Effect of Biosorption Parameters Kinetics Isotherm and Thermodynamics for Acid Green Dye Biosorption from Aqueous Solution by Brewery Waste

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Abstract

Biosorption of Acid Green (AG 25) was investigated using Spent Brewery Grains (SBG) a brewing industry waste in a batch system with respect to initial pH, temperature, initial dye concentration, biosorbent dosage, and contact time. The biomass exhibited the highest dye uptake capacity at 303 K, initial pH value of 3, the initial dye concentration of 90mg/L, biosorbent dosage of 0.2 g and contact time of 75 min. The extent of dye removal increased with increase in time, biosorbent dosage and decreased with increase in temperature. The equilibrium sorption capacity of the biomass increased on increasing the initial dye concentration up to 90 mg/L and then started decreasing in the studied concentration up to 300 mg/L. The experimental result has shown that the acidic pH favours the biosorption. Langmuir and Freundlich adsorption model is used for the mathematical description of the biosorption equilibrium and isotherm constants are evaluated. Equilibrium data fitted very well to the Langmuir model. The pseudo first- and second-order kinetic models were also applied to the experimental data. The results indicated that the dye uptake process followed the pseudo second-order rate expression and biosorption rate constants increased with increasing concentration.

Keywords: Biosorption, Acid green, Spent brewery grains, Isotherm, Kinetics, Thermodynamics

1. Introduction

Worldwide textile industries consumes very large volumes of water for wet processing of textiles such as scouring, bleaching, mercerizing, dyeing, printing and final finishing. These operations contribute to significant quantities of effluents and their pollution loads are considerable. Dyeing and printing is the most complex of the wet processes and includes hundreds of dyes and auxiliary chemicals which contribute to major pollution load of the receiving water bodies and ground water aquifers. Over 100,000 commercially available dyes exist and more than 7×10^5 tonnes per year are produced annually (Zollinger, 1987). Innumerable dyes are employed in the textile and dyeing industries. They are classified according to their chemical composition. However in textile processing dyes are classified based on their applications. Some prominent types of dyes used in India and other parts of the world are acid dyes, basic dyes, direct dyes, mordant dyes, pre-metallaized dyes, reactive dyes, sulfur dyes and vat dyes. The major constituent that causes difficulties in the treatment of dye house effluents is the colour. Color is the first contaminant to be recognized in wastewater and the presence of very small amounts of dyes in water is highly visible and undesirable (Robinson et *al.*, 2001).

Dye wastewater is usually treated by physical or chemical treatment processes. These include chemical coagulation/flocculation, precipitation, ozonation, adsorption, oxidation, irradiation, ion exchange and photo

degradation. Some of these techniques have shown to be effective, although they have limitations. Among these are: excess amount of chemical usage, or accumulation of concentrated sludge with disposal problems; expensive plant requirements and operational costs; lack of effective color reduction; and sensitivity to a variable wastewater input (Robinson et *al.,* 2001).

The use of biomaterials as biosorbents for the treatment of wastewaters will provide as a potential alternate to the conventional treatment methods. The process of uptake of solute using biomaterials including microbial cells, whether dead or alive, is known as biosorption. The main advantages of biosorption are high selectivity, cost effectiveness and good removal performance. World wide numerous low cost bio materials have been tried for biosorption of dyes (McKay et *al.*, 1983); Silica (McKay, 1984); the hardwood sawdust (Asfour et *al*., 1985); Bagasse pith (McKay et *al.*, 1987); Fly ash (Khare et *al*., 1987); Paddy straw (Deo, 1993); Rice husk (Lee & Low, 1997); Palm fruit bunch (Nasser, 1997). In the present investigation, the biomass SBG a brewery industry waste was used as biosorbent and its capacity to remove acid green an anionic dye was evaluated. A survey of literature showed that no work has been done so far on dye removal process using SBG as biosorbent for the removal of acid green dye stuffs from their aqueous solutions. Few studies have been conducted on spent grains as biosorbent of heavy metals Cadmium, lead (Low, 2000) and Copper (Lu & Gibb, 2008). Acid green has wider applications, which include paper industry, leather industry, dyeing and textile industries etc.

