International Journal of Applied Science and Engineering
2009. 7, 2: 115-125

Biosorption of acid dyes using spent brewery grains: Characterization and modeling

Dr.V.Jaikumar [a,*], K.Sathish Kumar [b], D.Gnana Prakash [b]

[a] *Department of Medical Bio-Nanotechnology, Chettinad University, Kelambakkam*
Rajiv Gandhi Salai (OMR), Chennai-603103, INDIA
[b] *Department of Chemical Engineering, SSN College of Engineering, Rajiv Gandhi Salai (OMR),*
Kalavakkam,Chennai- 603110, INDIA

Abstract: In the present work the brewery industry waste is taken as a low cost biosorbent for the removal of acid dyes from the aqueous solution. Biosorption of acid dyes (Acid Yellow - AY 17 and Acid Blue - AB 25) onto spent brewery grains (SBG) was investigated. The biosorbent material is characterized using scanning electron microscopy, FT-IR spectroscopy, XRD and BET surface area. The dye binding capacity of biosorbent was shown as a function of initial pH, initial dye concentration, biosorbent dosage, contact time and temperature. Equilibrium uptake was found to be pH dependent and maximum uptake was observed at a pH of 2 for both the dyes. Colour removal was found to decrease with initial dye concentration, temperature and increase with biosorbent dosage and time. The equilibrium data fitted very well to Freundlich adsorption model. The results showed that both the dyes uptake processes followed the second-order rate expression. The study confirms that the spent brewery grains can be used as biosorbent for the removal of acid dyes from its aqueous solution.

Keywords: Biosorption; Acid dyes; Spent brewery grains; Isotherm; Kinetics.

1. Introduction

Dyes are synthetic aromatic water-soluble dispersible organic colorants, having potential application in various industries [1]. Textile and dyeing industry are among important sources for the continuous pollution of the environment. The effluents of these industries are highly coloured and the disposal of these waste into environment can be extremely deleterious. It is reported that there are over 100,000 commercially available dyes [2] and most of them are difficult to decolorize due to their complex aromatic molecular structure and they are also stable to light, water, heat and oxidizing agents. There are many structural varieties of dyes such as acidic, basic, reactive, azo, disperse, direct, vat and metal complex dyes. All of these dyes are harmful, when in contact with living tissues for a long time. The discharge of these dye bearing effluents to the river stream without proper treatment causes severe irreparable damage to the living beings and crops, both aquatic and terrestrial.

The most widely used methods of dye removal from dye containing industrial effluents are categorized into chemical, physical and biological. Currently chemical and physical methods are used in industries for

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[*] Corresponding author; e-mail: jaikumarphd@gmail.com

Accepted for Publication: January 28, 2010,

their treatment of effluents with research concentrating on bio-based cheaper and effective alternatives. In physical treatment, adsorption technique has gained more importance due to their high efficiency in the removal of dyes from effluents and it is a process which is economically feasible compared to membrane filtration, ion exchange, irradiation and electro chemical methods. Activated carbon is the most widely used adsorbent for the removal of colour and treatment of textile effluents but due to its high price it is not used on a great scale [3]. This has led researchers to search for the use of cheap and efficient alternative material from various natural [4-10] and industrial waste products or biomass [11-12]. The industrial wastes that are available may be either organic or inorganic in nature. The survey of literature shows that various industrial waste or biomass from various industries such as sugar, fermentation, fertilizer, steel, pharmaceutical industries have been tried as biosorbent but not much work is done using spent brewery grains a brewery industry waste as biosorbent for the removal of dyes from aqueous solutions. Spent grains are normally utilized as cattle feed in countries where dairy farming is practiced. In many parts of world, spent grains are not fully utilized due to the absence of this activity. Also, due to the prosperous market of the brewing industry, the production of this material has steadily increased in the last years. Few studies have been conducted on spent grains potential as adsorbent of acid orange 7 dye [13] and heavy metal removal cadmium and lead from aqueous solutions [14]. The purpose of this study is to investigate the removal of acid dyes by spent brewery grains a cheap and abundant biomass obtained from brewery industry.

