g), the weight of the biomass. Effects of various parameters like concentration of dye, amount of biosorbent and pH of the solutions and temperature was studied using reported method (Haq*et al*., 2011). The equilibrium data commonly known as adsorption isotherms are basic requirements for the design of adsorption systems. Various adsorption isotherm models like Freundlich, Langmuir, Tempkin, Dubinin-Radushkevich and Harkins-Jura were applied to the equilibrium data for process optimization (Safa and Bhatti, 2010).Modeling of the contact time data was carried out using pseudo-first-order, pseudo-second order and intraparticle diffusion model (Safa and Bhatti, 2010).The effect of presence of salt (NaCl), heavy metal ion ($PbNO_3$) and surfactants (Triton X-100, CTAB, SDS, Arial and Excel)on the biosorption capacity of sugarcane bagasse was also investigated.

**Functional groups analysis:** Fourier transform infrared (FT-IR) spectrumof sugarcane bagasse was recorded using IR spectrophotometer (Bruker Tensor 27, USA) with the samples prepared as KBr discs to determine the various functional groups involved in biosorption of FBdye.

**Surface area analysis:** The surface area of sugarcane bagasse biomass was determined using surface area analyzer (Quantachrome v2.1 (Nova Station B) using Brunauer, Emmett and Teller (BET) method (Safa and Bhatti, 2010). Results were obtained by adsorption of pure liquid $N_2$ at 77±0.5 K.

## RESULT AND DISCUSSION

Sugarcane bagasse was treated physically and chemically under appropriate conditions as described in the experimental section. The results showed that the glutaraldehydetreated biomass exhibited maximum biosorption capacity (54.24 mg/g)as compared to other chemical and physical treatments. Minimum biosorption capacity (2.1 mg/g) was observed with surfactant CTAB. The dye loading capacity of a particular biomass could be taken as an equivalent measure of binding sites on the adsorbent. Glutaraldehyde is an amine-reactive homo-functional cross-linker which reacts with the amino groups of the biomass and enhances the binding sites. Hence Glutaraldehyde treated biomass was selected as one biosorbent for subsequent studies. The experiments were run with native, immobilized and chemically treated sugarcane bagasse for the removal of FBdye from simulated aqueous solutions.

The results regarding the effect of pH on the biosorption capacity of native, immobilized and pretreated sugarcane bagasse are depicted in Fig. 1. The results showed that an increase in pH increased the biosorption capacity for all biomasses. Maximum biosorption capacity of native biomass was observed at pH 4.0, while immobilized and chemically treated biomasses exhibited maximum capacity at pH 7.0. Further increase in pH resulted into a decrease in the biosorption capacity. pH is an important factor in the adsorption process. The ionic forms of the dye in solution and the surface electrical charge of the biomass depend on the solution pH. Therefore, the interaction between a dye and biosorbent is mainly affected by ionization states of the functional groups on both dye molecule and biosorbent surface (Maurya*et al*., 2006; Asgher and Bhatti, 2012). At lower pH, the biosorbent surface turned out to be positively charged and electrostatic attraction developed between positively charged biomass and negatively charged anionic dyes (Bhatti, and Safa, 2012).

The effect of biosorbent dose (0.05 - 0.3g) on the biosorption of FBdye by bagassebiomass is represented in Fig. 2. The maximum dye removal was observed at 0.05g biosorbent dose of native, pretreated immobilized biomass. When the biosorbent dose was further increased there was decrease in the biosorption capacity of biosorbent. Adsorption efficiency decreased with increase in the biosorbent dose.Biosorbent dose plays a very important role in the process of biosorption. The dye biosorption capacity decreased at higher biosorbent doses due to the aggregation of the biomass which results in the decrease in active sites on the surface of biosorbent available for the attachment of dye molecules. Another important factor is that at high biosorbent dose, the available dye molecules are insufficient to completely cover the available binding sites on the biosorbent, which usually results in low solute uptake (Tangaromsuk*et al*., 2002).Ahmad*et al*.(2007) reported that the biosorption of direct dye decreased with increase of biomass dose. Bullut*et al*. (2007) reported that the sorption of Direct Blue 71 by wheat shells from aqueous solution occurred at low biosorbent doses. Similar behavior regarding the biosorption of anionic dyes on rice milling waste has been reported (Bhatti, and Safa, 2012)

