Equilibrium Modeling of Removal of Drimarine Yellow HF-3GL Dye from Aqueous Solutions by Low Cost Agricultural Waste

Sana Nausheen, Haq Nawaz Bhatti*, Sana Sadaf, Zobia Farrukh and Saima Noreen
Environmental Chemistry Laboratory, Department of Chemistry and Biochemistry, University of Agriculture, Faisalabad 38040, Pakistan
hnbhatti2005@yahoo.com; haq_nawaz@uaf.edu.pk*

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Summary: Pollution control is one of the leading issues of society today. The present study was designed to remove the Drimarine Yellow HF-3GL dye from aqueous solutions through biosorption. Sugarcane bagasse was used as biosorbent in native, acetic acid treated and immobilized form. Batch study was conducted to optimize different system variables like pH of solution, medium temperature, biosorbent concentration, initial dye concentration and contact time. Maximum dye removal was observed at pH 2, biosorbent dose of 0.05 g/50 mL and 40°C temperature. The equilibrium was achieved in 45-90 min. Different kinetic and equilibrium models were applied to the experimental results. The biosorption kinetic data was found to follow the pseudo second order kinetic model. Freundlich adsorption isotherm model showed a better fitness to the equilibrium data. The value of Gibbs free energy revealed that biosorption of Drimarine Yellow HF-3GL dye by native and pretreated sugarcane bagasse was a spontaneous process. Presence of salt and heavy metal ions in aqueous solution enhanced the biosorption capacity while presence of surfactants decreased the biosorption potential of biosorbent. Dye was desorbed by 1M NaOH solution. Fixed bed column study of Drimarine Yellow HF-3GL was carried out to optimize different parameters like bed height, flow rate and initial dye concentration. It was observed that biosorption capacity increases with increase in initial dye concentration and bed height but decreases with the increase in flow rate. The data of column study was explained very well by BDST model. FT-IR analysis confirmed the involvement of various functional groups, mainly hydroxyl, carboxyl and amine groups. The results proved that sugarcane bagasse waste biomass can be used as a favorable biosorbent for the removal of dyes from aqueous solutions.

Keywords: Biosorption; Kinetic study; Adsorption isotherms; Thermodynamic study.

Introduction

Dyes and pigments are one of the most hazardous groups of pollutants [1]. They are produced by various industrial processes including dyestuff manufacturing, printing, dyeing, bleaching and textile finishing [2]. Dyes are mostly stable molecules which are intentionally synthesized to withstand fading against photodegradation, oxidizing agents, biodegradation, soaps and detergents [3]. A significant amount of research on wastewater treatment has focused on the removal of reactive dyes, essentially due to three reasons: firstly, reactive dyes constitute 20-30% of the total dye market. Secondly, a large amount of reactive dyes (10-15%) are eliminated during the dyeing process (up to 0.6-0.8 g/dm^3 can be observed in dyestuff matter) [4]. Thirdly, conventional wastewater treatments which depend upon biodegradation were found to be incompetent for complete removal of several reactive dyes [5].

There has been an increasing interest in the use of biosorption techniques for the removal of dyes from wastewater rather than following conventional treatment methods e.g., chemical precipitation, solvent extraction, photolysis, flocculation, coagulation, membrane filtration, chemical oxidation and reverse osmosis [6]. These methods have some limitations like less efficiency and high cost. Biosorption techniques are becoming popular due to its advantages of simple operation, availability of wide range of adsorbents, high efficiency, easy recovery and reuse of adsorbents [7]. It is proved to be an effective and attractive process for the removal of non biodegradable pollutants e.g. dyes from wastewater. Activated carbon is widely used as an adsorbent for the removal of dyes from water due to its excellent adsorption capacity [8]. Due to its high cost researchers are busy in finding low cost alternate adsorbents. Recently, a number of researches have been carried out to explore cheaper and effective adsorbents from different materials [9]. The use of proper adsorbent can reduce the cost of operation and increase its efficiency thus making the technique economically viable. Industrial wastes, agricultural byproducts and natural ores can be used as low cost adsorbents. Some low cost biosorbents used include rice husk [10], fruit peel [11], apple pomace and wheat straw [4], peat and pith [10], de-oil soya [12], cereal chaff [13], rice husk [14] and citrus wastes [15]. Sugaracane bagasse consists of cellulose (50%), polyoses (27%) and lignin (23%) [16]. It is a sugar industry waste by-product, which is easily available in large amount at no cost and thus it can form a good basis for the development of adsorbing materials. Literature had reported that it could be used for the

*To whom all correspondence should be addressed.

adsorptive removal of different dyes [17]. To attain better results different treatments and modifications can be performed with the biomass which will increase its biosorption capacity. Immobilization is another technique that can be used to make biosorbents more suitable for industrial applications. Immobilization enhances the process efficiency by regeneration of biomass and maximum exposure of binding sites of the biomass. Some important immobilization matrices used for biosorbent immobilization are polysulfone, polyurethane, sodium alginate and polyacrylamide. The selection of the immobilization matrix should be carefully done to avoid practical problems and additional process costs [18].

The focus of present research was to evaluate the biosorption capacity of untreated, treated and immobilized sugarcane biomass for Drimarine Yellow HF-3GL dye. Continuous mode study was conducted with native sugarcane bagasse biomass to check out its biosorption capacity for the real application.

Results and Discussions

Screening of Biosorbent

The reactive dye (Drimarine Yellow HF-3GL) was treated with five different biosorbents at pH 3 and 30 ^{0}C temperature. The samples were shaken for 2 hours. The results indicated that Drimarine Yellow HF-3GL showed highest biosorption on sugarcane bagasse. For further research this biosorbent was selected.

Pretreatments of Biomass

The selected biomass was pretreated with acids, alkalis, surfactants, organic solvents and chelating agents. Biosorption capability was highly enhanced after treatment with acid. Maximum dye removal was obtained by using acetic acid treated biomass. Cellular constituents of the biomass determine the success of pretreatment. The biomass was given physical treatments i.e., boiling and autoclave. The biosorption was not much affected by physical treatments. The biosorption capacity can be slightly enhanced by heating biomass at 100°C [19]. Acidic pretreatments gave better results for removal of reactive dyes because the impurities and the ions causing blockage can be easily removed by acid. After acidic treatment the biomass becomes positively charged due to which electrostatic interactions increased between the negatively charged dye molecules and positively charged biomass which resulted in more biosorption [20]. The dyes showed poor biosorption with alkali treatments. After treatment with alkali the functional group on the surface of biosorbent got deprotonated as a result of which electrostatic repulsion occurs between negatively charged dye molecules and biosorbent surface. Treatments with surfactants, alcohol and glutaraldehyde showed no good effect on biosorption capacity of tested biomass. SDS decreased the biosorption capacity of bagasse. Anionic dyes are less soluble in SDS micelles than in aqueous solution [21]. Decrease in biosorption after treatment with alcohol may be due to the formation of esters. The carboxylate functional groups present on the surface of biomass form ester after treatment with alcohol [22]. Hence CH_3COOH treated biomass was selected for further study.

