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Removal of Crystal Violet dye from aqueous solution using water hyacinth: Equilibrium, kinetics and thermodynamics study

M. Rajeswari Kulkarni *, T. Revanth, Anirudh Acharya, Prasad Bhat

Department of Chemical Engineering, M.S.Ramaiah Institute of Technology, Bangalore 560054, India

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Abstract

Effluent water from dyeing industries has now for long been a taxing issue. Of the various dyes which are extremely toxic, Crystal Violet which is used in the dyeing industry is known for its mutagenic and mitotic poisoning nature. Water hyacinth (*Eichhornia crassipes*) is a perennial aquatic plant notorious for its rapid invasive growth on the surface of water bodies causing ill-effects on the biodiversity. The potential of powdered roots of water hyacinth was studied for decolorization of Crystal Violet dye. Influence of parameters such as initial pH (2.0–10.0), initial dye concentration (100–500 ppm), biosorbent dosage (0.5–5 g/l), contact time (10–240 min) and temperature (300–323 K) were examined. Maximum removal of dye was observed at pH 7.8. The obtained data were fit into different kinetic models and the biosorption was found to follow pseudo second order kinetic model. The Langmuir monolayer biosorption capacity of water hyacinth was estimated as 322.58 mg/g. The study has demonstrated water hyacinth as a potential low cost biosorbent for effective removal of Crystal Violet dye from aqueous solution.

Keywords: Crystal Violet; Water hyacinth; Dye removal; Isotherm; Thermodynamics; Kinetics

1. Introduction

The rising existence of dyes in the aqueous bodies is one of the most significant environmental issues. The dyes do not undergo natural degradation; hence the persisting color hinders the passage of light into water and spoils the ecosystem [1,2]. Crystal Violet (CV) enters into the aquatic systems from the effluents of textile industry, paint industry and also from medical and biotechnology industry. Crystal Violet is well known for its mutagenic, teratogenic and mitotic poisoning nature. Among the several techniques employed for dye removal, the most feasible technique was found to be the use of biosorbent to adsorb the dye from waste water [3]. Several low cost adsorbents (agricultural, domestic or plant biomass waste) have been used for removal of CV dye such as grapefruit peel [4], rice husk [5], jackfruit leaf powder [6], ginger waste [7], etc. Water hyacinth, a perennial aquatic plant, was studied for its adsorptive capacities in the removal of CV dye. Water hyacinth is infamous for its rapid invasive growth, uncontrolled growth of its weed affects the biodiversity. But, along with the notoriety, the plant is now also at the center of many studies and researches, pertaining to wastewater treatment, for the removal of contaminants such as heavy metals, coloring agents and other organic and carcinogenic compounds, owing to its adsorptive properties. The root powder of this plant was utilized as the biosorbent to decolorize the waste water. The present study is addressing the problem of both the solid and liquid wastes by making use of water hyacinth to remove CV dye and thus finding a feasible solution to the environmental contamination.

2. Materials and methods

2.1. Adsorbate

Crystal Violet dye was purchased from Merck (India) Ltd. Stock solution of CV was prepared by dissolving 0.5 g of accurately weighed dye in 1000 ml of distilled water to obtain 500 ppm dye solution. The solution was then diluted to prepare standard solutions of different concentrations to study the effect of initial dye concentration. The dye concentration was measured in the UV spectrophotometer at the wavelength of 580 nm. The initial pH of dye solution was adjusted by using dilute hydrochloric acid or sodium hydroxide solution.

* Corresponding author. Department of Chemical Engineering, M.S.Ramaiah Institute of Technology, Bangalore 560054, Karnataka, India. Tel.: +91 8023600822; fax: +91 80 2360 3124.

E-mail address: rmkulkarni@msrit.edu (M.R. Kulkarni).

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2.2. Biosorbent preparation

Water hyacinth plants were obtained from Hebbal Lake, Bangalore and were extensively washed with water to remove earthly impurities. The roots were separated from the rest of the plant; the initial moisture content was 88.89%. The roots were sun dried for 5 days to reduce the moisture content to 10%, crushed and then sieved to an average particle size of 100 µm.