The results of experiments conducted to determine the equilibrium time are shown in Fig. 3.The results revealed that the equilibrium time for the removal of the FB dyewas 90min for immobilized form of biosorbent while for native and pretreated forms of sugarcane bagasse, the equilibrium was achieved after 120 min.Maximum biosorption capacity was depicted by pretreated form of sugarcane bagasse as compared to native and immobilized biomasses. Aksu and Isoglu (2006) reported that a contact time ranging from 2-4 hours was sufficient to achieve equilibrium for the removal of direct dye by waste sugar beet pulp.Experimental data related to the adsorption of FBdyewas subjected to the pseudo-first-order and the pseudo-second-order, and intra-particle diffusion models.

Pseudo-first order kinetic model is based on the fact that the change in dye concentration with respect to time is proportional to the power one. The differential equation is described as follows:-

$$\log (q_e - q_t) = \log (q_e) - k_1/2.303.t \qquad 2$$

Pseudo-second order kinetic model is also based upon the biosorption capacity of the biosorbent material. The biosorption mechanism over a complete range of the contact time is explained by the pseudo-second order kinetic model. The differential equation is shown below:-

$$(t/q_t) = 1/k_2 q_e^2 + 1/q_e. (t) \qquad 3$$

The movement of dye molecules (adsorbate) from aqueous solution to the biosorbent surface takes place through various steps. In the first step called bulk diffusion, the transportation of dye molecules to the solid biosorbent phase takes place. Second step involves the boundary layer diffusion of adsorbate molecules on the biosorbent surface which is called film diffusion. In the third step called pore or intraparticle diffusion, the dye molecules move from outer surface of biosorbent into the internal pores. The fourth step involves a chemical reaction in which the dye is adsorbed onto the active binding sites of the biosorbent material. The biosorption mechanism may be controlled by single step or combination of many steps.

Intraparticle diffusion based mechanism was studied. It is an empirically found functional relationship, common to the most adsorption processes, where uptake varies almost proportionally with $t^{1/2}$ rather than with the contact time t. The intraparticle diffusion equation is written as follows;

$$q_t = K_p t^{1/2} + C_i \qquad 4$$

Where;$q_t$= mass of dye adsorbed at time, $C_i$= initial dye concentration, $K_p$= rate constant of intraparticle diffusion

It was observed that experimental data fitted well to pseudo-second-order equation. The linearity of plot also showed the appropriation of the model (Table 1).The correlation coefficient ($R^2$ =0.99) of the pseudo-second-order model were higher than those of the correlation coefficients of the intra particle model ($R^2$=0.91) and so much highest than pseudo 1st order model. It is clear from the accuracy of the model that the sorption kinetics of the synthetic dyes are described by a pseudo-second-order chemical reaction and that, this reaction is significant in the rate controlling step. Based on the assumption that the rate limiting step may be chemical or chemisorption involving valence forces through sharing or exchange of electrons between adsorbent and adsorbate as covalent forces. Similar trend has also been observed in the biosorption of metal-complexed dye onto *Posidoniaoceanica* (Ncibi*et al*., 2008).

The results regarding the removal of FBdyeby native, pretreated and immobilized bagasse as a function of different initial dye concentration are shown in Fig. 4. The results revealed that an increase in initial dye concentration led to an increase in the amount of dye adsorbed by all types of bagasse.Maximum biosorption capacity of all biomasses was observed with 100 ppm dye concentration. Further increase in dye concentration did not affect the biosorption capacity of biomass. When the available binding sites became saturated, no further adsorption took place. The initial dye concentration is an important parameter in the process of biosorption. A higher initial dye concentration provides an important driving force to overcome all mass transfer resistances of the dye between the aqueous and solid phases, thus increases the uptake capacity.Almeida *et al*. (2009)

reported that more methylene blue was retained by the adsorbent, and the adsorption mechanism also became more efficient, as the initial dye concentration increased, but the percentage removal was higher at low concentration.

Equilibrium data, commonly known as adsorption isotherms, are basic requirement for the analysis and design of adsorption system (Aksu and Isoglu, 2006). In order to discover the biosorption capacity of bagasse waste biomass for the FBdye, the experimental data points were fitted to the Langmuir, Freundlich, Tempkin, isotherms, Dubinin-Radushkevich and Harkins Jura isotherms (Bhatti and Safa, 2012**)** which are the most frequently, used two parameters. These models are simple, give a good description of experimental behavior in a large range of operating conditions and are characterized by a limited number of adjustable parameters (Aksu and Isoglu, 2006).