In the brewing process, barley is initially steeped, germinated, kilned and then sent for mash conversion and lautertun, the grain obtained from lautertun is the spent grain used in the present study. Spent grains are normally utilized as feed for cow, cattle and like animals, but due to absence of this activity in industrialized and urbanized countries it is difficult to dispose it, since large amounts are produced annually and also difficult to store it due to formation of microorganism and fly on it. Also due to prosperous market of the alcohol industry in India, the production of alcohol has steadily increased in the last years from 1654 million liters in 1999-2000 to 2300 million liters in 2007-2008.

The aim of this present work is to explore the possibility of utilizing SBG for the biosorptive removal of AG 25 dye from aqueous solution. The effect of factors such as initial pH, temperature, initial dye concentration, biosorbent dosage, and contact time was investigated. The kinetics of AG 25 biosorption onto SBG was analyzed by fitting to kinetics models. Experimental equilibrium data were fitted to Langmuir and Freundlich isotherm equation. Thermodynamics parameters Gibb's free energy changes (ΔG), enthalpy changes (ΔH) and entropy changes (ΔS) were estimated for the biosorption of acid green onto SBG.

2. Materials and methods

2.1 Biosorbent

Spent Brewery Grains, taken from Mohan breweries and distilleries Limited, Chennai, India, was suspended in 0.13M Sulphuric acid solution (12g of SBG per 100mL of acid solution) for one hour. 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 $60^{\circ}C$ for 24 hours. The dried biomass was ground, seived and stored for further use in the experiments. SBG with a particle of 0.25mm was used in the experiments.

2.2 Adsorbate

The adsorbate AG 25 dye (C.I. number = 61570, C.I. name = AG 25, Chemical formula = $C_{28}H_{20}N_2Na_2O_8S_2$, F W = 622.58, Commercial name = Alizarin cyanin green G, Chemical class = anthraquinone, nature = acid) was supplied by Sigma-Aldrich Chemicals Ltd., India. The structure of AG 25 is given in Fig. 1. An accurately weighed quantity (1 g) of AG 25 was dissolved in double distilled water to prepare stock solution of 1000 mg/L. Experimental solutions of the desired concentrations were prepared by dilution of stock solution with double-distilled water.

2.3 Analytical measurements

The concentration of the dye AG 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} = 642 nm). 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 a temperature –controlled orbital shaker at a constant speed of 150 rpm to study the effect of important parameters like pH, adsorbent dosage, initial dye concentration, contact time and temperature. 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 AG 25 solution of different concentrations with the known amount of SBG till the equilibrium was achieved. The effect of temperature on the sorption characteristics was investigated at 303,313,323 K. Initial dye concentration varied from 30 to 300 mg/L.

3. Results and discussion

3.1 Effect of pH

pH affects not only the biosorption capacity, but also the color of the dye solution and the solubility of some dyes (Fu & Viraraghavan, 2001). Therefore, the pH value of the solution was an important controlling factor in the biosorption process (Waranusantigul et *al., 2003*). The effect of initial pH on AG 25 biosorption by SBG is shown in the Fig. 2. The maximum dye sorption occurred at pH 3 and the removal decreased thereafter. This may be due to high electrostatic attraction between the positively charged surface of the SBG and anionic dye AG 25. 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 (Namasivayam & Kavitha, 2002). In general, the acidic dye uptakes are much higher in acidic solutions than those in neutral and alkaline conditions (Chiou & Li, 2002).

3.2 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. The biosorption of AG 25 on SBG was investigated as a function of temperature and maximum uptake value was obtained at 303 K as can be seen from Fig. 3. biosorption decreased with further increase in temperature due to the decreased surface activity suggesting that biosorption between AG 25 and SBG was an exothermic process and the mechanism was mainly physical adsorption enhanced by a chemical effect (Aksu & Tezer, 2005).

3.3 Effect of biosorbent dosage

The effect of biosorbent dosage on the removal of AG 25 by SBG at Co = 100 mg/L is shown in the Fig. 4. It can be seen that the AG 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 biosorption sites (Mane et *al.,* 2007). At biosorbent dosage greater than 0.2 g the surface AG 25 concentration and the solution AG 25 concentration come to equilibrium with each other. However the biosorption capacity (mg/g) decreased with increase in SBG dosage and this may be attributed to overlapping or aggregation of biosorbent sites resulting in decrease in total biosorbent surface area available to dye and an increase in diffusion path length.