Effect of pH

The most important controlling parameter for biosorption is pH. Effect of pH on the removal of the Drimarine Yellow HF-3GL is shown in Fig. 1. Biosorption increased with decrease in pH and best removal observed was 21.69, 23.93 and 17.96 mg/g for native, pretreated and immobilized biomass respectively at pH 2. Biosorption mechanism involved in this process depends upon the initial pH of solution. Zhang *et al.* studied the biosorption of reactive dyes by *Penicillium oxalicum* [23]. They observed that dye biosorption was favoured by low pH. Tobin *et al.* suggested that at low pH, a large number of weak base groups present on the biomass become protonated and acquire positive charge which makes it easier for the anionic dyes to bind with the biomass [24]. With decrease in pH, the positively charged groups of biosorbent increase resulting in increase in binding sites due to which anionic/reactive dye uptake is enhanced. High pH causes an increase in OH^- ions which compete with dye anions to adsorb the biosorbent [18].

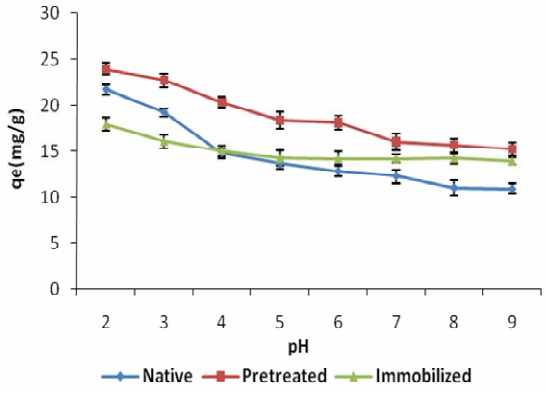

Fig. 1: Effect of pH on the biosorption of Drimarine Yellow HF-3GL by native, pretreated and immobilized sugarcane bagasse.

Effect of Biosorbent Dosage

Biosorption is greatly influenced by the amount of biosorbent used for the removal of constant amount of dye from aqueous solutions. Biosorption capacity of the reactive dye was investigated by varying the amount of biosorbent from 0.05-0.3g/50mL dye solution and results are presented in Fig. 2. Results indicate that maximum dye removal (24.25, 39.75 and 30.53 mg/g) for native, pretreated and immobilized biomass respectively was achieved with 0.05 g biosorbent. Thus 0.05g was taken as optimum dosage for further studies. Mostly, low biosorbent dose results in higher uptakes but less percentage removal. As the biosorbent dosage increases the amount of biosorbed solute per unit weight of the biosorbent decreases. This decrease is the consequence of several factors. The most important factor is that with increase in biosorbent dose the present solute cannot completely cover the exchangeable sites of the biosorbent causing less solute uptake [25]. Hence it results in decrease in biosorption capacity (mg/g) of biosorbent.

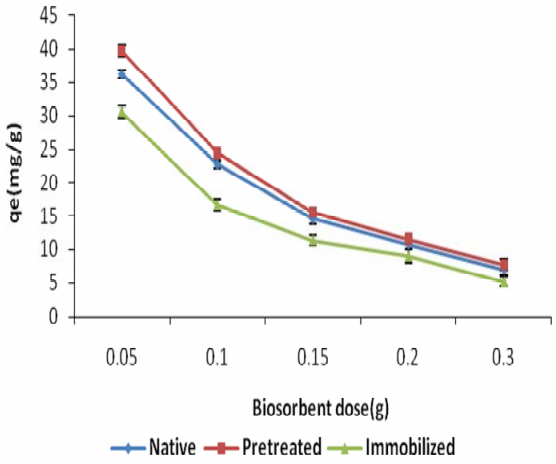

Fig. 2: Effect of biosorbent dose on the biosorption of Drimarine Yellow HF-3GL by native, pretreated and immobilized sugarcane bagasse.

Effect of Contact Time

The contact time is of great importance in the design of the biosorption system and its large scale applications. Therefore, time-dependent experiments were carried out in the time range of 5–180 min at room temperature. The results were shown in Fig. 3. An initial rapid biosorption was observed in the first 45, 60 and 90 min by native, pretreated and immobilized biomass respectively. After this equilibrium period, the biosorption capacity of sugarcane bagasse for Drimarine Yellow HF-3GL did not considerably changed with time. Therefore 45, 60 and 90 min was selected as the optimum contact time for the batch experiments by native, pretreated and immobilized biomass respectively, in order to make sure that equilibrium was attained.

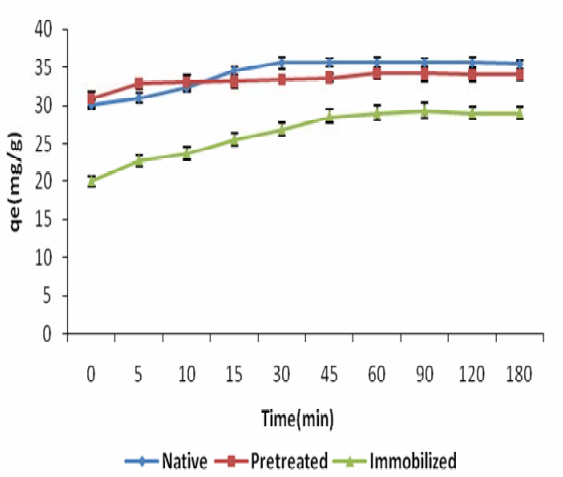

Fig. 3: Effect of contact time on the biosorption of Drimarine Yellow HF-3GL by native, pretreated and immobilized sugarcane bagasse.

Biosorption capacity increased with the passage of time but after certain time equilibrium was established. In the beginning, the fast biosorption may be due to the presence of positively charged groups present on the biosorbent surface which developed interaction with the negatively charged molecules of dye. After that biosorption began to slow down due to the movement of the molecules into the interior of the biosorbent which is a slow process [26]. In the beginning, a large number of exchanging sites are present which helped in biosorption but after a certain period of time saturation occurred. Akar *et al*. [27] studied the removal of reactive dye (RR198). They observed that dye removal density increased with the passage of time and equilibrium was established after 40 minutes.

Kinetic Study

Kinetics of the biosorption process expressed in terms of the rate of solute removal is one of the most important aspects of the operation defining the efficiency of the pollutant removal

process. The kinetic data for the biosorption of Drimarine Yellow HF-3GL onto sugarcane bagasse at the room temperature are evaluated by three different equations namely pseudo-first-order [28], pseudo-second-order [29] and intraparticle diffusion model [30]. The applicability of these kinetic models was determined by measuring the coefficients of determination (R^2).When the value of R^2 is high, the model is best applicable to data [31]. The pseudo-first-order kinetic equation is commonly expressed as follows:

$$\log(q_e - q_t) = \log q_e - K_1 \cdot \frac{t}{2.303} \quad (1)$$

where q_e and q_t (mg/g) are the biosorption capacity at equilibrium and at time t, respectively, as well as k_1 is the rate constant of pseudo-first-order biosorption (L/min).Using the following model, the value of k_1 and q_e were calculated from the slope and intercept of the plot of log(qe _ qt) versus t, respectively.

$$\frac{dq_t}{d_t} = K_2(q_e - q_t)^2 \quad (2)$$

By rearranging the above equation, following linear form is obtained.