2.3. Biosorption experiments

The effects of initial pH (2.0–10.0), contact time (10–240 min), biosorbent dosage (0.5–5 g/l), initial dye concentration (100–500 ppm) and temperature (300–323 K) on biosorption of CV were examined in a batch system. One hundred milliliters of dye solution was in contact with water hyacinth root powder in an incubator orbital shaker. After biosorption, the samples were filtered and residual dye concentration was analyzed. All the biosorption experiments were performed in duplicate and deviations were within 5%; average values were used in the result analysis. Dye uptake and percentage removal were calculated by using Eq. (1) and Eq. (2).

$$q = \frac{v(c_i - c_f)}{m} \tag{1}$$

$$\%\, CV\ removal = \frac{(c_i - c_f)}{c_i} \times 100 \tag{2}$$

where q is the dye uptake (mg/g), V is volume of dye solution (l), C_i is the initial concentration of Crystal Violet in the solution (ppm), C_f is the final concentration of Crystal Violet in the solution (ppm) and m is the amount of water hyacinth root powder (g).

2.4. Surface characterization

2.4.1. FTIR analysis

Fourier transform-infrared spectrometer (Bruker alpha) was used in the range of 4000–500 cm^{-1} to determine the functional groups present on the surface of the biosorbent. The spectra obtained are shown in Fig. 1(a) and (b). The presence of peak at 533.41 cm^{-1} indicates the probability of an alkyl halide C—Br stretching with a strong absorption band. Peak at 1004.05 cm^{-1} indicates a strong bending of a = C—H bond. After biosorption, peaks at 1583.02 cm^{-1} indicates probable C=C stretching and peaks at 1360.33 cm^{-1} and 1170 cm^{-1} can be attributed to stretching of C=H and C—N groups. A decrease in the frequency at 1002.56 cm^{-1} from 1004.05 cm^{-1} and a peak at 534.81 cm^{-1} indicates a role of C—Br and C—H bond in the biosorption of the dye onto biosorbent.

2.4.2. SEM analysis

SEM imaging of the biosorbent surface was carried out before and after biosorption of CV, using scanning electron microscope (JEOL, Japan) with 30 kV and at 10,000 times of magnification. The images are presented in Fig. 2(a) and (b) respectively. In Fig. 2(a), the surface was relatively free of any kind of aggregations. Fig. 2(b) shows image of the surface after biosorption of CV, with aggregations on the surface, possibly be

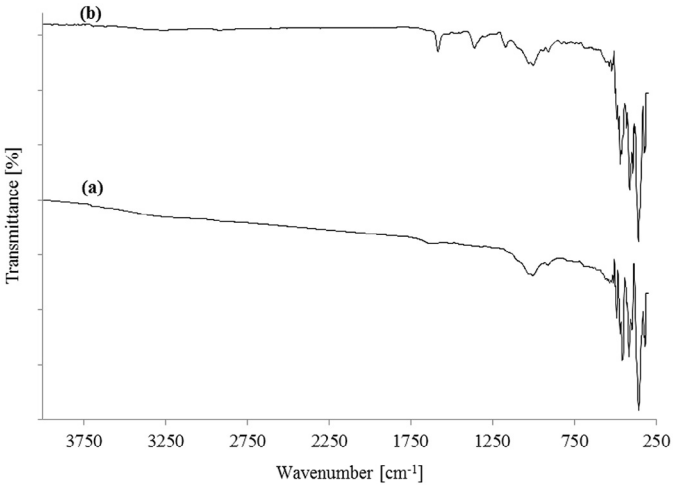


Fig. 1. FTIR of biosorbent (a) before biosorption and (b) after biosorption of CV.

the particles of the dyes adsorbed onto the surface at the pores and the pore walls. The surfaces of CV-loaded water hyacinth root powder was appeared to be rough and wrinkled by the dye molecules, indicating involvement of ion exchange in the dye removal.