3.4 Effect of initial dye concentration

The effect of initial dye concentration on the biosorption of dye was investigated and shown in Fig. 5. 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 equilibrium uptake values increased from 7.05 to 65.17 mg/g with increasing initial dye concentration from 30 to 300 mg/L as a result of the increase in the driving force. However, AG 25 removal yield increased from 94 to 98 % from 30 to 90 mg/L concentration, and then started to decrease from 97 to 86 % for initial dye concentration of 120 to 300 mg/L. At lower dye concentrations solute concentrations to biosorbent sites ratio is higher, which cause an increase in color removal (Ozer et *al.,* 2005). At higher concentrations, lower adsorption yield is due to the saturation of adsorption sites (Ozer et *al.,* 2005).

3.5 Effect of contact time

The effect of contact time on biosorption of AG 25 by SBG at Co = 100 mg/L for biosorbent dosage 0.2 g was studied. It was observed that rapid biosorption of dye has taken place in the first 15 minutes and thereafter, the rate of biosorption decreased gradually and reached equilibrium in about 75 min. around 98 % of AG 25 removal was obtained in about 75 min. This may be due to strong attractive forces between the dye molecules and the adsorbent. Fast diffusion on the external surface was followed by fast pore diffusion into the intra particle matrix to attain rapid equilibrium (Ho & Chiang, 2001).   Further increase in contact time showed that there is no significant increase in the removal of AG 25 by SBG, so further experiments were conducted for 75 min contact time only.

3.6 Kinetic modelling

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

3.6.1 Pseudo-first-order model

The pseudo-first-order equation is given as (Lagergren, 1898):

$$dq_t \, / \, dt = k_f \, (q_e - q_t) \tag{1}$$

Where q_t is the amount of adsorbate adsorbed at time t (mg/g), q_e is the biosorption capacity at equilibrium (mg/g), k_f is the pseudo-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:

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

The values of biosorption rate constant (k_f) for AG 25 adsorption on SBG were determined from the plot of log (q_e-q_t) against t (not shown here).

3.6.2 Pseudo-second-order model

The pseudo-second-order model is given as (McKay & Ho, 1999):

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

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

$$q_t = \frac{q_e^2 k_s t}{1 + q_e k_s t} \tag{4}$$

Eq. (4) is the integrated rate law for a second-order reaction (Ho, 2006) and can be rearranged to obtain

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

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 biosorption 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 (Fig. 6). Values of $k_{s,}\ q_{s,\ h}$ and correlation coefficient R^2 are listed in Table 1.The Table 1 indicates that the pseudo second order model rate constant k values and initial biosorption rate h values increased with increasing the initial dye concentrations. It suggests that k and h values are affected by the initial dye concentrations. 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 AG 25 by SBG.

3.7 Equilibrium modelling

The equilibrium sorption isotherm is fundamentally important in the design of biosorption system. Equilibrium studies in biosorption 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 (Ho et al., 2002). Langmuir and Freundlich isotherm constants were determined from the plots of $C_e/\ q_e$ versus Ce (Fig. 7) and ln q_e versus ln C_e (Fig.8) respectively. It was found that the Langmuir isotherm best represents the equilibrium adsorption of AG 25 on SBG. The isotherm constants and the correlation coefficient, R^2 with the experimental data is given in Table 2.

3.7.1 Langmuir isotherm

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 biosorption (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).

The Langmuir isotherm is applicable to monolayer sorption of adsorbate onto SBG, as shown in Fig. 7. The correlation coefficient, R^2, was 0.905. According to Eq. (9), the maximum sorption capacity, q_m was calculated to be 212.76 mg/g, and the equilibrium constant, b, 0.03566 L/mg. A large value of b implies strong bonding of AG 25 dye to SBG at this temperature.

The favourable nature of adsorption can be expressed in terms of dimensionless separation factor of equilibrium parameter, which is defined by Eq. (10)

$$R_L = \frac{1}{1 + bC_o} \tag{10}$$

Where b is the Langmuir constant and C_o is the initial concentration of the adsorbate in solution.

The values of R_L indicates the type of isotherm to be irreversible ($R_L = 0$), favourable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavourable ($R_L > 1$). R_L values for acid green adsorption onto SBG were less than 1 and greater than zero indicating favourable adsorption (Table 2).