$$\log(q_e - q_t) = \log q_e - K_1 \cdot \frac{t}{2.303} \quad (3)$$

The correlation coefficient R^2 for the dye was very low for native biomass as compared to pretreated and immobilized biomass, which indicates that the biosorption of Drimarine Yellow HF-3GL onto native adsorbent was not a first-order reaction. Therefore, another experimental model is necessarily required to explain the data. The biosorption kinetics may be described by the pseudo-second-order model, which is generally given by the following equation:

$$\frac{dq_t}{d_t} = K_2(q_e - q_t)^2 \quad (4)$$

where k_2 (g/mg min) is the second order rate constant of biosorption process.
Integrating the above equation in the interval 0 to t for t and 0 to qt for qt, gives:

$$\left(\frac{t}{q_t}\right) = \frac{1}{K_2 qe^2} + \frac{t}{qe} \quad (5)$$

The plot of t/q_t versus t explains the whole sorption process very well by native, pretreated and immobilized biomass. Values of k_2 and equilibrium biosorption capacity q_e were calculated from the intercept and slope of the plot of t/q_t versus t, respectively. The values of correlation coefficient R^2 were greater than pseudo-first-order model for all types of adsorbents. This indicates that pseudo-second-order kinetic model fitted best to the biosorption system for the entire sorption period. The validity of pseudo-second-order model suggests that the biosorption can occur in two stages: fast and slower reactions. Besides pseudo-second-order model, intra particle diffusion model [30] was also investigated to search for possible mechanism of biosorption. The model is given as under:

$$q_t = K_{pi} t^{1/2} + C_i \quad (6)$$

where q_t (mg/g) is the biosorption capacity at any time t, Kpi (mg/g min1/2) is the intra-particle diffusion rate constant, and Ci is the boundary layer thickness. The results showed that the straight line did not pass through the origin which indicates that the intraparticle diffusion was not only the rate controlling step [32]. However immobilized biomass fairly followed this model as compared to native and pretreated biomass. According to this model two possible mechanistic phases of biosorption take place. The first phase represents a rapid biosorption due to the mass transfer from the dye solution to the external surface of adsorbent. First phase of speedy diffusion is followed by a slower phase of intra-particle diffusion . This implies that more than one processes affected the biosorption of Drimarine Yellow HF-3GL onto the biosorbent. Thus, combination of mechanisms was involved in the biosorption of dye onto the biosorbent. The results of application of kinetic models were presented in Table-1. Similar results have been reported in the literature [31].

Table-1: Comparative study of kinetic parameters for the biosorption of Drimarine Yellow HF-3GL.

Kinetic models	Native	Pretreated	Immobilized
Pseudo-first order	-0.018	-0.017	-0.018
K_1(1/min), q_e (mg/g)	0.922	1.463	4.486
R^2	0.211	0.671	0.699
Pseudo-second order	0.112	0.120	0.02
K_2 (g/mg min), q_e (mg/g)	35.71	34.48	29.41
R^2	0.999	1	0.99
Intraparticle diffusion	0.406	0.197	0.70
K_{pi} (mg/g min $^{1/2}$)	31.57	32.07	21.97
C_iR^2	0.629	0.690	0.799

Effect of Initial Dye Concentration

The influence of the initial concentration of Drimarine Yellow HF-3GL (10-200 mg/L) on the biosorption capacity of native, pretreated and immobilized sugarcane bagasse was studied. The experiments were carried out at fixed biosorbent dose

(0.05g), at room temperature (28 ±1 ºC) and pH (2.0) for equilibrium time. Dye removel capacity of native, pretreated and immobilized biomass increased from 5.52-87.21, 6.18-104.67 and 3.77-95.56 mg/g respectively with increasing dye concentration from 10-200 mg/L. The results regarding the influence of initial dye concentration of the reactive dye (Drimarine Yellow HF-3GL) are presented in **Fig**. 4. Biosorption capacity of biosorbent is increased with the increase of initial dye concentration. It is because of the fact at higher concentration, the ratio of the initial number of dye molecules to the available surface area is high, subsequently the fractional biosorption becomes dependent of initial concentration. However, at lower concentration the available sites of biosorption becomes fewer and hence the biosorption capacity of dye dependents upon concentration. 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. In addition, increasing initial dye concentration increases the number of collisions between dye anions and biosorbents, which enhances the biosorption process [33]. Bulut and Aydin reported the same results [34]. They observed 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.

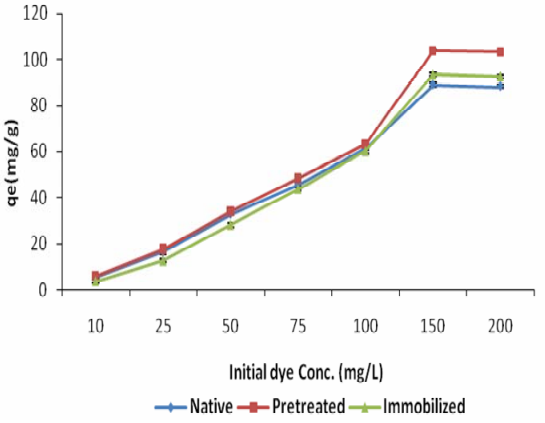

Fig. 4: Effect of initial dye conc. on the biosorption of Drimarine Yellow HF-3GL by native, pretreated and immobilized sugarcane bagasse.

Biosorption Isotherms

Biosorption isotherm studies are carried out in order to correlate biosorption capacity and residual concentration of adsorbate present in the aqueous solution. Several isotherm models i.e., Langmuir [35], Freundlich [36], Temkin [37], Harkins–Jura [38] and D–R isotherm [39] are applied to search for such correlations. By comparing the Correlation Co-efficient (R^2) of the five models, the applicability of the isotherm equation was suggested. Various types of constants related to the isotherms used were thus determined. The biosorption parameters of the isotherm models often give some insight into the biosorption mechanism, surface properties and affinity of the biosorbent with the adsorbate [40].

The Freundlich isotherm model suggests that the concentration of adsorbate on the biosorbent surface increases as the adsorbate concentration increases. Theoretically, using this expression, an infinite amount of biosorption can occur [41].

$$logq_e = logK_F + \frac{1}{n} logC_e \qquad (7)$$

here K_F (L/ g) and n (dimensionless) are Freundlich isotherm constants which represent the biosorption and the degree of nonlinearity between solution concentration and biosorption, respectively. A plot of lnq_e versus lnC_e results in a straight line with a slope of (1/n) and intercept of lnK_F. The Langmuir isotherm model is based on the following principles [41]: adsorbates are chemically adsorbed at a fixed number of well-defined sites; each site can only hold one adsorbate species; all sites are energetically equivalent; and there are no interactions between the adsorbate species. The linear form of Langmuir model is represented by the following equation;

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \qquad (8)$$

here Ce (mg/L) is the equilibrium concentration of Drimarine Yellow HF-3GL in the solution, qe (mg/g) is the amount of Drimarine Yellow HF-3GL biosorbed at equilibrium. q_{max} (mg/g) is monolayer biosorption capacity of the biosorbent and b is the binding energy of biosorption. The essential features of the Langmuir isotherm can be expressed by means of 'R_L', a dimensionless constant referred to as separation factor or equilibrium parameter which is defined

$R_L > 1$: Unfavorable
$R_L = 1$: Linear
$0 < R_L < 1$: Favorable
$R_L = 0$: Irreversible

Another model for the analysis of isotherms is Dubinin–Radushkevich isotherm [40] which has the following form:

$$\ln q_e = lnq_m - \beta\varepsilon^2 \quad (9)$$

q_m is the maximum biosorption capacity, β is the activity coefficient related to mean adsorption energy and ε is the Polanyi potential which can be calculated from the equation given below:

$$\varepsilon = RTln(1 + \frac{1}{C_e}) \quad (10)$$

R (J mol^{-1} K^{-1}) is the gas constant, and T (K) is the absolute temperature. The objective of applying equilibrium data to the D–R model is primarily to clarify the adsorption type and assess the nature of interaction between sorbate and solid.