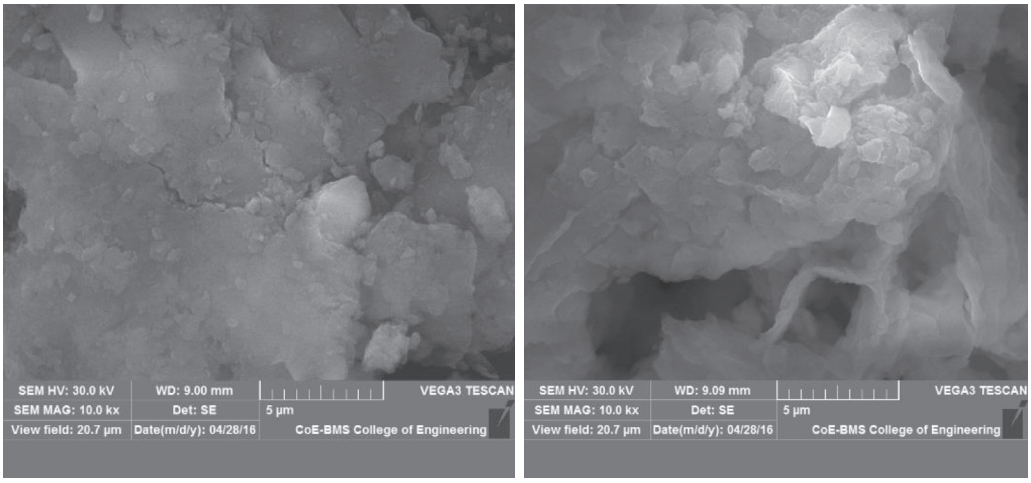
3. Results and discussion

3.1. Effect of pH on biosorption of CV

The effect of initial pH on dye removal was investigated at different initial CV concentrations (100–500 ppm) by maintaining a fixed contact time of 120 min, ambient temperature of 27 °C and biosorbent dosage of 1 g/l. The percentage removal was observed to increase sharply with an increase in pH from 2.0 to 4.0. The removal was found to be high thereafter but with a constant trend until pH 10.0. The variation has been depicted in Fig. 3. The maximum removal was observed at pH 7.8. Low biosorption of CV at lower pH is due to the high concentration of H^+ ions which result in repulsion and hence cause the reduced biosorption at lower pH [4,8]. As the pH increases, more negatively charged surfaces are available resulting in decrease in repulsion between the positively charged dye molecule and the biosorbent [5,9].

3.2. Effect of contact time on biosorption of CV

The study on the effect of contact time provides useful information on time taken to attain equilibrium. Time taken to achieve equilibrium depends on the rate of mass transfer, which, in turn, depends on the conditions provided for the contact between the solid and the liquid phase [10]. The effect of contact time (10–240 min) on the removal of CV dye was studied for an initial dye concentration of 500 ppm, ambient temperature of 27 °C, biosorbent dosage of 1 g/l and pH 7.8. It can be observed from Fig. 4 that the initial rate of CV biosorption is rapid within 40 min of contact time due to high concentration gradient and the availability of large surface area for biosorption. The rate slows down after 40 min due to the



(a) (b)

Fig. 2. SEM image of water hyacinth root powder (a) before biosorption and (b) after biosorption of CV.

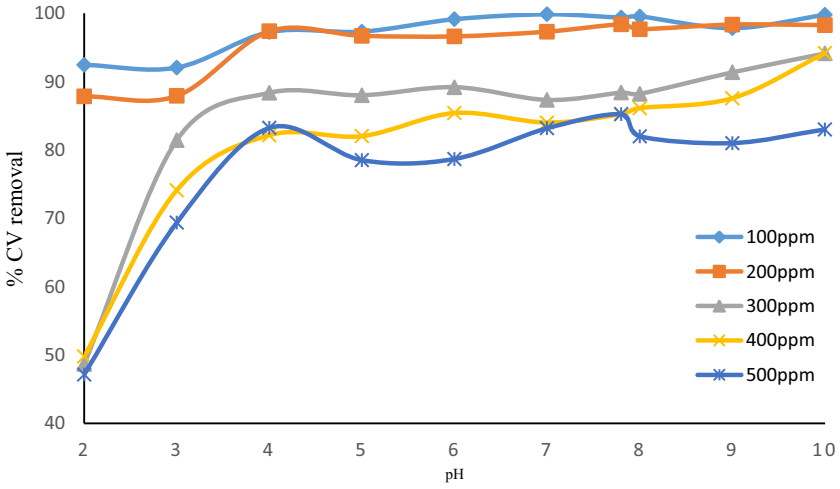


Fig. 3. Percentage removal of CV variation with initial pH for different dye initial concentrations.

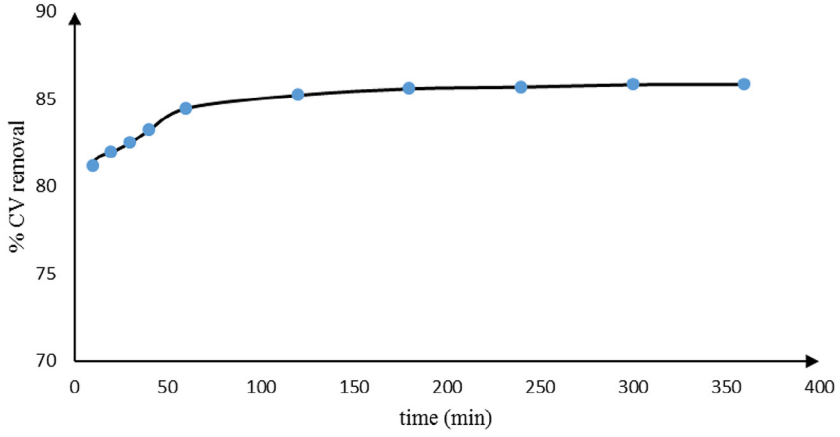


Fig. 4. Percentage removal of CV variation with time.