3.8 Estimation of thermodynamic parameters

The thermodynamics parameters Gibb's free energy changes (ΔG), are calculated using the following equations (Wang et *al.,* 2008)

$$\Delta G = -RT \ln K_c \tag{11}$$

$$K_c = \frac{C_{Ae}}{C_e} \tag{12}$$

Where K_c is the equilibrium constant, C_{Ae} is the amount of dye adsorbed on the biosorbent per liter of the solution at equilibrium (mg/L), C_e is the equilibrium concentration of the dye in the solution (mg/L), T is absolute temperature and R is the universal gas constant (8.314 J/mol K). Also, enthalpy changes (ΔH) and entropy changes (ΔS) can be estimated by the following equations, respectively (Jain et *al.,* 2004)

$$\Delta H = -R \left(\frac{T_2 T_1}{T_2 - T_1} \right) \ln \frac{K_2}{K_1} \tag{13}$$

$$\Delta S = \frac{\Delta H - \Delta G}{T} \tag{14}$$

Where, K_1 and K_2 are the values of the equilibrium constant at temperatures T_1 and T_2, respectively. The free energy of biosorption (ΔG), enthalpy (ΔH) and entropy (ΔS) changes were estimated by using Eq. (11)-(14) for the system AG 25/SBG. Table 3 shows negative values of ΔG and ΔH indicates that biosorption is spontaneous and exothermic in nature. The positive value of entropy reflects the affinity of the biosorbent for AG 25 dye.

ΔH for physical adsorption ranges from -4 to -40 kJ/mol, compared to that of chemical adsorption ranging from -40 to -800 kJ/mol.(Crini & Badot, 2008) As shown in Table 3, the ΔH values suggest that the adsorption process might be considered as physical adsorption in nature enhanced by a chemical effect.

3.9 Evaluation of spent brewery grain as biosorbent

Table 4 shows the comparison of the maximum monolayer adsorption capacities of various adsorbents for AG 25 dye. The value of q_{max} in this study (212.76 mg/g) is larger than those in most of previous studies except that of chitosan based biosorbents. More over the SBG used in this study does not require any pretreatment or processing such as chemical modification or activation making it as low cost biosorbent obtained from industrial waste. Furthermore, the industrial waste, SBG, used in this work could be easily obtained as low cost in India and other parts of the developing and developed countries where there is no activity of cattle farming. The results showed that SBG is effective for AG25 dye and could be an alternative for more costly biosorbents used for dye removal in waste water treatment processes.

4. Conclusions

The capability of the use of spent brewery grains for the removal of Acid Green dye was examined, including equilibrium and kinetic studies. Experiments were performed as a function of initial solution pH, temperature, initial dye concentration, biosorbent dosage and contact time. The solution pH, temperature and initial dye concentration played a significant role in affecting the capacity of biosorbent. The further increase in pH over 5.0, temperature over 303 K and initial dye concentration of 120 mg/L led to a reduction of the biosorption capacity of the biomass. Optimum biosorbent dosage was 0.2 g/L of solution. The equilibrium between the adsorbate in the solution and on the biosorbent surface was practically achieved in 75 min. Biosorption kinetics was found to follow pseudo-second-order rate expression. Equilibrium biosorption data for AG 25 on SBG were best represented by Langmuir isotherm. The typical dependence of dye uptake on temperature and kinetic studies indicated the biosorption process of AG 25 onto SBG to be physical adsorption enhanced with chemical effect and diffusion controlled. Thermodynamics parameters were estimated for the biosorption of acid green onto SBG. Negative values of ΔG and ΔH indicate that biosorption is spontaneous and exothermic in nature. The positive value of ΔS reflects the affinity of the biosorbent for AG 25 dye.

The present study concludes that spent brewery grains could be employed as a low-cost and ecofriendly biosorbent as an alternative to the current expensive methods of removing dyes from textile effluents. The scope of the further study is to try the feasibility of using SBG as biosorbent for the treatment of industrial effluents containing other dyes and mixture of dyes.