Temkin isotherm [37] consists of a factor that fairly explains the types of interactions present between adsorbent–adsorbate. The heat of biosorption of all the molecules in the layer decreases linearly with coverage as a result of adsorbent–adsorbate interactions. The biosorption process can be explained by a uniform distribution of binding energies, up to some maximum binding energy. The linear form of the Temkin isotherm is expressed as:

$$q_e = BlnA + BlnC_e \quad (11)$$

RT/bT = B (J mol^{-1}), which is the Temkin constant related to heat of sorption whereas A (L g^{-1}) is the equilibrium binding constant corresponding to the maximum binding energy. R (8.314 J mol^{-1} K) is the universal gas constant and T (K) is the absolute solution temperature. Due to presence of a heterogeneous pore distribution, a multilayer biosorption can be explained by the Harkins–Jura isotherm model. The linear form of the model is presented in equation below:

$$\frac{1}{qe^2} = \left(\frac{B}{A}\right) - \left(\frac{1}{A}\right) logCe \quad (12)$$

The values of various constants are shown in Table-2. The values of correlation coefficient showed that adsorbent does not possess heterogeneous pore distribution [26].

Freundlich isotherm model was fitted most excellent to the experimental data. The heterogeneity factor (n) obtained from Freundlich model was found to be 1.15, 1.11 and 0.82 for native, pretreated and immobilized biomass respectively, and indicated a chemical process [7]. The value of n indicated the favorable biosorption under selected experimental conditions The equilibrium data was fairly explained by Temkin isotherm model also. Biosorption of direct dyes by rice husk followed Temkin isotherm model [26]. Binupriya *et al*. reported that removal of Congo Red by different mycelia pellets also followed Temkin isotherm model [42]. The constants of the Temkin model are listed in Table-2. These results suggest that the biosorbent surface is heterogeneous in nature and did not possess equal distribution of binding energies on the available binding sites. This is also consistent with the hypotheses of the Freundlich equation that assumes the binding energies not being identical. The calculated isotherm parameters and R^2 values for the biosorption of Drimarne Yellow HF-3GL onto sugarcane bagasse were included in Table-2.

Table-2: Comparison of the isotherm parameters for the biosorption of Drimarine Yellow HF-3GL by sugarcane bagasse waste biomass.

Isotherm models	Native	Pretreated	Immobilized
Freundlich			
K_F	2.16	2.49	0.57
n	1.15	1.11	0.82
R^2	0.927	0.944	0.939
Langmuir			
q_{max}(mg/g)	200	250	-500
b	101.8	107.75	-510.5
R^2	0.661	0.580	0.049
Temkin			
a(1/g)	0.22	4.16	0.104
b	88.35	75.58	75.94
R^2	0.944	0.890	0.912
Harkins-Jurra			
A	58.82	-71.428	-21.276
B	1.764	1.714	1.680
R^2	0.539	0.560	0.552
Doubinin-Radushkevich			
q_m(mg/g)	58.03	64.39	58.38
β	-0.00001	0.000007	0.00002
R^2	0.853	0.830	0.835

Effect of Temperature

Biosorption is mostly favored by increase in temperature. Experiments were conducted at six different temperatures *i.e.,* 30, 35, 40, 45, 50 and 60 ^{0}C by keeping all other parameters constant such as pH, initial dye concentration, contact time and biosorbent dosage. Experimental results regarding the effect of temperature on the biosorption capacity of dye at different temperatures are demonstrated in **Fig**. 5. The results reveal that biosorption of Drimarine Yellow HF-3GL on sugarcane bagasse biomass increases when temperature of the solution is raised from 30 to 40^0 C for native, pretreated and immobilized biomass. It became clear from the results that the process of sorption was endothermic by nature. This trend has been reported by some

researchers while studying the biosorption behavior of different type of dyes and other organic compounds over several adsorbents [43-44]. McKay *et al*. suggested that this behavior is due to the possibility of an increased porosity and total pore volume of the adsorbent with the rise of the temperature [43]. Rise in temperature causes swelling of the internal structure of the adsorbent which results in increased penetration of the bigger dye molecules. However, increase of the color removal efficiency with the increase of the temperature is still not well understood and it is a phenomenon worthy of further investigation.

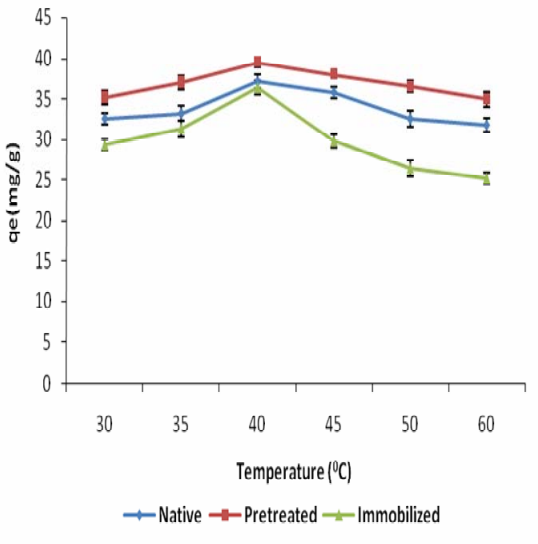

Fig.5: Effect of temperature on the biosorption of Drimarine Yellow HF-3GL by native, pretreated and immobilized sugarcane bagasse.

Thermodynamics of Biosorption

Thermodynamic parameters associated to the process of biosorption, *i.e.,* Gibb's free energy change, (ΔG^okJ mol^{-1}), enthalpy change (ΔH^0, kJ mol^{-1}) and entropy change (ΔS^o, J mol^{-1} K^{-1}) were determined by the following equations:

$$\Delta G° = \Delta H° - T\Delta S° \quad (13)$$

$$\Delta G° = -RTlnK_d \quad (14)$$

where K_d=qe/Ce

The combination of above Eqs.gives:

$$ln(K_d) = \frac{\Delta S^o}{R} - \frac{\Delta H°}{R} \times \frac{1}{T} \quad (15)$$

where R is the universal gas constant (8.314 J K^{-1} mol^{-1}), T is the absolute temperature (Kelvin) and K_d shows the equilibrium biosorption constants of the isotherm fits. The ΔH and ΔS values can be calculated from the slope and intercept of the linear plot of ln(K_d) versus 1/T. The thermodynamic results are depicted in Table-3. The magnitude of enthalpy for native biomass was consistent with a physical biosorption. The nature of interaction can be classified, up to some extent, by the magnitude of change in enthalpy. Enthalpy changes (ΔH^0) indicate that the biosorption by pretreated and immobilized biomass followed endothermic processes while process was exothermic for native biomass. Negative values of ΔG^0 for native and pretreated biomass showed that the Drimarine Yellow HF-3GL dye biosorption by sugarcane bagasse biosorbent was a spontaneous and feasible process at all the studied temperatures. The positive values of ΔS (Table-3) show the increased disorder and randomness at the solid solution interface of biosorbate with biosorbent that bring about some structural changes in the biosorbate and biosorbent.

