The study of Adsorption & Adsorption isotherms for color removal from water effluent

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ABSTRACT

Chitosan hydrogel nanobeads using glutaraldehyde as crosslinker has been studied as adsorbent by adopting batch method throughout the investigation for removing congo red (CR) from outflow water effluent. Results show that percent removal of CR dye has been found to be 35% to 63% at varying initial concentration of dye solution from 7000 to 1000 mg/l in 24 hours. The studies for adsorption isotherms were carried out at various temperature and initial dye concentration at pH 5.0 as dye is stable in acidic solution. The adsorption equilibriums were analyzed by applying three isotherm models: Langmuir, Freundlich and Temkin model. Adsorption data of the dye gave best linearity into the Langmuir model at various temperatures. Adsorption of dye decreases with increasing pH and dye initial concentration. It also increases with increasing temperature. Thermodynamic parameters such as changes in Gibbs free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) were also calculated. Adsorption process corresponds to physical adsorption as ΔG values lie between -6.95 and -12.85 KJ/mol.

Key words- Chitosan, adsorption, nanobeads, Congo red, dye etc.

INTRODUCTION

Dyes make most hazardous group of industrial pollutants and include a large variety of compounds that pollute the aquatic ecosystem. Though the environmental behavior of dyes is very unspecified, interest is conveyed essentially over their conceivable poisonousness. Discharged water from industries either manufacturing dye stuffs or using them like textile, leather, paper making, printing etc. are darkly colored due to containing enormous amount of dyes with a large quantities of broad range of dissolved and suspended inorganic and organic impurities and their adducts with dye molecules. Coloring molecules are known to cause unfavorably susceptible dermatitis, skin bothering, malignancy and even genetic changes. Expulsion of color from squander water is therefore of utmost importance to prevent pollution of water before receiving by societies.

In spite of the fact that various strategies are known to eliminate toxic matters yet, adsorption has awarded a tag of the best, cheap, effective and efficient method for the expulsion of color from squander water effluent. The significant point of interest of using adsorption to control water toxicity are less expenditure for initiation,

easily operated plant with simple activity, ineffectual to harmfulness of pollutants, and super expulsion of natural and commercial waste constituents in contrast to other conventional water treatment methods.

Initially activated carbon is the most favored substance because of its outstanding functioning in adsorption (Baccar et al., 2009) but its significant price and trouble in recovery restricts its relevancy (Mahmoodi et al., 2011). Recently, minimal expensive absorbents for squander water purification have captured full concentration. Horticultural squanders (Bhattacharyya and Sharma 2005; Vadivelan and Kumar 2005) and commercial byproducts (Batzias and Sidiras 2007; Hamdaoui 2006; Jain and Jayaram 2010; Kumar and Sivanesan 2007), fly ash (Acemigolu, 2004), generation of activated carbon from coir pitch, clay minerals (Gurses et al., 2004), leaf powder, rice husk (Bhattacharyya and Sharma 2004), fungus and bacterial bio sorbents (Fu and Viraraghavan, 2002) have been explored to utilize for the expulsion of colors in water reservoir. The low adsorption capabilities towards dyes and unavailability of these adsorbents at each and every site make their limited practical utility.

Chitosan (CS), obtained after deacetylation of chitin, shows a high adsorption capability towards numerous classes of dyes because of its various active functional groups, biocompatibility and biodegradability. CS-based adsorbents are flexible materials considering their utilization as hydrogel in forming various structures like powder or flake, pallet or bead type. Recent researches explained that chitosan containing adsorbents, typically utilized as hydrogel beads or nano particles have demonstrated excellent adsorption capability for various coloring molecules (Crini and Badot, 2008) with a limitation of mechanically weak particles that restricts their commercial benefit as adsorbent. A few chemical synthetic strategies like poly amination, carboxy alkyl replacement, chemical cross-linking (Chiou et al. 2004) etc. have been utilized to obtain the mechanically strong hydrogel globules of chitosan. We endeavored to obtain chitosan hydrogel nanobeads using glutaraldehyde as crosslinker to study them as adsorbent by adopting batch method throughout the investigation for removing congo red (CR) from outflow water effluent.

Materials

An organic polymer, chitosan of crustacean origin was bought by India Sea Food, Kerala, and was utilized as acquired. Its level of deacetylation was 89%. Glutaraldehyde was bought by Loba Chemie Pvt. Ltd, India and utilized for crosslinking chemical between chains of chitosan polymer. Analytical grade chemicals like acetic acid, methanol, NaOH, HCl, KCl, KH_2PO_4 were also used. Doubly refined distilled water was utilized in all the investigations.