2. Experimental

2.1 Materials

Spent Brewery Grains, obtained from Mohan breweries and distilleries Limited, Chennai, India, was suspended in 1M sulphuric acid solution (20g of SBG per 100mL of acid solution) for one hour to remove impurities. Then it was filtered and the acid solution was discarded. The biomass was washed with distilled water many times until it is completely free from the acid and dried at 60°C for 24 hours. The dried biomass was ground and sieved and stored for further use in the experiments.

The adsorbate AY 17 dye (C.I. = 18965, Chemical formula = $C_{16}H_{10}Cl_2N_4Na_2O_7S_2$ F W = 551.29, nature = acid yellow 17) and AB 25 (C.I. = 62055, Chemical formula = $C_{20}H_{13}N_2NaO_5S$, F W = 416.38, nature = acid blue 25) was supplied by Sigma-Aldrich Chemicals Ltd., India. The structure of AB 25 and AY 17 is given in (Figure 1) and (Figure2) An accurately weighed quantity (1 g) each of AY 17 and AB 25 was dissolved in double distilled water separately to prepare stock solution of 1000 mg/L each. Experimental solutions of the desired concentrations were prepared by dilution with double-distilled water.

2.2 Physical characterization

The physical properties of SBG relating to Brunauer-Emmett-Teller (BET) surface area and total pore volume were obtained by measuring their nitrogen adsorption isotherm at 77 K in a surface area and porosity analyzer (Model ASAP 2020 Micromeritics Co., USA). The surface morphology of SBG is characterized by scanning electron microscope (SEM) (JEOL JSM Model 6360). The SEM images of various magnifications are given in Figure 3a, 3b and 3c. The Figure 4 shows FT-IR of the material recorded on Perkin Elmer FT-IR Model RX_1 with KBR pellets for solid samples and XRD patterns were taken on a Rich Seifert (Model 3000) X- ray diffractometer using Cu-K_{α} radiation.

2.3. Analytical measurements

The concentration of the dye AY 17 and AB 25 were determined using a UV-vis spectrophotometer (HITACHI U 2000, spectrophotometer) at a wavelength corresponding to the maximum absorbance of the dye (λ_{max} = 401.5 nm and 600 nm) respectively. Calibration curves were plotted between absorbance and concentration of the dye solution.

2.4. Batch experiments

Batch experiments were conducted using 250 mL Erlenmeyer flasks to which 50 mL of dye containing waste water and biomass were added. These flasks were agitated in an orbital shaker at a constant speed of 150 rpm to study the effect of important parameters like pH, initial dye concentration and adsorbent dosage. Samples were withdrawn at appropriate time intervals and these samples were centrifuged (Research centrifuge Remi scientific work, India) at 4000 rpm. The supernatant was used for analysis of the residual dye concentration. The effect of pH on dye removal was studied over a pH range of 2-12. pH was adjusted by addition of dilute aqueous solutions of 0.1N HCl or 0.1N NaOH. For the optimum amount of adsorbent per unit mass of adsorbate, a 50mL dye solution was contacted with different amounts of SBG till equilibrium was attained. The kinetics of adsorption was determined by analyzing adsorptive uptake of the dye from the aqueous solution at different time intervals. The adsorption isotherm was found by agitating AY 17 and AB 25 solution of different concentrations with the known amount of SBG till the equilibrium was achieved. The studies were performed at room temperature of around 303 K.