Acknowledgements

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Table 1. Kinetic parameters for the removal of AG 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
60	14.7058	0.034715	7.5075	0.9999
90	22.2222	0.036096	17.8253	1
120	29.6735	0.036873	32.4675	1
150	37.1747	0.037299	72.2118	1
200	49.7512	0.037408	92.5925	1
250	62.1118	0.038119	147.0588	1
300	74.6268	0.038204	212.766	1

Table 2. Langmuir and Freundlich isotherm constants of AG 25 biosorption on SBG

Langmuir constants				Freundlich constants		
q_m (mg/g)	b (L/mg)	R^2	R_L	K_F (mg/g)(L/mg)^n	n	R^2
212.76	0.03566	0.905	0.2190	11.29	1.58	0.901

Table 3. Thermodynamics parameters for AG 25 dye biosorption onto SBG

Temperature (K)	ΔG (kJ/mol)	ΔH (J/mol K)	ΔS (J/mol K)
303	-8.84	-54.87	29.0
313	-10.95		
323	- 12.32		

Table 4. Comparison of biosorption capacities of various biosorbents for AG 25 dye

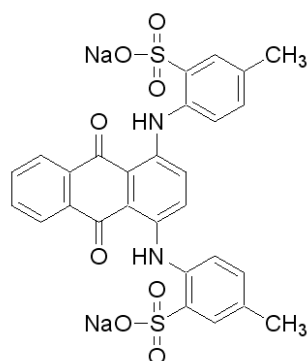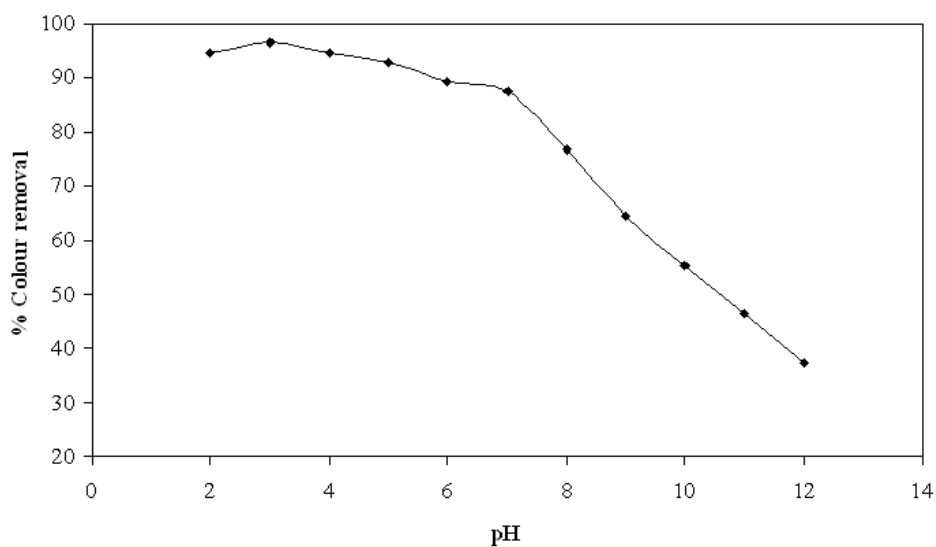| Biosorbent	q_{max} (mg/g)	Reference
Spent brewery grains	212.76	This study
Shells of bittim	16.0	(Aydın & Baysal 2006)
Durian peel	63.29	(Hameed & Hakimi 2008)
Activated palm ash	123.4	(Hameed et *al.*,2007)
Chitosan	525.0	(Gibbs et *al.*, 2003)
Crab shell	645.1	(Cheung et al., 2007)