Methodology

Preparation of chitosan beads

Chitosan beads preparation was carried out as described in our previous studies (Vaishali et al., 2018).

STABILITY OF AQUEOUS SOLUTIONS

Distilled water was used for the preparation of aqueous solution of dyes. Aqueous solution of dye was found to be stable at room temperature and in acidic medium at λ_{max} (497 nm) and absorbance remained unchanged in the pH range 4.0-7.0 for the CR dye.

Adsorption experiment

A conical flask was filled with CR dye solution (10 ml) of known concentration and CS beads (0.2 g) was added in it at desired pH and temperature, shaken and then retained for 24 h and ultimately CR dye concentration at equilibrium was estimated using spectrophotometer at CR-λ_{max} (497 nm).

Adsorbed quantity of CR dye was computed by following formula-

$$qe = (Co - Ceq) \times V/W$$

Where qe is amount of dye adsorbed per g dried CS beads in mg/g, C_o and C_{eq} are concentrations of dye solution initially and at equilibrium in mg/l, V is the volume of dye solution in ml and W is quantity of the dried CS beads in g. The experiments were performed at different temperatures 30°, 40°, 50° and 60°C and after attaining equilibrium the adsorbed dye quantity was computed by above formula.

RESULTS AND DISCUSSION

ADSORPTION ISOTHERMS

To examine the adsorption potential of crosslinked chitosan-glutaraldehyde beads as an adsorbent for removal of CR dye, the studies for adsorption isotherms were carried out at pH 5.0 as dye is stable in acidic solution. The adsorption isotherms for CR at various temperatures (30°, 40°, 50° and 60°C) are shown in figure 1.

The isotherms showed positive adsorption at all temperatures studied. These are regular and concave to equilibrium concentration axis. The adsorption mechanism appears to be more efficient as degree of dye adsorption increases with the increased dye initial concentration. This kind of behavior might be brought about by the increment in the mass concentration gradient pressure due to increasing dye initial concentration that furnished the required driving forces to transport dye molecules into bulk solution to reside at surface of the beads. The percentage removal of dye is quite high at low adsorbate concentration i.e. the process of adsorption is not uniform, there is relatively rapid initial rate of dye uptake from very dilute solutions which decreased remarkably as the dye concentration exceeds and finally approached slowly to saturation (Senthil et al., 2010).
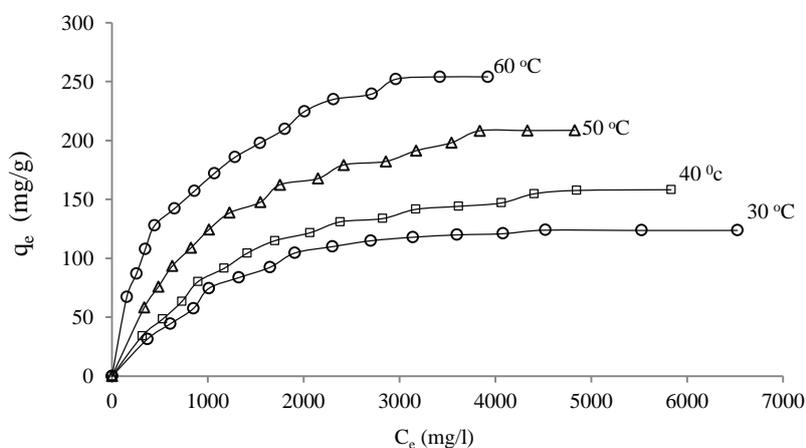

Figure -1 Adsorption isotherms showing effect of temperature for CR adsorption on CS beads.

At low dye concentration (1500 mg/l), 44.5-67.25 mg/g (59.33%-89.67 %) of CR dye get adsorbed by using CS beads (20 g/l) for CR solution. The results indicated high adsorption capacity for CR dye on beads. It is further noted that withdrawn percentage of CR dye diminished from 63% to 46% for CR with the increase in initial concentration from 1000 to 5000 mg.l^{-1} at 30^{0}C. Similar conclusions have also been noticed for the removal of colors by Annadurai and Krishnan, 1997 &1996.

The fact has been reported previously that temperature has two significant consequences for the adsorption cycle. An increment in temperature is well known to expand the pace of dispersion of the adsorbate units across the surface layer and to inward pores of the adsorbent because of the diminished viscosity of the medium (Al-Qodah, 2000). Almeida et al., 2009 recommended that a swelling impact inside the bead's mass of the adsorbent through which entering the large color units, probably going to happen when the temperature increased. In addition, Cestari et al., 2005 reported that the size of the chitosan holes enlargement occurred with the expansion of temperature. The extent of enlargement of holes favored the intraparticle diffusion with smoothly movement of dye units.