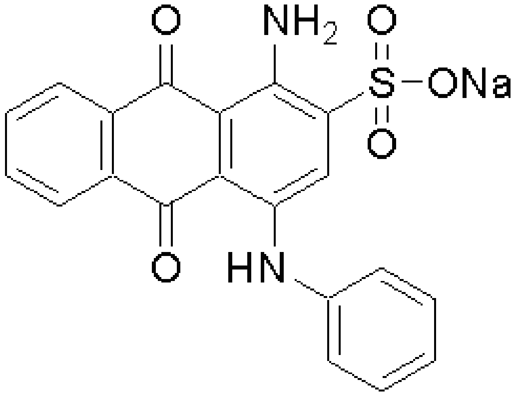

Figure 1. Chemical structure of AB 25

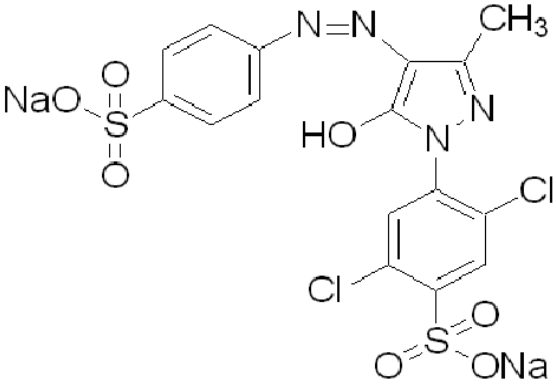

Figure 2. Chemical structure of AY 17

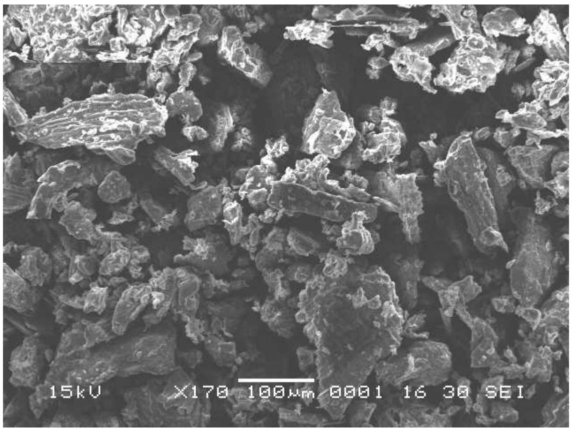

Figure 3a. SEM image of SBG 170x

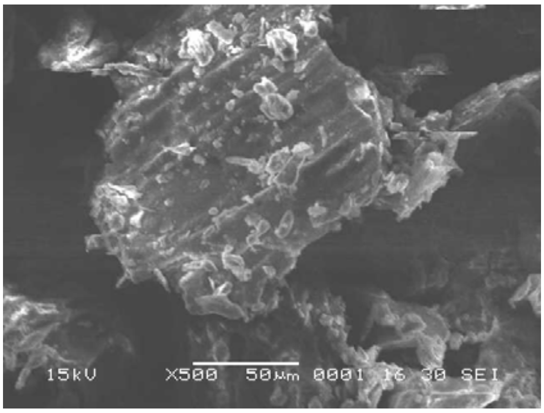

Figure 3b. SEM image of SBG 500x

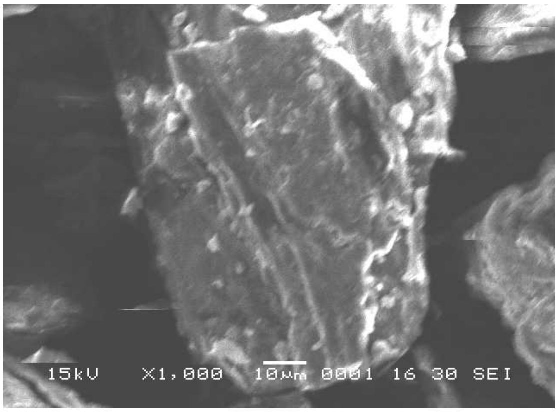

Figure 3c. SEM image of SBG 1000x

Table 1. Main physical properties of spent brewery grains (SBG)

Sample	S_{BET} (m^2/g) BET Surface area	V_t (cm^3/g) Total pore volume	W_{av} (A^o) Average pore width
SBG	1.748	0.0053	121.784