Table-3: Thermodynamic parameters for the biosorption of Drimarine Yellow HF-3GL by sugarcane bagasse waste biomass.

Temp (C°)	Native			Pretreated			Immobilized		
	ΔG°	ΔH°	ΔS°	ΔG°	ΔH°	ΔS°	ΔG°	ΔH°	ΔS°
30	-1.69	-27.49	5.49	-2.54	-9.95	8.36	0.41	-223.48	2.12
35	-1.71			-2.58			0.43		
40	-1.74			-2.62			0.44		
45	-1.77			-2.66			0.45		
50	-1.80			-2.71			0.46		
60	-1.85			-2.79			0.48		

ΔG° = kJ mol^{-1}; **ΔH°** = kJ mol^{-1}; **ΔS°** = J mol^{-1}K^{-1}.

Effect of Salt, Surfactants and Heavy Metals

The presence of different salts and metal ions in dyeing wastewaters causes high ionic strength and plays an important role on dye biosorption. Industrial water contains various salts/electrolytes which considerably affect the dye biosorption. Effect of the salt concentration (NaCl) on dye biosorption was investigated in the concentration range of 1-0.2%. The results reveal that the amount of dye adsorbed increased with increase in the concentration of salts. Increase in biosorption with increase in concentration of salt may be due to masking effect of Na^+ ion on the biomass surface and increased the biosorption of dyes onto the biosorbent [45]. Janos *et al*. investigated that the biosorption of dye increased with increase in the concentration of salts [46]. Effect

of heavy metals was studied at concentration range 1-0.2%. Sorption of Drimarine Yellow HF-3GL was not much affected by the presence of heavy metals. Textile industries also discharge surfactants along with dyes into the water stream. The effect of surfactants on the dye removal was determined in this study. The presence of surfactants reduced the sorption of Drimarine Yellow HF-3GL. The biosorption capacity of the dye reduced significantly by adding anionic surfactant, SDS (sodium dodecylsulfate). This was in agreement with the results obtained by Janos *et al*. [46] during the adsorptive study of basic (Methylene Blue) and acid (Egacid Orange) dyes. This reduction of biosorption capacity may be due to repulsive interactions between anionic surfactant and anionic dye molecules. The solubility of anionic dyes is less in SDS micelles than in the aqueous phase [22].

Desorption Study

The biomass used in biosorption should be reused to make the process attractive, efficient and economical. For successful desorption selection of eluent is important. Desorption depends upon the biosorption process, adsorbate and adsorbent. From the study of pH effect, it was observed that biosorption is maximum at low pH. Therefore, it would be logical that the adsorbed dyes could be recovered under reversely condition, i.e., strongly basic. Therefore, 0.2-1.0 M NaOH was used as eluent for unbinding the molecules. It was observed that Drimarine Yellow HF-3GL dye was satisfactorily desorbed. It was further noted that Drimarine Yellow HF-3GL desorbed more at higher concentration of eluent. Kavitha and Namasivayam [47] reported that insignificant biosorption at various pH values shows that chemisorption is the major mechanism of biosorption. Low biosorption at high pH shows that electrostatic attraction is not majorly involved in biosorption. Desorption of the dye molecules at higher pH has further confirmed the ionic interactions between the dye molecules and adsorbent.

Fixed-Bed Column Study of Drimarine Yellow HF-3GL

The capacity of breakthrough was calculated by using the formula given by Treybal and is described as the amount of dye in mg which is adsorbed on one g of biomass/adsorbant (Equation)

The biosorption capacity of dye in column was calculated at different flow rates, initial dye concentration and bed heights and results are presented in Table-4.

Table-4: Column biosorption capacities ($Q_{50\%}$) of Drimarine Yellow HF-3GL at different experimental conditions of flow rate (mL/min), bed height (cm) and initial dye concentration (mg/L).

Inlet Conc. (mg/L)	Break point (50%) (min)	Flow rate (mL/min)	Bed height (cm)	Biosorption capacity(mg/g)
50	25	3.6	3	3.96
50	45	3.6	4	5.67
50	70	3.6	5	7.35
50	40	5.4	5	6.30
50	30	7.2	5	5.99
75	58	3.6	5	9.61
100	46	3.6	5	9.77

Effect of Bed Height

The breakthrough curves attained for the biosorption of Dimarine Yellow HF-3GL for three varying bed heights 3 cm, 4 cm and 5 cm (1g, 1.25g and 1.5g respectively) at the constant inlet concentration of 50 mg/L of Dimarine Yellow HF-3GL solution and flow rate 3.6 mL/min and the breakthrough curves were plotted between time and ratio of outlet (final) and inlet (initial) Dimarine Yellow HF-3GL concentrations (C_{out}/C_{in}).

An increase in the bed height increased both the breakthrough time and the saturation/exhaustion time. When the bed height is increased, the breakthrough time increased because the zone of mass transfer had to travel more distance from the entering point of the bed to the exit point [48]. An increase in the bed height provides greater number of fixation sites for binding of dye molecules and thus causing more biosorption of dye resulting in the higher removal of Dimarine Yellow HF-3GL. The reduction in the bed height causes the predominance of phenomenon of axial dispersion rather than mass transfer therefore the solute had not good time for diffusion into the whole bed of biosorbant and thus reducing solute diffusion. The biosorption capacities of three bed heights i.e. 3 cm, 4 cm and 5cm were found 3.94 mg/g, 5.67 mg/g and 7.35 mg/g respectively. The maximum biosorption capacity was found 5 cm at constant flow rate 3.6 mL/min and 50 mg/L initial dye concentration. This 5 cm bed height was then selected and was used as optimum bed height for further studies.

Break through capacity ($Q_{50\%}$)=

$$\frac{\text{time for breakthrough (at 50\%)} \times \text{flow rate} \times \text{initial conc. of dye solution}}{\text{Amount of biosorbent used}} \quad \text{(Equation)}$$

Effect of Flow Rate

The breakthrough curves for biosorption of Dimarine Yellow HF-3GL onto bagasse at three flow rates 3.6 mL/min, 5.4 mL/min and 7.2 mL/min were studied while keeping the initial dye concentration 50 mg/L constant and using the optimized bed height 5 cm. It was observed that with higher flow rates, the occurrence of breakthrough was faster. At the lower flow rates more time was required for exhaustion/saturation. The different biosorption capacities and breakthrough curve slope at different flow rates can be described on the principles of mass transfer. The higher flow rate caused the saturation of bagasse more rapidly because there was an increase in mass transfer rate and thus causing the quick saturation of biomass [49].