The Langmuir model is valid for monolayer adsorption onto a surface with a finite number of identical sites. The well-known expression of the Langmuir model is given by Eq.

$q_{e=}Q_m K_a C_e/1+ K_a C_e$ 5

Where $q_e$ is the amount of dye biosorbed on the biomass (mg/g) at equilibrium, $C_e$ is the equilibrium concentration of dye solution, $Q_m$ is the maximum biosorption capacity describing a complete monolayer adsorption (mg/g) and $K_a$ is adsorption equilibrium constant (l/mg) that is related to the free energy of biosorption.The theoretical Langmuir isotherm is valid for sorption of a solute from a liquid solution as monolayer adsorption on a surface containing a finitenumber of identical sites.

The Freundlich isotherm is used for a heterogeneous surface energy system. The sorption isotherm is the most convenient form of representing the experimental data for different particle sizes. The Freundlich expression is an exponential equation and therefore, assumes that as the adsorbate concentration increases, the concentration of adsorbate on the adsorbent surface also increases theoretically using this expression

$q_e = K_F C_e^{1/n}$ 6

Where $K_F$ is the Freundlich isotherm constant (mg/g) related to the bonding energy. $K_F$ is defined as the distribution coefficient and suggests the amount of dye sorbed on the biosorbent for unit equilibrium concentration. The value of n indicates whether the biosorption process is favorable or not.

The Tempkin isotherm contains a factor that explicitly takes into account adsorbing species_adsorbent interactions. Temkin and Pyzhev (1940) considered the effects of some indirect adsorbate/adsorbate interactions on adsorption isotherms and suggested that because of these interactions the heat of adsorption of all the molecules in the layer would decrease linearly with coverage. The Temkin isotherm has been used in the following form

$q_e = B\ln A + B\ln C_e$ 7

Where B=RT/b, T is the absolute temperature in Kelvin, b is Temkin constant and R is the universal gas constant (8.314J $mol^{-1}$ $K^{-1}$).

The D-R isotherm is more general because it does not assume a homogenous surface or constant adsorption potential. It was applied to estimate the porosity apparent free energy and the characteristics of adsorption. The linear form can be represented as

$\ln q_e= \ln q_D- \beta\varepsilon^2$ 8

Where,β is a constant related to the mean free energy of adsorption ($mol^2$ $(kJ^2)^{-1}$), $q_D$ is the theoretical saturation capacity (mg/g), ε is the polyani potential, and calculated as follows:

$\varepsilon = RT\ln (1+1/Ce)$ 9

The slope of the plot of $\ln q_e$ versus $\varepsilon^2$ give β and the intercept yields the adsorption capacity, qD.

Langmuir, Freundlich. Tempkin, D-R and Harkins-Jura coefficients for the removal of FB dye by native pretreated and immobilized bagasse are reported in Table 2. In view of the values of linear regression coefficients in Table 2, the Langmuir model exhibited better fit ($R^2$=0.929 for native and $R^2$ =0.9 for pretreated bagasse to the sorption data of FB dye than other models. This indicated that biosorption of FB dyeis chemisorption in nature.

The result of biosorption experiments performed at different temperature showed that the biosorption of FB dye onto native, pretreated and immobilized bagasse biomass was an exothermic in nature (Fig. 5). Biosorption capacity of bagasse decreased with increase in temperature. Maximum biosorption capacity was observed at 30 °C (303 K) and equilibrium biosorption capacity decreased as the temperature is increased. Temperature is well known to play an important role in both biosorption rate and equilibrium uptake of dyes by different biosorbents. Kumar*et al*. (2010) reported that adsorption of the dye by cashew nut shell was highest at $30^oC$ and decreased with increase in temperature. Similarly biosorption of reactive dyes by citrus waste biomass decreased at higher temperature as compared to lower temperature (Asgher and Bhatti, 2012).

The effect of presence of NaCl on the removal of FB dye by using sugarcane bagasse was investigated at different salt concentrations (0.2 - 1 %). The results revealed that by increasing the salt concentration, the biosorption potential of sugarcane bagasse increased. Maximum dye removal was achieved at 1 % NaCl concentration. This might be due to the fact that increase in the ionic strength increases the positive charge of the surface of biosorbent hence it increases the electrostatic interaction between dye anions and biosorbent which results in increase in biosorption potential of biosorbent (Haq *et al*., 2011).