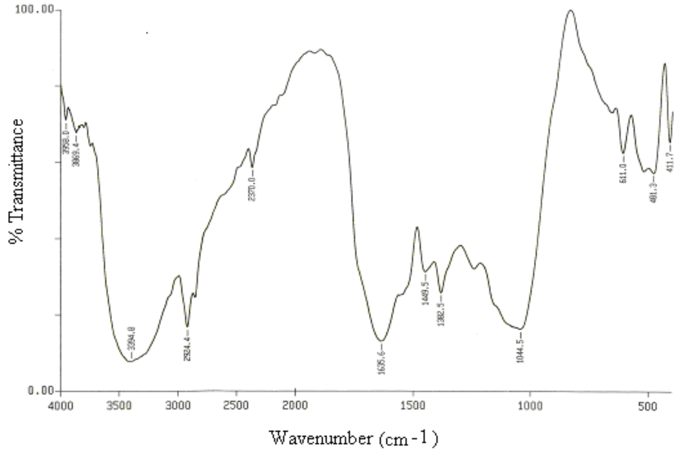

Figure 4. FTIR spectra for SBG

3. Results and discussion

3.1 Physical characterization of SBG

The data in Table 1 indicates the BET surface area, total pore volume and average pore width of SBG biosorbent. The results show that the pores of SBG are macroporous and possess fewer adsorption properties but have great ability to trap suspended solids for separation from liquid solutions [15]. The textural structure examination of SBG can be observed from the SEM photographs. It could be seen that the observation was consistent with the results from the measurements of physical properties given in Table 1. The IR Spectrum of SBG shown in Figure 4 exhibited broad adsorption bands in the region of 3400 cm-1 that represent bounded –OH and –NH groups. The bands at 1382 cm^{-1} and1044 cm^{-1} represents carbonate and carbohydrates. –CH stretch could be ascribed to the band that appeared at 2924 cm^{-1}. The carboxyl ions give rise to two bands: a strong asymmetrical stretching band at 1635 $cm^{-1}$and a weaker symmetrical band at 1449 cm^{-1} for the SBG. Wide angle X-ray spectra were obtained using a Rich Seifert (Model 3000) diffractometer with Cu K_α radiation ($\lambda = 1.5418$ $A^{0)}$ ($\theta = 3^0$) for the ground powder of SBG is 1.4722 nm.

3.2. Effect of pH

pH is an important parameter affecting the biosorption process. The effect of initial pH on the equilibrium uptake is given in (Figure 5) for each dye at 100 mg/L initial dye concentration at the liquid to solid ratio of 50 mL solution / 0.5 g biosorbent for AY 17 and 50 mL solution / 0.4 g biosorbent for AB 25 at room temperature. The maximum dye sorption occurred at pH 2 and the removal decreased thereafter for both the dyes. This may be due to high electrostatic attraction between the positively charged surface of the SBG and anionic dyes. The $-SO_3$ group present in the dyes plays a major role in enhancing the dye adsorption process. Acid dyes are also called as anionic dyes because of the negative electrical structure of the chromophore group. As the initial pH increases, the number of negatively charged sites on the biosorbent surfaces increases and the number of positively charged sites decreases. A negative surface charge does not favor the biosorption of dye anions due to electrostatic repulsion [16]. In general, the acidic dye uptakes are much higher in acidic solutions than those in neutral and alkaline conditions [17].

3.3. Effect of initial dye concentration

The effect of initial dye concentration on the adsorption of dye was investigated and shown in (Figure 6). Experiments are carried out at initial pH 2, room temperature 303K and biosorbent dosage of 0.5g/l for AY 17 and 0.4 g/l for AB 25. It provides an important driving force to overcome all mass transfer resistances of the dye between the aqueous and solid phases, thus increases the uptake. The removal yield of AY 17 and AB 25 increased from 90 to 94 % and 97.6 to 99.5 % respectively from 25 to 150 mg/L initial dye concentration, and then started to decrease from 94 to 77 % and 99.4 to 93.8 % for initial dye concentration of 175 to 600 mg/L. At lower dye concentrations solute concentrations to biosorbent sites ratio is higher, which cause an increase in color removal [18]. At higher concentrations, lower adsorption yield is due to the saturation of adsorption sites.