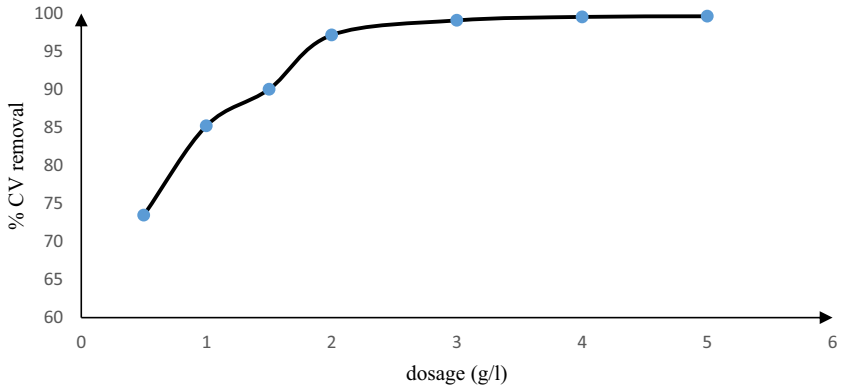


Fig. 5. Effect of biosorbent dosage on percentage removal of CV.

decrease in surface area and binding sites, the concentration approaches a constant value after 120 min [11,12]. The equilibrium time was found to be 120 min, after which the percentage removal of the dye was almost constant.

3.3. Effect of biosorbent dosage on biosorption of CV

The biosorbent dosage was varied from 0.5 g/l to 5 g/l to evaluate the effect of dosage on biosorption of CV dye. The initial dye concentration was 500 ppm, ambient temperature was 27 °C, contact time was maintained for 120 min and pH at 7.8. It was observed that with the increase in dosage from 0.5 to 1.5 g/l, the percentage removal was found to increase from 73.48% to 90% (Fig. 5), due to increase in the biosorbent surface area [13–15]. A further increase in dosage yielded an almost constant percentage removal which may be attributed to the saturation of binding sites due to aggregation of adsorbed particles [5,16]. According to these results, it is inferred that percentage removal of CV increases with biosorbent concentration, reaches a maximum and remains almost constant with further increase in dosage.

3.4. Effect of initial dye concentration and effect of temperature on biosorption of CV

The effect of initial dye concentration (100–500 ppm) on the biosorption of CV was studied at different temperatures 300 K, 313 K and 323 K using a biosorbent dosage of 1 g/l, pH of 7.8 and employing a contact time of 120 min. The results have been shown in a plot of percentage removal versus initial dye concentration at different temperatures (Fig. 6). It was observed that at 100 ppm initial dye concentration and temperature 300 K, very significant removal of 99.36% was attained. With increase in the initial CV concentration, the percentage biosorption was decreased. The ratio of biosorptive surface to ion concentration decreased with increase in dye concentration [2,17]. The removal was decreased to 85% at 500 ppm and temperature 300 K.

It can also be noted that with increase in temperature for all the initial dye concentrations, the percentage removal of CV was found to be increasing. This can be attributed to the strong bond between the CV dye molecules and the binding sites of water hyacinth, at higher temperatures. Higher temperatures

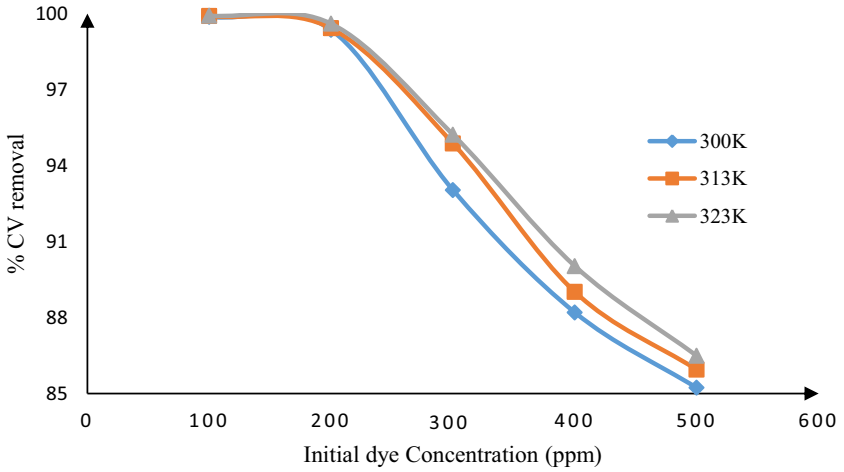


Fig. 6. Percentage removal of CV variation with initial dye concentration at different temperatures.