At the start of the column experiment and at the lowest flow rate 3.6 mL/min greater removal of Dimarine Yellow HF-3GL on bagasse was observed. However by the continuous flow of dye solution through the column, the outlet concentration of Dimarine Yellow HF-3GL rapidly increased and the biosorbent became exhausted rapidly with Dimarine Yellow HF-3GL and the effluent concentration increased to the initial concentration of Dimarine Yellow HF-3GL. At higher flow rates breakthrough curves became much sharper.

An increase in the flow rate also decreased the time of breakthrough point and total amount of Dimarine Yellow HF-3GL adsorbed on bagasse. It can be described that the biosorption of Dimarine Yellow HF-3GL on bagasse is affected by less time of residence of the dye solution in the column, less number of sites for binding and insufficient diffusion of dye solution in the pores of bagasse and the dye exit the column before the occurrence of equilibrium as reported by

The biosorption capacities of three flow rates 3.6 mL/min, 5.4 mL/min and 7.2 mL/min were found to be 7.35 mg/g, 6.30 mg/g and 5.99 mg/g respectively. The maximum biosorption capacity was found for flow rate 3.6 mL/min, at 5 cm bed height and 50 mg/L initial dye concentration. This 3.6 mL/min flow rate was then selected and was used as optimum flow rate for next study [25].

Effect of Initial Dye Concentration

The effect of different initial concentrations was investigated by using Dimarine Yellow HF-3GL solution of 50 mg/L, 75 mg/L and 100 mg/L keeping the bed height 5 cm and flow rate 3.6 mL/min constant. The breakthrough curves were plotted between $C_{ou}t/C_{in}$ against time. An increase in the initial concentration of Dimarine Yellow HF-3GL resulted in the less service time and sharpness of breakthrough curves. The bagasse fixed-bed column was exhausted /saturated more rapidly at 100 mg/L which resulted in less time for both the breakthrough point and saturation point. The performance of the column was affected by the change in the initial solution of Dimarine Yellow HF-3GL. With an increase in the inlet concentration from 50 mg/L to 100 mg/L, both the breakthrough time of Dimarine Yellow HF-3GL and treated effluent volume decreased. However the biosorption capacity of the bed at the breakthrough point and saturation were found to increase from 7.35 mg/g to 9.77 mg/g at 5 cm bed height and 3.6 mL/min flow rate. The biosorption capacities of three different concentrations 75 mg/L, 75 mg/L and 100 mg/L were found to be 7.35 mg/g, 9.61 mg/g and 9.77 mg/g respectively at 3.6 mL/min flow rate and 5cm bed height. The maximum biosorption capacity was found to be 9.77 mg/g for 100 mg/L. The transport of dye is slow from the layer of film to the adsorbent surface due to less inlet concentration which implies the less driving force for mass transfer and small coefficient of diffusion. The reason of biosorption is the difference in concentration between the dye present in the solution and the amount of dye on the biosorbant and this high difference in concentration gives more driving force for the biosorption [50].

Kinetic Modeling of Experimental Data

Three kinetic models, BDST, Yoon-Nelson and Thomas models were applied to experimental data of continuous mode study.

Bed-Depth Service Time Model

The model of BDST describes that there is a linear relationship between the service time (t) and the bed height (z). The equation of BDST is expressed as:

$$t = \frac{NoZ}{CoU} - \frac{1}{K_a C_o} ln(\frac{C_o}{C_b} - 1) \quad (16)$$

here C_b is the concentration (mg/L) of dye solution at breakthrough point, initial concentration is C_i, U (cm/min) is the linear velocity, N_0 (mg/L) is the capacity of biosorption and the rate constant is K_a (L/mgmin). The plot of t-Z at the 0.2, 0.4, 0.6 C_b/C_{in} values at the 3.6 mL/min flow rate and 50 mg/L initial concentration are (R^2= 0.996, 0.999, 0.964) respectively showing the very good validation of model of BDST for Dimarine Yellow HF-3GL. By keeping the C_i and V as constant values, the slope of

the BDST line gave the biosorption capacity N_0, and k_a was calculated from the value of the intercept. The K_a, constant of the rate of reaction, describes the rate of transfer of the dye from the liquid solution to the solid surface of the biosorbent.

It was observed that with an increase in the values of C_b/C_{in} from 0.2 to 0.6 at 3.6 mL/min flow rate and 50 mg/L C_i, there was an increase in the value of N_0 from 2785.68 mg/L to 5014.22 mg/L while the value of K_a decreased [14]. The biosorption capacity of bed N_0 (mg/L), K_a (L/mgmin), together with their R^2 values at C_b/C_i values of 0.2, 0.4 and 0.6 are represented in Table-5.

Table-5: The calculated BDST model constants for the biosorption of Drimarine Yellow HF-3GL on bagasse (V=3.6 mL/min and Ci=50 mg/L).

C_b/C_{in}	m(min/cm)	c (min)	N_0 (mg/L)	K (L/mg min)	R^2
0.20	20	−52.66	2785.68	0.00059	0.996
0.40	21	−45.33	2924.9	0.00020	0.999
0.60	36	−80.00	5014.22	−0.00011	0.964

Thomas Model

This model is suitably used for the determination of concentration (q_0) of solid phase of the sorbate and the rate constant (K_{th}) of the sorbate [14] by using the linearized form of this model given below:

$$ln\left(\frac{C_o}{C_t}-1\right)=\frac{K_{Th}\times q_o\times W}{Q}-K_{Th}\times C_o\times t \quad (17)$$

The data of the column experiments of Dimarine Yellow HF-3GL at different bed heights, flow rates and initial concentrations of Dimarine Yellow HF-3GL was fitted to this model and q_0 and K_{th} were determined. The values of q_0 and K_{th} were determined from the plot of t versus ln(Cin/Ct-1) and coefficient (R^2) of linear correlation were attained for Dimarine Yellow HF-3GL.

Table 6 shows the comparison of q_0 predicted by model of Thomas and experimentally determined q_0 values gives a summarized form of the parameters of model of Thomas attained at varying heights of the biosorption bed, inlet concentration of Dimarine Yellow HF-3GL and flow rates. The q_0 values were found to increase from 4.50 mg/g to 6.01 mg/g with an increase in bed height from 3 cm to 5 cm and 6.01 mg/g to 13.01 mg/g with increase in initial dye concentration from 50 mg/L to 100 mg/L but a decrease was observed in the value of k_{th} in the same manner as observed by.

Table-6: Parameters of Thomas model at different experimental conditions for Dimarine Yellow HF-3GL.

Bed height (cm)	Flow rate (mL/min)	Initial dye conc. (mg/L)	Q_{exp} (mg/g)	Q_{cal} (mg/g)	K_{Th} (L/mgmin)	R^2
3	3.6	50	3.94	4.50	0.00021	0.926
4	3.6	50	5.67	5.11	0.000208	0.909
5	3.6	50	7.35	6.01	0.00016	0.959
5	5.4	50	6.30	4.34	0.000181	0.913
5	7.2	50	6.30	4.15	0.000183	0.931
5	3.6	75	9.61	10.00	0.00013	0.939
5	3.6	100	9.77	13.01	0.00011	0.885

While with the increasing flow rates from 3.6 mL/min to 7.2 mL/min, the value k_{th} increased and of q_0 decreased.