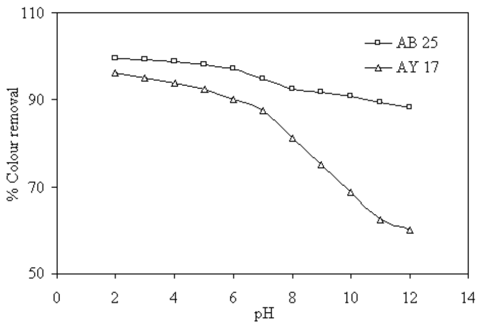

Figure 5.The effect of initial pH of dye solution

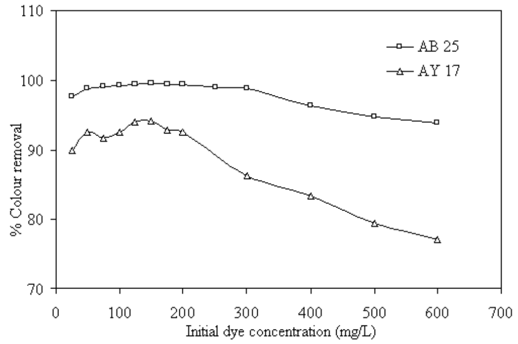

Figure 6. Effect of initial dye concentration

3.4. Effect of biosorbent dosage

The effect of biosorbent dosage on the removal of AY 17 and AB 25 by SBG at Co = 100 mg/L, pH 2 and at 303K temperature is shown in the (Figure 7). It can be seen that the AY 17 and AB 25 removal increases up to a certain limit and then it remains constant. The increase in the biosorption with the biosorbent dosage can be attributed to greater surface area and the availability of more adsorption sites [19]. At biosorbent dosage greater than 0.5 g for AY 17 and 0.4 g for AB 25 the surface dye concentration and the solution dye concentration come to equilibrium with each other.

3.5. Effect of contact time

The effect of contact time on adsorption of AY 17 by SBG at Co = 100 mg/L for adsorbent dosage 0.5 g and 0.4g for AB 25, pH 2 and at room temperature 303K is presented in Fig. 8. It can be observed from the figure that rapid adsorption of dye has taken place in the first 10 min and, thereafter, the rate of adsorption decreased gradually and reached equilibrium in about 40 min. around 94 % of removal was obtained in about 40 min. for both the dyes. This may be due to strong attractive forces between the dye molecules and the adsorbent [20]. Fast diffusion on the external surface was followed by fast pore diffusion into the intra particle matrix to attain rapid equilibrium [21]. Further increase in contact time showed that there is no significant increase in the removal of dyes by SBG.

3.6. Effect of temperature

Investigation of temperature effect on the biosorption of acidic dyes is very important in the real application of biosorption as various textile and other dye effluents are produced at relatively high temperatures. Experiments are carried out at Co = 100 mg/L, initial pH 2, and biosorbent dosage of 0.5g/l for AY 17 and 0.4 g/l for AB 25. The biosorption of AY 17 and AB 25 on SBG was investigated as a function of temperature and maximum uptake value was obtained at 30 ºC as can be seen from Fig. 9. Adsorption decreased with further increase in temperature due to the decreased surface activity suggesting that biosorption between both the dyes (AY 17 and AB 25) and SBG was an exothermic process and the mechanism was mainly physical adsorption [22].