ADSORPTION MODELS

The nature of interactions between the solute i.e. dye and the adsorbent material chitosan bead is better described by adsorption models. The experimentally obtained data for the adsorption equilibriums were analyzed by applying three isotherm models: Langmuir, Freundlich and Temkin models.

LANGMUIR MODEL

The broadly utilized Langmuir equation (Lambanda et al., 2009) has obtained fruitful application in numerous sorption processes and is computed by following expression:

$$q_e = \frac{q_m \, K_L \, C_e}{(1 + K_L C_e)} \qquad \text{.......(1)}$$

The constants K_L and q_m are the Langmuir constants and can be find out from a linearized form of Langmuir equation, expressed as:

$$\frac{C_e}{q_e} = \frac{1}{q_m \, K_L} + \frac{C_e}{q_m} \qquad \text{............(2)}$$

Hence, a plot of C_e/q_e versus C_e produces a straight line with a slope $1/q_m$ and an intercept $1/q_m K_L$, demonstrating the utility of the Langmuir model for formation of monolayered covering of adsorbate units at the surface of the sorbent.

Basic qualities of Langmuir model can be communicated with dimensionless constant termed as equilibrium parameter or partitioning factor, R_L (Mohan et al., 2006) which is defined by the given equation:

$$R_L = \frac{1}{1 + K_L C_0} \qquad \text{............(3)}$$

Where,

C_0 implies Initial dye concentration in mol/l and K_L, a Langmuir constant measuring adsorption energy. R_L determines Efficiency of the process. It directs the behavior and shape of the isotherm. Values of R_L in the range of zero to one represent favorable adsorption.

Experimentally obtained adsorption data was applied to equation 2 of Langmuir model and the Langmuir plots for the dye was drawn by plotting Ce/qe versus Ce at different temperatures as represented in figure 2.
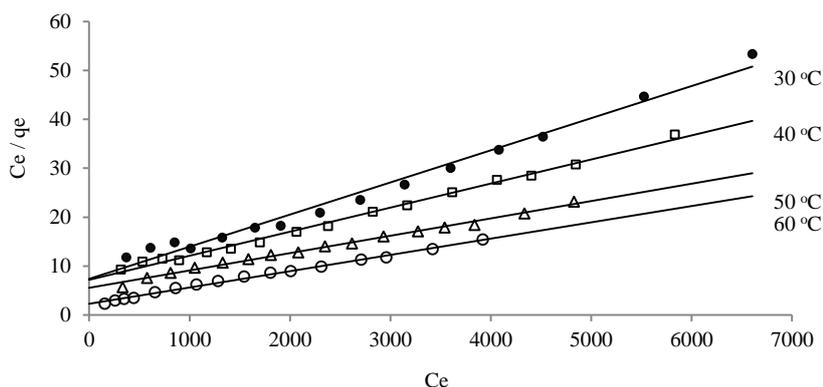

Figure- 2 Linear Langmuir plots for adsorption of CR dye on CS beads.

The resulted linear plots (R^2=.977 to .997) shows that adsorption data fitted well for the Langmuir model in the entire range of initial concentration studied. The increase in adsorption capacity (q_m) of dye on increasing the temperature demonstrating that a higher amount of dye is needed to form a monolayer at the exterior of adsorbent. The increased quantity of dye removal with increasing temperature is supported by q_m values.

Thermodynamic parameters of the adsorption process can be evaluated by using the van't Hoff equation with the value of K_L obtained at different temperatures (Crini et al., 2008).

$$\ln K_L = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \qquad\qquad ……….(4)$$

Here, change in enthalpy and entropy is denoted by ΔH and ΔS respectively and a universal gas constant, R=8.314 J mol^{-1} K^{-1} and T is absolute temperature in K.

The thermodynamic variables for dye adsorption on chitosan beads were evaluated using van't Hoff's equation 4 (plots of ln K_L vs 1/T) gives linear plots having R^2=0.96 from which thermodynamic parameters were calculated and given in table:1. The negative values of Gibbs free energy (ΔG) for CR at all the studied temperatures confirm that the process is feasible with spontaneous dye adsorption onto CS-beads and also indicated that the system did not gain energy from an external source.