Effect of presence of heavy metal ions was also explored by using $PbNO_3$ at different concentrations (0.2 - 1 %) and results showed that by increasing the heavy metal ion concentration, there was a significant decrease in the dye removal. This fact can be explained as some of the heavy metal ions may occupy the binding sites on the surface of biosorbent which leads to the decreased biosorption of dyes (Asgher and Bhatii, 2010)

Surfactants are used in the textile industries during different washing processes. The effect of presence of surfactants on the adsorption capacity of sugarcane bagasse was investigated by using different surfactants (Triton X-100, CTAB, SDS) and two commercial detergents (Arial and Excel). All these surfactants were used in 1 % concentration. The results showed that in the presence of surfactants, there was a significant decrease in the adsorption potential of biosorbent.

**Table 1 Kinetic parameters for the adsorption of FB dye by native, pretreated and immobilized sugarcane bagasse**

| Kinetic Models | Native | Pretreated | Immobilized |
|---|---|---|---|
| **Pseudo First Order** | | | |
| $q_e$(Calculated) | 14.90 | 17.36 | 2.67 |
| $k_1$ | 0.011 | 0.013 | 0.014 |
| $R^2$ | 0.489 | 0.653 | 0.288 |
| **Pseudo Second Order** | | | |
| $q_e$ (Calculated) | 75.76 | 89.29 | 86.21 |
| $k_2$ | 0.278 | 0.236 | 0.11 |
| $R^2$ | 0.997 | 0.996 | 0.969 |
| **Intra-particle diffusion** | | | |
| $C_i$ (Calculated) | 54.04 | 65.58 | 0.55 |
| $K_p$ | 1.168 | 1.849 | 0.75 |
| $R^2$ | 0.917 | 0.917 | 0.82 |

**Table 2 Isotherm parameters for the biosorption of FB dye by native, pretreated and immobilized sugarcane bagasse**

| Equilibrium models | Native | Pretreated | Immobilized |
|---|---|---|---|
| **Langmuir** | | | |
| $q_{max}$(mg/g) | 81.301 | 96.15 | -1.06 |
| b | 14.02 | 15.16 | 0.007 |
| $R^2$ | 0.929 | 0.90 | 0.226 |
| **Freundlich** | 2.57 | | |
| $k_F$ | 1.31 | 9.79 | 9.24 |
| n | 0.338 | 1.81 | 8.21 |
| $R^2$ | | 0.564 | 0.011 |
| **Temkin** | | | |
| a (l/g) | 0.0400 | 1.1398 | 2.659 |
| b | 103.86 | 123.26 | 697.4 |
| $R^2$ | 0.539 | 0.728 | 0.873 |
| **Dubinin-Radushkevich** | | | |
| $q_{max}$(Calculated) | 4.29 | 23.05 | 1.801 |
| β | $3\times10^{-6}$ | $7\times10^{-7}$ | $5\times10^{-5}$ |
| $R^2$ | 0.81 | 0.659 | 0.82 |
| **Harkins Jura** | | | |
| A | -0.345 | -2.36 | -0.013 |
| B | -2.550 | -6.079 | -1.938 |
| $R^2$ | 0.154 | 0.223 | 0.569 |

The FT-IR spectrum of FB dye loaded sugarcane bagasse was studied in the range of 400 – 4000 $cm^{-1}$ and illustrated in Fig. 6. FT-IR analysis was performed to elucidate the active sites present on the biosorbent to check out the pattern of biosorption of FB dye. A broad band at $3346.50 cm^{-1}$ indicated the presence of O-H group (carboxylic acids, phenols and alcohols) on the surface of biosorbent as in cellulose, pectin and lignin. Presence of peak at 2920.06 cm$^{-1}$ indicated the asymmetric and symmetric vibrations of C-H of aliphatic acids. The peak present at 1634.49cm$^{-1}$ was because of stretching vibration of C=O bond which is due to presence of nonionic carboxylic groups which might be assigned to carboxylic acids and their esters(Sadaf *et al*., 2013).

The surface features of sugarcane bagasse biomass were analyzed by surface area studies. The results revealed that the BET specific surface area of sugarcane bagasse biomass was 89.49 m$^2$/g. The results revealed that the structure of sugarcane bagasse biomass is favorable for the adsorption process.