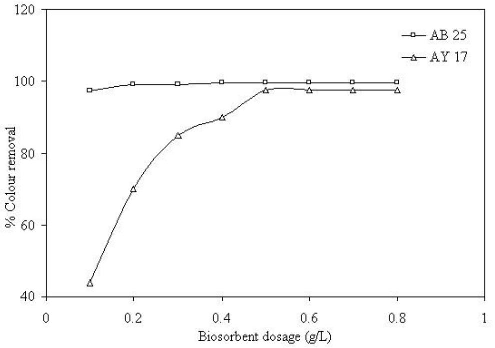

Figure 7. Effect of biosorbent dosage

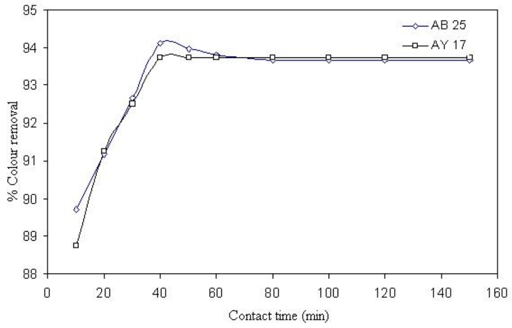

Figure 8. Effect of contact time

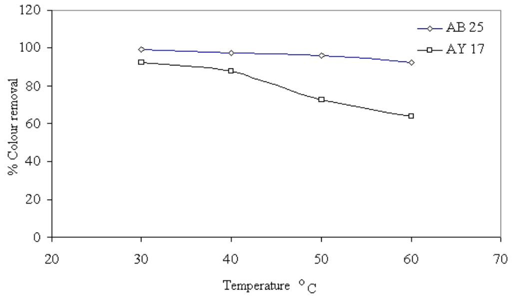

Figure 9. Effect of temperature

3.7. Kinetic modeling

In order to investigate the biosorption processes of AY 17 and AB 25 on the SBG, pseudo-first order and pseudo-second order kinetic models were used.

3.7.1. Pseudo-first-order model

The pseudo-first-order equation is given as: [23]

$$dq_t \;/ dt = k_f\; (q_e - q_t) \qquad (1)$$

where q_t is the amount of adsorbate adsorbed at time t (mg/g), q_e is the adsorption capacity at equilibrium (mg/g), k_f is the seudo-first-order rate constant (min^{-1}), and t is the contact time (min). The integration of Eq. (1) with the initial condition, $q_t = 0$ at $t = 0$ leads to:

$$\log(q_e - q_t) = \log q_e - \frac{k_f}{2.303} t \qquad (2)$$

The values of adsorption rate constant (k_f) for AY 17 and AB 25 adsorption on SBG were determined from the plot of log (q_e-q_t) against t (not shown here). These values are given in Table 2a and 2b.

Table 2a. Kinetic parameters for the removal of AY 17 by SBG, Pseudo-first-order model

C_o (mg/L)	q_e (mg/g)	k_f (1/min)	R^2
100	0.904	0.066	0.9278
150	0.904	0.066	0.9278
200	0.904	0.066	0.9278
300	3.773	0.283	0.7987

Table 2b. Kinetic parameters for the removal of AB 25 by SBG, Pseudo-first-order model

C_o (mg/L)	q_e (mg/g)	k_f (1/min)	R^2
100	1.034	0.073	0.9633
150	1.034	0.073	0.9633
200	1.034	0.073	0.9633
300	1.034	0.073	0.9633

3.7.2. Pseudo-second-order model

The pseudo-second-order model is given as: [24]

$$\frac{dq}{dt} = k_s (q_e - q_t)^2 \qquad (3)$$

Where k_s is the pseudo-second-order rate constant (g/mg min), q_e is the amount of dye adsorbed at equilibrium (mg/g), and q_t is the amount of dye adsorbed at time t (mg/g). Integrating Eq. (3) for the boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$ gives

$$q_t = \frac{q_e^{\,2} k_s t}{1 + q_e k_s t} \qquad (4)$$

Eq. (4) is the integrated rate law for a second-order reaction (25) and can be rearranged to obtain