Figure 1. Chemical structure of AG 25

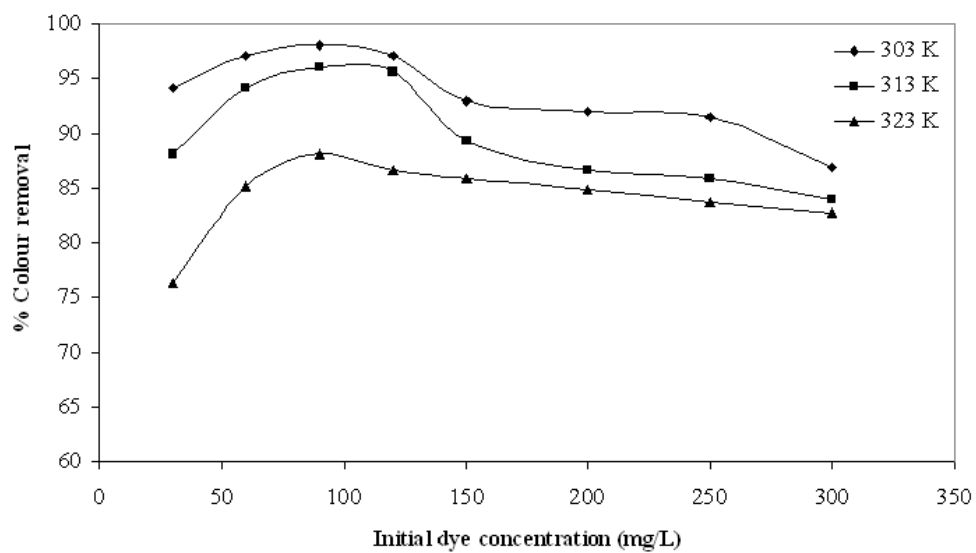Figure 2. The effect of initial pH of dye solution
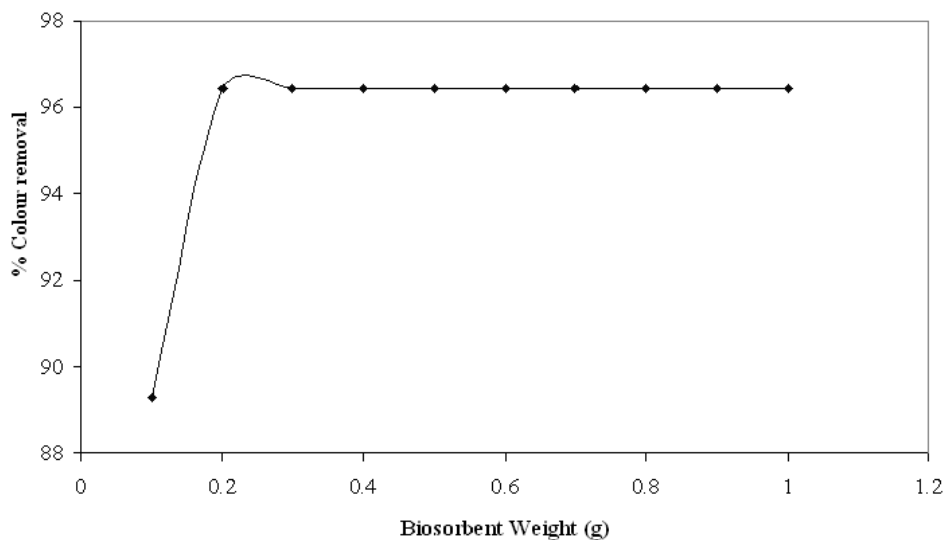