When the temperature was increased, the magnitude of ΔG shifted a high negative value suggesting that the adsorption was more spontaneous on increasing temperature. In adsorption processes, ΔG values were noticed in the range of -6.95 to -12.81 KJ/mol, hence adsorption process corresponds to physical adsorption. Positive values for enthalpy change (ΔH) demonstrated an endothermic adsorption process means heat absorbing during adsorption. These estimations seem to be clarified by the ionic interaction between the dye unit and chitosan beads (McMullan et al., 2001 & Anjos et al., 2002). As the values of entropy change (ΔS) are also positive this suggests that it is accountable for negative ΔG during dye adsorption on CS beads with a spontaneity and there was increased randomness at the site uniting dye unit with chitosan bead under circumstances.

Table- 1. Thermodynamic Parameters for adsorption of CR on CS beads.

S.No.	Temperature (°K)	ΔG (kJ mol⁻¹)	ΔH (kJ mol⁻¹)	ΔS (kJ mol⁻¹)
1	303	-6.9453		
2	313	-8.304	51.322	0.19131
3	323	-9.991		
4	333	-12.807		

FREUNDLICH MODEL

The sorption of solutes from a solution onto a solid is an extraordinary example of heterogeneous distribution of energies at surface where the energy variations with the coverage of surface is governed by varying heats of adsorption. The equation given by Freundlich can be expressed as:

$$q_e = K_f \cdot C_e^{1/n} \qquad\qquad \text{....……...(5)}$$

The logarithmic form of the equation is:

$$\ln q_e = \ln K_f + \frac{1}{n} (\ln C_e) \qquad\qquad \text{……….(6)}$$

Where Freundlich constant K_f, is an indicative for sorption capacity of the adsorbing species, n is an another constant that implies energy or potency of adsorption.

Freundlich isotherms were obtained for adsorption data of CR on CS-beads at various temperatures which obtained as linear (figure-3) plots. K_F and n constants were calculated from their intercept and slope. The relative high value (n > 1 i.e.1.7544 to 2.3202) on increasing temperature from 30°C to 60°C may suggest the existence of a significant affinity and interaction between dye and chitosan. The Freundlich constant (K_F) is a relative measure of the adsorption capacity and its increased values with temperature indicates that the interaction between the chitosan and dye is an endothermic process. The value of correlation coefficient (R^2=0.94 to 0.986) are although close to unity yet it is not enough as in Langmuir model where R^2 is always greater than 0.98. This evidence leads to the hypothesis that the Langmuir isotherm model is more appropriate than the freundlich model.
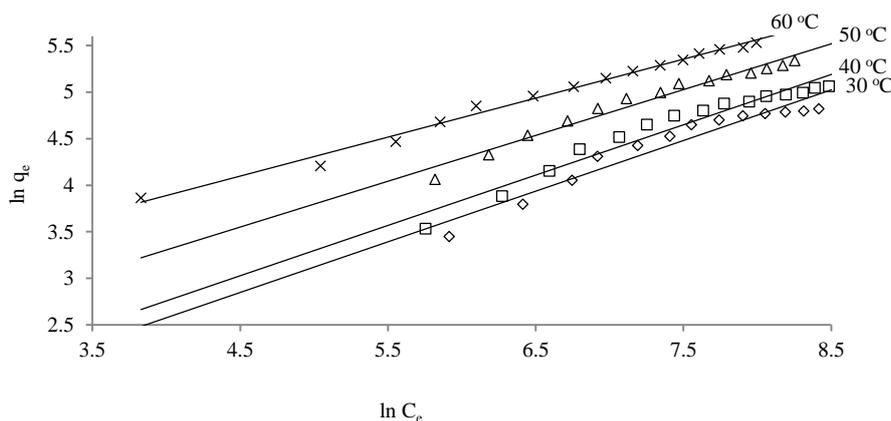

Figure- 3 Freundlich plots of Congo red dye adsorption on CS beads at various temperatures.

TEMKIN ISOTHERM MODEL

It describes adsorption mechanism in such a process where a linear reduction in the heats of adsorption is expressed for all the particles adhere in the layer because of interlinks between the adsorbent and the adsorbate become lesser with the filling of adsorbing locations at surface. The equation is further computed to linear form as given below:

$$q_e = \frac{RT}{\Delta Q}\ln K_T + \frac{RT}{\Delta Q}\ln C_e \qquad\qquad\qquad ....(7)$$

In equation 7, C_e is the equilibrium dye concentration in mg/l, q_e is the dye quantity adsorbed on sorbent in mg/g and K_T is a constant demonstrating binding capacity of adsorbent in l/g at equilibrium.