$$q_t = \frac{t}{\dfrac{1}{k_s q^2{}_e} + \dfrac{t}{q_e}} \qquad (5)$$

This has a linear form of

$$\frac{t}{q_t} = \frac{1}{k_s {q_e}^2} + \frac{1}{q_e} t \tag{6}$$

The initial adsorption rate, h (mg/g min) is defined as:

$$h = k_s {q_e}^2 \tag{7}$$

The rate parameters k_s and q_e can be directly obtained from the intercept and slope of the plot (t/ q_t) against t (Figure 10) and (Fig. 11) for AB 25 and AY 17 respectively. Values of $k_{s,}$ $q_{s,\,h}$ and correlation coefficient R^2 are listed in Table 3a and 3b. The calculated correlation coefficients are closer to unity for pseudo-second-order kinetics than that for the pseudo-first-order kinetic model. Therefore, the sorption can be approximated more appropriately by the pseudo-second-order kinetic model for the biosorption of AY 17 and AB 25 by SBG.

Table 3a. Kinetic parameters for the removal of AY 17 by SBG, Pseudo-second-order model

C_o (mg/L)	q_e (mg/g)	k_s (g/mg min)	h (mg/g min)	R^2
50	3.753	0.165	2.329	0.9998
100	7.911	0.181	11.335	0.9999
150	12.077	0.185	27.086	1
200	16.233	0.187	49.491	1
300	24.570	0.190	114.942	1

Table 3b. Kinetic parameters for the removal of AB 25 by SBG, Pseudo-second-order model

C_o (mg/L)	q_e (mg/g)	k_s (g/mg min)	h (mg/g min)	R^2
50	5.455	0.827	24.630	1
100	11.709	0.900	123.456	1
150	17.953	0.940	303.030	1
200	24.213	0.947	555.555	1
300	36.764	0.924	1250.00	1

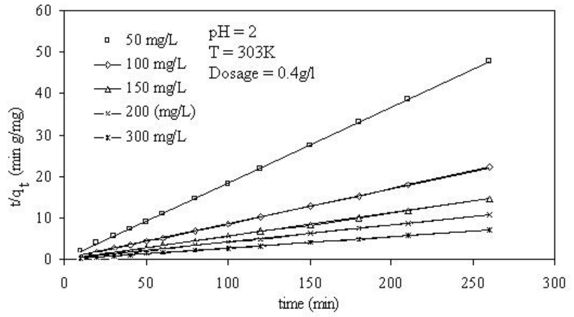

Figure 10. Pseudo-second-order kinetic plots for the removal of AB 25

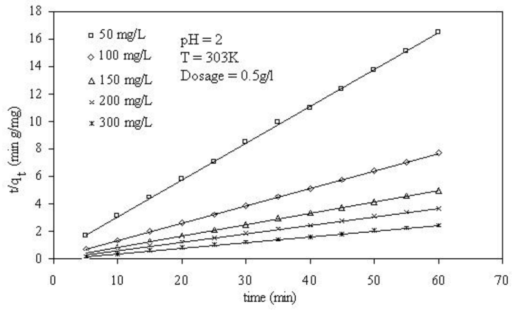

Figure 11. Pseudo-second-order kinetic plots for the removal of AY 17

3.8. Equilibrium modeling

The equilibrium sorption isotherm is fundamentally important in the design of adsorption system. Equilibrium studies in adsorption gives the capacity of the sorbent. Equilibrium relationships between sorbent and sorbate are described by adsorption isotherms, usually the ratio between the quantity sorbed and that remaining in the solution at a fixed temperature at equilibrium [25].The Langmuir and Freundlich isotherm models are generally used two parameter models for description of the nonlinear equilibrium between biosorption capacity and adsorbate equilibrium concentration at a constant temperature.