Table 1
Isotherm comparisons for biosorption of CV on water hyacinth root powder.

Temperature (K)	Langmuir isotherm $\frac{1}{q_e}=\frac{1}{q_{max}bc_e}+\frac{1}{q_{max}}$					Freundlich isotherm $lnq_e=\frac{1}{n}lnC_e+ln\,K$				
	q_{max} (mg/g)	b (l/mg)	R^2	ND	NSD	n	K	R^2	ND	NSD
300	322.58	0.688	0.9644	12.806	15.332	3.792	121.63	0.9394	11.480	12.357
313	323.18	0.885	0.9611	13.102	15.719	3.793	128.36	0.963	9.304	9.617
323	333.33	1.000	0.9706	12.003	14.354	3.951	137.55	0.9496	10.504	11.204

usually enhance biosorption due to the increased surface activity and kinetic energy of the solute [18,19].

3.5. Adsorption isotherms

The two most frequently used isotherm equations: the Langmuir and Freundlich equations were tested for the equilibrium data obtained from initial dye concentration study. The models are simple, well-established and have physical meaning and are easily interpretable, which are some of the important reasons for their frequent and extensive use. The Langmuir isotherm model considers monolayer biosorption whereas Freundlich isotherm model describes biosorption onto a heterogeneous surface [20,21]. The values of coefficient of determination being near to one (>0.94) suggest that both Langmuir and Freundlich models provide best fit to the equilibrium biosorption data at all the studied temperatures (Table 1). Error analysis was carried out by estimating the normalized deviation (ND) and normalized standard deviations (NSD) using Eqs. (3) and (4) [22].

$$ND=\frac{100}{n}\sum\left|\frac{q_{e(exp)}-q_{e(pre)}}{q_{e(exp)}}\right| \tag{3}$$

$$NSD=100\sqrt{\frac{\sum\left(\frac{q_{e(exp)}-q_{e(pre)}}{q_{e(exp)}}\right)^2}{n}} \tag{4}$$

$q_{e(exp)}$ and $q_{e(pre)}$ are the experimental and predicted CV uptake ($mg\cdot g^{-1}$) respectively, where n is the number of observations made. But, based on normalized and standard normalized deviations, the best fit for the equilibrium data was found in the Freundlich isotherm suggesting sorption to heterogeneous surfaces or surfaces supporting sites with various affinities.

The maximum biosorption capacity q_{max} for CV at 300 K was obtained as 322.58 mg of dye/g of biosorbent. The biosorption equilibrium constant b was found to be 0.688 g/l. Table 2 summarizes the maximum biosorption capacity of different types of biosorbents used for the removal of CV and also presents the results of the current study. It is clearly evident from the comparison; the value of q_{max} in this study is fairly high compared to the reported biosorbents. Larger value of q_{max} and Freundlich constant n (>3) implies stronger interaction between CV dye and water hyacinth root powder and also more negatively charged surfaces are available for biosorption. Water hyacinth root powder, owing to its high biosorption intensity for CV and large availability from the local supply, is a better biosorbent for economical treatment of CV contaminated water. Endothermic nature of the process reveals that chemisorption is the dominant mechanism of metal ion removal from the solution.

3.6. Adsorption kinetics

To determine the mechanism and the rate controlling step of the process of biosorption of CV on the powdered roots of water hyacinth, pseudo first order, pseudo second order and intra-particle diffusion models were tested with the data obtained from the contact time studies [25–28]. The values of the rate constant are presented in Table 3 along with the coefficient of determination values (R^2). The pseudo second order kinetic model fits well with the kinetic data over the entire contact time range. This states that chemical sorption involving valence force induced by sharing or exchange of electrons between adsorbate and adsorbent is the rate controlling step [26,27]. Weber and Morris intra-particle diffusion model was also tested to identify the involvement of intra-particle diffusion during the biosorption process by plotting graph of q v/s $\sqrt{t}$ [28].