Yoon-Nelson model

The Yoon-Nelson model assumed that the decrease in the rate of biosorption probability of every sorbate molecule is directly proportional to the sorbat sorption probability and breakthrough probability of sorbat on the biosoabant. The linearized equation of Yoon-Nelson can be expressed as:

$$\ln\left(\frac{Ct}{Cin}-Ct\right)=K_{YNT}-\tau K_{YN} \quad (18)$$

This model was applied to find out the breakthrough behavior of Dimarine Yellow HF-3GL on bagasse. The values of the rate constant (k_{YN}) and the time for 50 % breakthrough point of the bagasse (τ) were calculated from the plot of t against ln (C_t/C_{in}-C_t) at different bed heights varying from 3cm to 5cm and concentrations of initial solution of Dimarine Yellow HF-3GL varied from 50 mg/L to 100 mg/L and flow rates varied from 3.6 mL/min to 7.4 mL/min. These values were then used for the determination of breakthrough curves. The values of τ and k_{YN} are represented in Table-7. From the table values it was found that the value of k_{YN} increased for both the increase in flow rate and initial concentration of Dimarine Yellow HF-3GL but the value of τ (time for 50 % breakthrough) decreased.

Table-7: Parameters of Yoon–Nelson model for Dimarine Yellow HF-3GL biosorption on bagasse at different flow rates and initial concentrations.

Z (cm)	Q (mL/min)	C_0 (mg/L)	τ_{exp} (min)	τ_{cal} (min)	K_{YN} ($Lmin^{-1}$)	R^2
3	3.6	50	25	23	0.0091	0.926
4	3.6	50	45	36	0.0085	0.909
5	3.6	50	70	54	0.0073	0.959
5	5.4	50	40	21	0.0074	0.913
5	7.2	50	30	14	0.0077	0.931
5	3.6	75	58	30	0.0075	0.939
5	3.6	100	46	25	0.0083	0.885

Fourier Transform Infrared (FTIR) Studies

The FT-IR analysis was performed to identify the possible interactions between the

functional groups of sugarcane bagasse and Drimarne Yellow HF-3GL (Fig. 6). The broad and strong vibration at 3338.40 cm $^{-1}$ is indicative of the presence of the –OH and -NH groups on sugarcane bagasse biomass. The peak at 2923.77 cm^{-1} is assigned to the asymmetric and symmetric C-H stretching vibrations of the aliphatic groups. Presence of peak at 1650.63 cm^{-1} was attributed to stretching vibration of carboxyl group (-C=O). The band observed at 1033.48 cm^{-1} was assigned to C-O stretching vibration of alcohols and carboxylic acids. Presence of peak in the range of 2,360.73 – 2,339.81 cm−1 suggests the participation of functional group O–H (carboxylic acid and derivates) in dye biosorption on the surface of sugarcane bagasse. These observations indicate that various functional groups (hydroxyl, carboxyl, amine) on the surface of the sugarcane bagasse are responsible for the binding of Drimarine Yellow HF-3GL.

Point of Zero Charge

Point of zero charge of sugarcane bagasse biomass was determined by solid addition method and it was found to be 4.8. This indicates that below this pH the sugarcane bagasse biomass acquires positive charge due to protonation of functional groups which results in electrostatic attraction between dye anions and whereas above this pH a negative charge exists on the surface of sugarcane bagasse biomass. Anionic dye biosorption is favored at pH□Hpzc where the surface becomes positively charged.

Experimental

Chemicals

All the analytical grade chemicals were taken from Sigma–Aldrich Chemical Co. (USA) and Merck (Germany).

Preparation of Biomass

Different agricultural waste materials (bagasse, peanut husk, corncobs, cotton sticks and sunflower) were collected from different areas of Punjab, Pakistan to use as biosorbents in this study. These biomasses were cut into small pieces and were rinsed several times with distilled water to remove dust and foreign particles. The cleaned biomasses were dried in sunlight and oven dried overnight at 60 °C. The dried biomasses were ground with a food processor (Moulinex, France) and sieved using Octagon sieve (OCT-DIGITAL 4527-01) to a 0.250 mm mesh size.

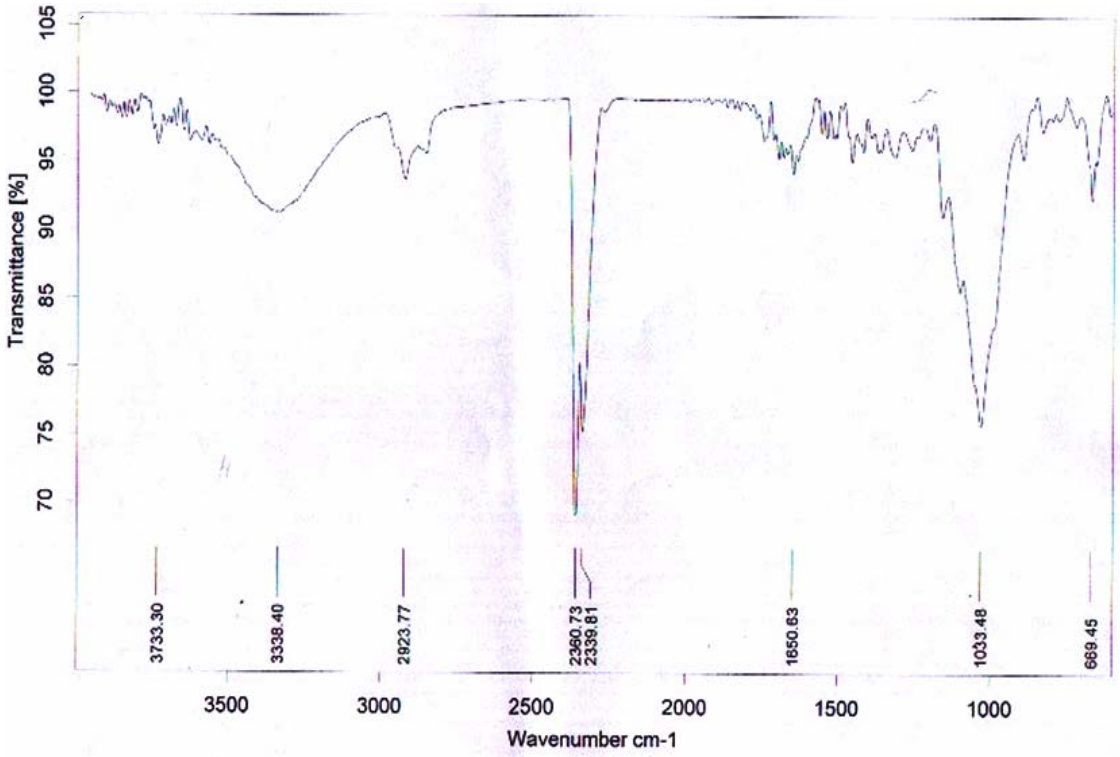

Fig. 6: FT-IR spectrum of sugarcane bagasse loaded with Drimarine Yellow HF-3GL.