The highest binding energy, and constant $RT/\Delta Q$ is interrelated to the heat of adsorption. Temkin isotherm equation 7 was used to draw linear plots between adsorption capacity and concentration at equilibrium (qe vs ln Ce) for various temperature presented in figure 4. The Temkin models also show a strong conformation to the experimental data, judging by the satisfactory values of the obtained linear regression coefficient ($R^2 = 0.99$) for CR dye except at 30°C. It again leading the calculation that the Langmuir isotherm model describes better the adsorption mechanism of dyes studied onto chitosan beads.
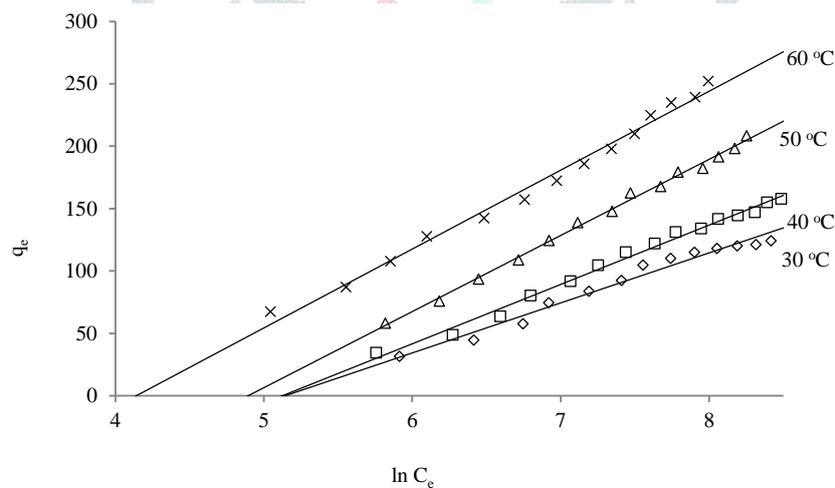

Figure- 4 Temkin plots for Congo red dye adsorption on CS beads at various temperature.

The comparison of R^2 values for the linear plots obtained for isotherm models tested may suggest the following order: Langmuir > Temkin > Freudlich. The sorption of the solute on a sorbent can involve physical bonding, ion exchange, complexation, and chelation or a coalescence of these interactions. Taking in consideration the special features of chitosan and reasonable arguments of the appropriate isotherm model, one can conclude that the interaction between chitosan and dye involves different mechanisms, but the electrostatic interaction appears as a dominant one.

Table- 2 Constant values for Isotherm models given by Langmuir, Freundlich and Temkin at various temperatures for adsorbing CR dye by CS beads.

S.no.	Parameters		Temperature (°C)			
			30	40	50	60
1.	Langmuir	R^2 Values	0.985	0.994	0.992	0.994
		R_L Values	0.149-0.551	0.204-0.641	0.208-0.648	0.098-0.431
		K_L (L/mg) x 10^{-4}	8.14	5.59	5.43	13.2
		q_m (mg/g)	167.67	250	333.33	333.33
2.	Freundlich	R^2 Values	0.94	0.953	0.968	0.986
		K_F (mol/mg)	1.242	1.136	3.815	8.314
		N	1.754	1.802	2.037	2.32
3.	Temkin	R^2 Values	0.973	0.991	0.996	0.989
		K_T (L/mol) x 10^{-3}	5.83	5.945	7.489	15.9
		Q (J/mol)	62.92	54.727	44.031	43.79

CONCLUSION

Results shows that chitosan beads crosslinked with glutaraldehyde can act as a good sorbent for removing congo red dye. It is possible to remove 63% of congo red using 20 g chitosan beads in 24 hours from 1000 mg/L dye solution. The adsorption capabilities of chitosan is because of its electropositive nature as it has amino group ($-NH_2$) that can undergo protonation ($-NH_3^+$) and able to provide site for adsorbing dye ions or dye molecules through an electrostatic interaction. Adsorption of dye decreases with increasing pH and dye initial concentration. Adsorption also increases with increasing temperature. Adsorption data of the dye fits into Freundlich, Temkin, and Langmuir models but it gave best linearity into the Langmuir model at various temperatures. The values for Gibbs free energy 'ΔG' are negative indicated spontaneous dye adsorption with no gain of energy from external source. These negative value for ΔG increases with increase of temperature, showing more spontaneous adsorption on increasing the temperature. Adsorption process corresponds to physical adsorption as ΔG values are in the range -20 to 0 KJ/mol. An endothermic process for adsorbing dye is indicated due to obtaining positive enthalpy change (ΔH) values. The Gibbs free energy (ΔG) concluded that the adsorption process favored greatly at the connecting sites and bonds between the CS and dye molecule produce reflection by estimating in positive values of change in entropy (ΔS).

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