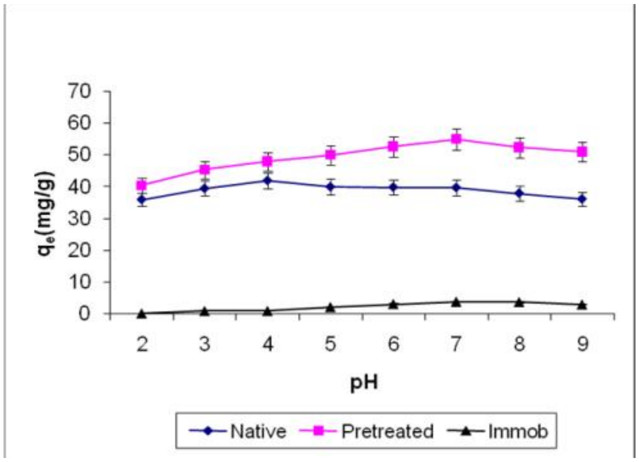

**Fig.1. Effect of pH on the biosorption of FB dye by native, pretreated and immobilized sugarcane bagasse**

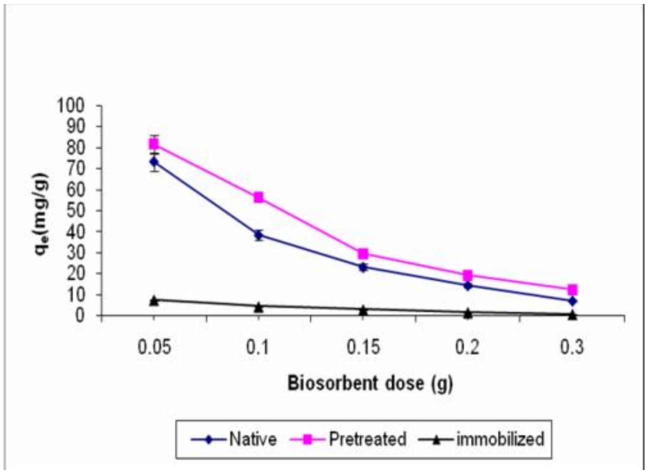

**Fig. 2: Effect of biosorbent dose on the biosorption of FB dye by native, pretreated and immobilized sugarcane bagasse**

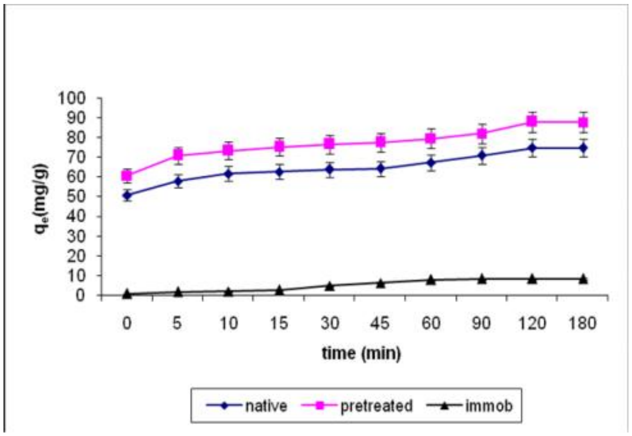

**Fig. 3. Effect of contact time on the biosorption of FB dye by native, pretreated and immobilized sugarcane bagasse**

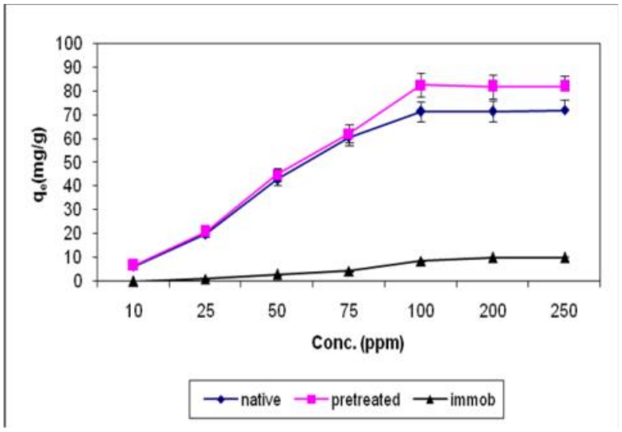

**Fig.4.Effect of initial dye concentration on the of biosorption of FB dye by native, pretreated and immobilized sugarcane bagasse**