3.8.1. Langmuir isotherm

Langmuir proposed a theory to describe the adsorption of gas molecules onto metal surfaces. Langmuir model of adsorption depends on the assumption that intermolecular forces decrease rapidly with distance and consequently predicts the existence of monolayer coverage of the adsorbate at the outer surface of the adsorbent. The isotherm further assumes that adsorption takes place at specific homogeneous sites within the adsorbent. It is also assumed that once a dye molecule occupies a site, no further adsorption can take place at that site. The Langmuir isotherm is often used to describe the sorption of solute from solution as

$$\frac{q_e}{q_m} = \frac{bc_e}{1+bc_e} \tag{8}$$

This relation can be written in linearized form as

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m} \tag{9}$$

Where q_e is the amount of adsorbate adsorbed at equilibrium (mg/g), b is the Langmuir constant related to the energy of sorption (L/mg), q_m is the maximum sorption capacity corresponding to complete monolayer coverage (mg/g), and C_e is the equilibrium solute concentration (mg/L).

3.8.2. Freundlich isotherm

The empirical Freundlich equation that corresponds to the sorption on heterogeneous surface is given below:

$$q_e = K_f C_e^{1/n} \tag{10}$$

Where K_f and n are the Freundlich constants characteristics of the system (n, dimensionless; K_f, ($\mathrm{mg}^{1-1/n}\ \mathrm{g}^{-1}\ \mathrm{l}^{1/n}$). Eq. (10) can be linearized in logarithmic form and the Freundlich constants can then be determined.

Freundlich and Langmuir isotherm constants were determined from the plots of ln q_e versus ln C_e and for AB 25 and AY 17 respectively and C_e/ q_e versus Ce (not shown here) respectively, at 303, 313, 323 K. The data poorly fit to Langmuir model suggesting the interactions were not simple surface adsorption. It was found that the Freundlich isotherm best represents the equilibrium adsorption of AY 17 and AB 25 on SBG. The isotherm constants and the correlation coefficient, R^2 with the experimental data is given in Table 4a and 4b. As seen from Table 4, the parameter K_F (Freundlich constant) related to the adsorption density increased with a decrease in temperature. This was consistent with the experimental observation; it also indicates that n (intensity of adsorption) is greater than unity, indicating that the dye is favourably adsorbed by biomass at all temperatures studied.

4. Conclusions

The present investigation clearly demonstrated the applicability of SBG as biosorbent for AY 17 and AB 25 dye removal from aqueous solutions.

Table 4a. Freundlich isotherm constants for the biosorption of AY 17 onto SBG at varying temperatures

T (K)	K_F (mg/g)(L/mg)^n	n	R^2
303	1.934	1.534	0.8937
313	0.828	1.195	0.8213
323	0.474	1.073	0.7465

Table 4b. Freundlich isotherm constants for biosorption of AB 25 onto SBG at varying temperatures

T (K)	K_F (mg/g)(L/mg)^n	n	R^2
303	13.953	1.130	0.8007
313	9.466	0.971	0.8640
323	1.612	0.640	0.9978

Experiments were carried out covering a wide range of operating conditions. The influence of time, pH, adsorbent dosage, temperature and initial dye concentration was critically examined. The solution pH, and initial dye concentration played a significant role in affecting the capacity of biosorbent. The further increase in pH over 2.0 initial dye concentration of 150 mg/L and temperature over 303 K led to decrease in colour removal capacity of the biomass. Optimum sorbent dosage was 0.5 g/L and 0.4 g/L for AY 17 and AB25 respectively. The equilibrium between the adsorbate in the solution and on the adsorbent surface was practically achieved in 40 min and biosorption kinetics was found to follow pseudo-second-order rate expression for both the dyes. Equilibrium biosorption data were best represented by Freundlich isotherm. The used biosorbent SBG can be regenerated, sent for landfills or can be incinerated. The present study concludes that spent brewery grains could be employed as a low-cost and eco friendly biosorbent and as an alternative to the current expensive methods of removing dyes from textile effluents.

Acknowledgements

The financial support for this investigation given by Council of Scientific and Industrial Research (CSIR), Ministry of Human Resources Development, New Delhi, India under the grant CSIR Lr. No. 9/468(371)/2007-EMR-1 dated 30.03.2007 is gratefully acknowledged.

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