Figure 3. The effect of temperature

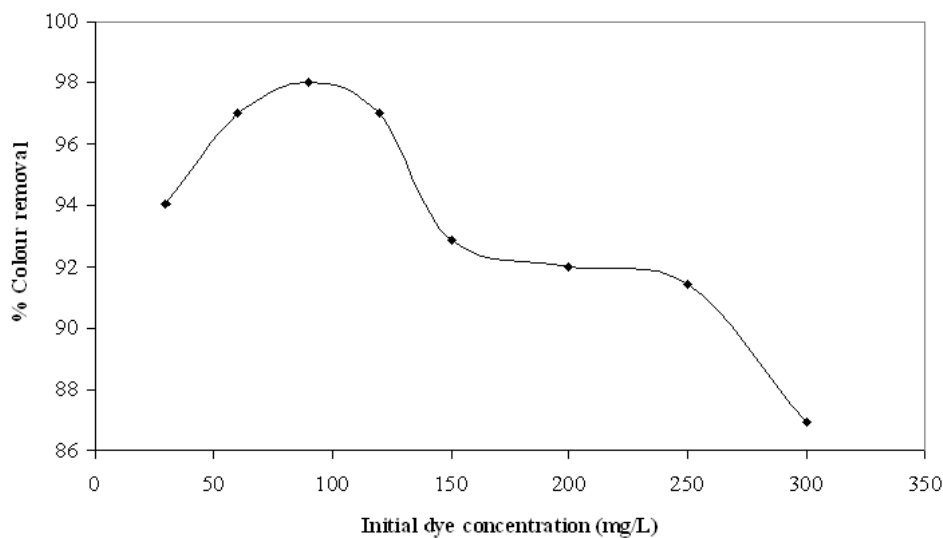Figure 4. Effect of biosorbent dosage

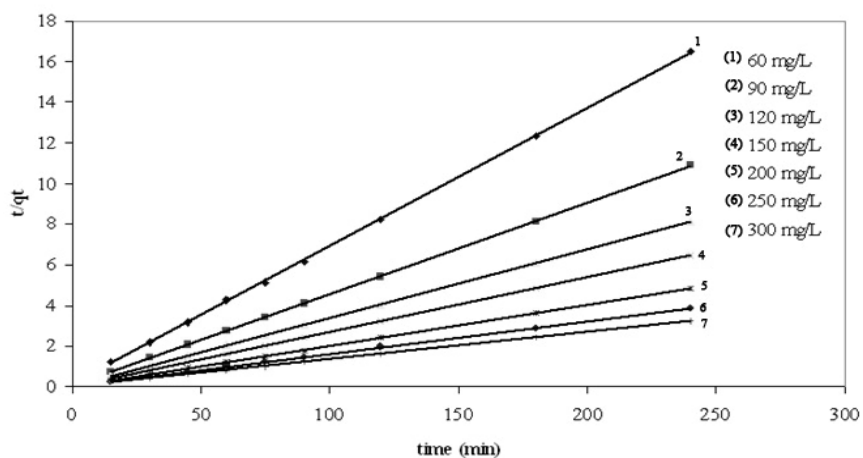Figure 5. Effect of initial dye concentration

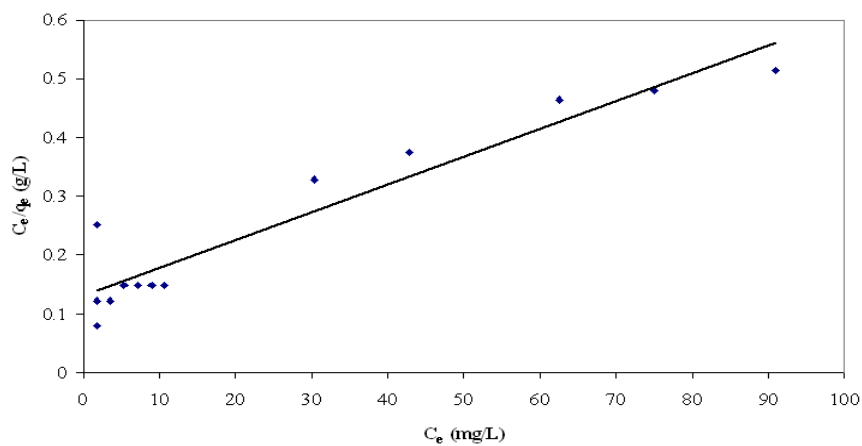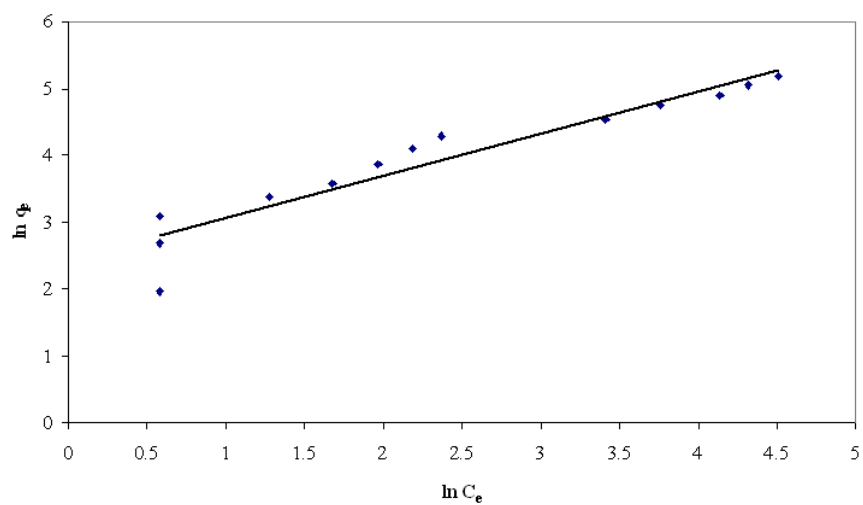Figure 6. Pseudo-second-order kinetic plots for the removal of AG 25

Figure 7. Langmuir isotherm

Figure 8. Freundlich isotherm