The intra-particle diffusion plot q v/s $\sqrt{t}$ at 500 ppm CV concentration has indicated that the biosorption process displayed three distinct steps: (i) transport of the CV dye molecules from the boundary liquid film to the surface of the water hyacinth root powder (external film mass transfer); (ii) transfer of solute from the surface to the internal active binding sites (intraparticle diffusion); (iii) interaction of the solute with the

Table 2
Adsorption capacities of different biosorbents for CV.

Adsorbents	Maximum biosorption capacity (mg/g)	References
Grapefruit peel	254.16	[4]
NaOH-modified rice husk	44.876	[5]
Magnetic nanoparticles (MNPs) modified with sodium dodecyl sulphate (SDS)	166.67	[14]
Punica granatum shell	50.21	[16]
Powdered mycelial biomass of *Ceriporia lacerate*	239.25	[17]
Leaf biomass of *Calotropis procera*	4.14	[23]
Artocarpus heterophyllus (jackfruit) leaf powder (JLP)	43.39	[6]
Treated ginger waste (TGW)	64.93	[7]
palm kernel fiber (PKF)	95.4	[24]
Present study	322.58	

Table 3
Kinetic parameters for the biosorption of CV on water hyacinth root powder.

Experimental q_e (mg/g)	Pseudo first order model $\log(q_e - q) = \log q_e - \left(\frac{k_1 \cdot t}{2.303}\right)$			Pseudo second order model $\frac{t}{q} = \frac{1}{h} + \frac{t}{q_e}$, $h = k_2 q_e^2$			Intraparticle diffusion model $q = k_3 \times \sqrt{t} + C$		
	k_1 (min^{-1})	$q_{e,cal}$ (mg/g)	R_1^2	k_2 (g/mg.min)	$q_{e,\ cal}$ (mg/g)	R_2^2	C	k_3 (mg/g)$min^{-1/2}$	R_3^2
426.12	0.033	32.3	0.948	0.05	434.78	1.0	488.22	0.6164	0.711

Table 4
Thermodynamic parameters for the biosorption of CV.

Adsorbent	ΔG^0 (kJ mol^{-1}) $\Delta G^0 = -RTlnb$			$lnb = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}$	
	300 K	313 K	323 K	ΔH^o (kJ mol^{-1})	ΔS^o (J K^{-1} mol^{-1})
Water hyacinth root powder	−14.092	−15.273	−16.182	13.172	90.88

active binding site. Since a deviation from the origin was observed, intra-particle diffusion was not the only rate limiting step [29,30].

3.7. Thermodynamic analysis

Thermodynamic feasibility of the biosorption process can be determined by evaluating the thermodynamic parameters of biosorption such as ΔG^0, ΔH^0 and ΔS^0 [31].

In biosorption studies, equilibrium constant K will be replaced with Langmuir isotherm constant b (l/mol). The enthalpy change ΔH^0 (kJ mol^{-1}) and entropy change ΔS^0 (J/mol^{-1} K^{-1}) of biosorption of CV were calculated from the slope and intercept of plot of ln(b) v/s 1/T. The negative values of ΔG^0 (Table 4) obtained illustrate that the biosorption process is favorable and that it is spontaneous and is observed to decrease with increase in the temperature. Positive value of ΔH^0 13.172 kJ mol^{-1} indicates endothermic nature of the biosorption process and positive ΔS^0 value 90.88 J/mol^{-1} K^{-1} indicates the randomness that prevails in the system.

4. Conclusions

This study has dealt with the biosorption of CV using water hyacinth root powder. The potential of water hyacinth was studied for decolonization of CV. Influence of different parameters such as initial pH (2.0–10.0), initial dye concentration for CV (100–500 ppm), contact time (10–240 min), biosorbent dosage (0.5–5 g/l) and temperature (300–323 K) on biosorption of CV were examined. Thermodynamic analysis suggests that the biosorption of CV is spontaneous process and endothermic in nature. Maximum removal of dye was observed at pH 7.8 and the biosorption process has reached equilibrium at 120 min.

The best fit for the equilibrium data was found in the Freundlich isotherm. The maximum biosorption capacity was found to be 322.58 mg/g, which is high when compared to other biosorbents. The biosorption process followed the pseudo second order kinetic model. It seems that the use of readily available water hyacinth weed offers an alternative economic and environment-friendly process in the treatment of dye effluents.

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