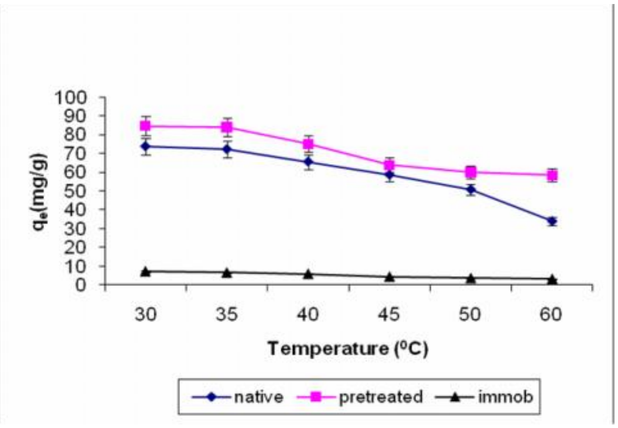

**Fig.5: Effect of temperature on biosorption of biosorption of FB dye by native, pretreated and immobilized sugarcane bagasse**

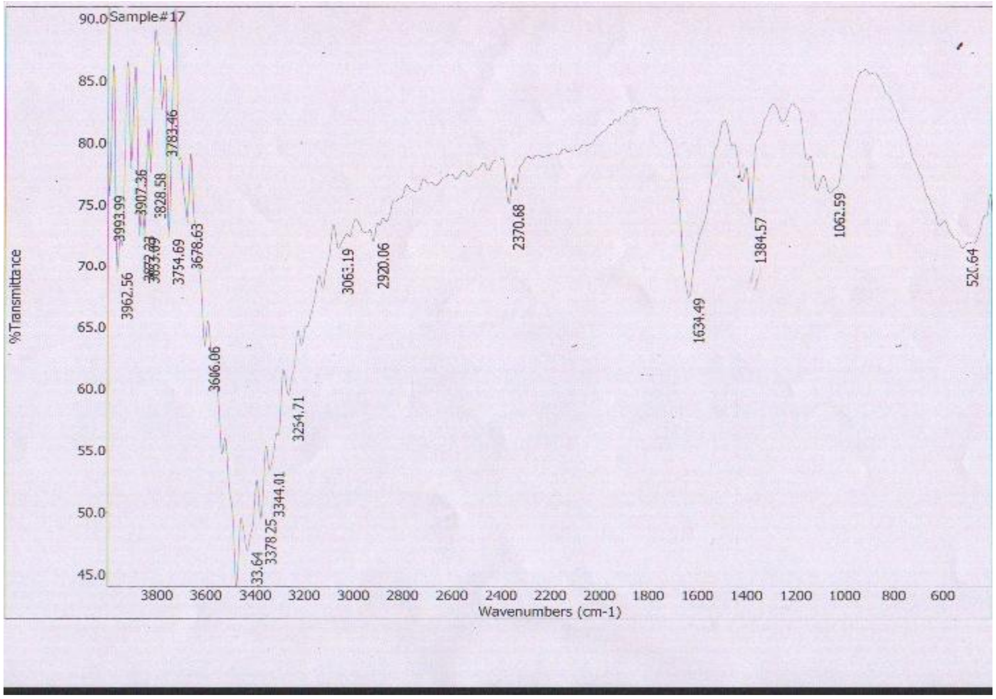

**Fig. 6. FT-IR spectrum of FB dye loaded sugarcane bagasse**

**Conclusion:** In the present study sugarcane bagasse was used as s low cost biosorbent for the removal of FB dye from aqueous solution. The sorption was found to be strongly dependent on solution pH and initial dye concentration. Biosorption was favored at pH 4 for native and 7 for pretreated and immobilized biosorbent. Langmuir adsorption isotherm described well biosorption data which indicated that chemisorption mechanism was majorly involved in the adsorption of FB dye onto sugarcane bagasse. Kinetics of biosorption followed the pseudo-second-order mechanism. Maximum dye removal was achieved with pretreated form of biosorbent. The immobilized form of biosorbent depicted decreased dye removal which might be due to the blocking of binding sites thorough immobilization. The results proved that sugarcane bagassewaste biomass could be used as a favorable biosorbent for application on industrial scale.

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