Preparation of Aqueous Dye Solutions

Drimarine Yellow HF-3GL dye was obtained from Clariant Pakisatn Limited, Faisalabad, Pakistan and was used without further purification. Stock solution of dye was prepared by dissolving 1g of dye in 1000 mL of double distilled water. The experimental solutions of different concentrations ranging from 10-200 mg/L were made by further dilutions. Standard curve was developed through the measurement of the dye solution absorbance by UV/Visible Spectrophotometer (Schimadzu, Japan). Drimarine Yellow HF-3GL dye was anionic in nature and its $\lambda_{max}$was found to be 429 nm.

Batch Experimental Program

Screening test was carried out with five agricultural wastes for the selection of best biosorbent to use in the further study. Optimization of important process parameters such as pH, contact time, biosorbent dose, initial dye concentration and temperature for the removal of Drimarine Yellow HF-3GL was carried out by using classical approach. The 250-mL conical flasks containing 50 mL of dye solution of known pH, concentration and biosorbent dose were shaken in orbital shaking incubator (PA250/25H) at 120 rpm. Blank solutions were run under same conditions except the addition of biosorbent. pH of the solution was adjusted using 0.1M HCl and NaOH solutions. All the experiments were performed in triplicate and reported values are mean ± SD. After certain time, the samples were taken out and centrifugation was performed at 5000 rpm for 20 min and concentration of remaining dye solution was determined by using UV-Vis spectrophotometer (Schimadzu, Japan).

The equilibrium biosorption uptake, qe (mg/g), was calculated using the following relationship:

$$q_e = \frac{(C_o - C_e)V}{W} \qquad (19)$$

where C_o is the initial dye concentration (mg/L), C_e is the equilibrium dye concentration (mg/L), V is the volume of the solution (L) and w is the mass of the biosorbent (g).

Immobilization of Biomass

Sodium–alginate (2.0 g) was dissolved in 100 mL of water by heating and then the solution was cooled down. Sugarcane biomass (1g/100 mL) was added to above mixture and mixed until to form a homogeneous mixture. Then the mixture was dropped into a solution of 0.1 M $CaCl_2$ to form uniform beads of immobilized biomass. The beads were washed with distilled water and stored at 4 ^oC in 0.05 M $CaCl_2$ solution [51].

Pretreatment of Selected Biosorbent

Sugarcane bagasse biomass was pretreated physically and chemically. During physical treatments autoclaving (the sugarcane bagasse biomass was autoclaved at 121 ^oC for 15 min) and boiling (5 g of biomass/100 mL of H_2O and boiled for 30 min) was carried out. In chemical modifications, 1 g of the biosorbent was treated with 5 % of different acids (HCl, H_2SO_4 and HNO_3 and CH_3COOH), alkalis (NaOH, KOH, NH_4OH), Surfactants (CTAB, SDS, Triton X-100), chelating agents (PEI, EDTA and glutaraldehyde) and organic solvents (benzene and methanol). Then all the modified biomasses were washed with double distilled water and filtered. Then the modified biosorbents were dried in oven at 60° C for 24 hours and ground it [19].

Biosorption Kinetics

Biosorption kinetics experiments were carried out in 250 mL flasks containing 50 mL of the dye solutions using a known amount of sugarcane bagasse. The flasks were agitated for various time intervals (0–180 min) in an orbital shaker at 120 rpm under constant temperature (30 °C). The samples were taken at different time intervals, centrifuged and analyzed for remaining dye concentrations as described before. The kinetic data was analyzed using pseudo-first order [28], pseudo-second order [29] and intraparticle diffusion [30] kinetic models.

Biosorption Equilibrium

Equilibrium experiments were carried out by taking known amount of Sugarcane bagasse in 250-mL flasks containing 50 mL of the dye solution of different initial dye amounts (10–200 mg/L). The mixture was shaken in an orbital shaker at 120 rpm keeping temperature constant (30 °C). Then most commonly employed biosorption isotherm models were applied in this present investigation viz. the Langmuir [36], Freundlich [37], Temkin [38], Harkins Jura [39] and Doubinin– Radushkevich [40].

Biosorption Thermodynamics

Biosorption of Drimarine Yellow HF-3GL was investigated at different temperatures (30 to 60 C^o) in the orbital shaking incubator under pre-optimized conditions. Various thermodynamic

parameters such as enthalpy changes (ΔH°), entropy changes (ΔS°) and Gibbs free energy changes (ΔG°) were used to determine the spontaneity of biosorption process.

Column Studies

Biosorption performance of biosorbents in continuous system is important factor in accessing the feasibility of biosorbent in real applications. Continuous biosorption experiments in a fixed-bed column were conducted in a glass column (20 mm ID and 43 cm height), packed with a known quantity of sugarcane bagasse biomass. At the bottom of the column, a stainless sieve was attached followed by a layer of glass wool. A known quantity of the sugarcane bagasse was packed in the column to yield the desired bed height of the biosorbent (3, 4 and 5 cm). Drimarine Yellow HF-3GL dye solution of known concentrations (50, 75 and 100 mg/L) at pH 2 was pumped upward through the column at a desired flow rate (3.6, 5.4 and 7.2 mL/min) controlled by a peristaltic pump (Prominent, Heidelberg, Germany). The dye solutions at the outlet of the column were collected at regular time intervals and the concentration was measured using a double beam UV-visible spectrophotometer (Shimadzu, Japan) at 429 nm. All the experiments were carried out at room temperature (28 ± 1°C).

FTIR Studies

The chemical characteristics of sugarcane bagasse biomass were analyzed and interpreted by Bruker Tensor 27 Fourier transform infrared spectrometer with the samples prepared as KBr discs.

Determination of Point of Zero Charge (pHpzc)

The point of zero charge (pHpzc) was determined by solid addition method [52]. A series of 0.1 $MKNO_3$ solutions (50 mL each) were prepared and their pH was adjusted in the range of 1.0 to 12.0 by addition of 0.1 NHCl and NaOH. To each solution, 0.1 g of biosorbent was added and the suspensions were shaked manually and solution was kept for a period of 48 h with intermittent manual shaking. The final pH of the solution was recorded and difference between initial and final pH (ΔpH) (Y-axis) was plotted against initial pH (X-axis). The point of intersection of this curve yielded point of zero charge.

Conclusions

Sugarcane bagasse has been proved as an efficient biosorbent for the removal of Drimarine Yellow HF-3GL from aqueous solution. Batch mode of biosorption was influenced by some experimental parameters i.e., pH, biosorbent dose, contact time, initial dye concentration and temperature. The kinetic, thermodynamic and equilibrium studies were also carried out to understand the process of biosorption. Isotherm parameters of Langmuir, Freundlich, Temkin, H-R and D-R models were calculated and data was better explained by Freundlich isotherm model. Thermodynamic studies proved that biosorption by native and pretreated biomass was spontaneous. Kinetic study revealed that the biosorption process followed pseudo-second-order kinetic model. The column mode of study showed that biosorption increases with increase in bed height and initial dye concentration but decreases with increase in flow rate. The mechanism of dye biosorption was confirmed by FTIR analysis. In view of these results it can be concluded that sugarcane bagasse can be used as a low cost and proficient biosorbent for the removal of reactive dyes from waste effluents.

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