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Removal of Harmful Textile Dye Congo Red from Aqueous Solution Using Chitosan and Chitosan Beads Modified with CTAB

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ABSTRACT
Color is an important aspect of human life. Textile industries are the major consumers of dye stuffs. During coloration process, 10 to 15 percent of the dyes will be lost and this will be discharged with the effluents coming from textile industries. These are very difficult to degrade and they may degrade to form products that are highly toxic to human. Today, methods such as coagulation, flocculation, activated carbon adsorption, etc. are available for the removal of dyes. These are all quite expensive and difficult to degrade. Chitosan is a natural hetero polymer derived from chitin. Chitosan has proved to be effective in removing hazardous compounds from environment due to its multiple functional groups. It is available as flakes and powder. In the present work, chitosan beads were prepared and modified with a cationic surfactant CTAB for the removal of dye Congo Red. Batch experiments were conducted to study the effect of CTAB concentration, contact time, agitation speed, adsorbent dosage, initial dye concentration and pH. Batch equilibrium data were analyzed using Langmuir and Freundlich isotherm. Bach kinetic data were analyzed using Pseudo first order kinetic model and pseudo second order kinetic model.
Key words: Batch studies, chitosan, Congo Red, Freundlich model. Langmuir model

I. INTRODUCTION

Color is an important aspect of human life. Coloring process in industries are done using dyes. A dye is a colored substance that has an affinity to the substrate to which it is being applied.Today there are more than 10,000 dyes available commercially. Synthetic dyestuffs widely exist in the effluents of industries such as textiles, printing, paper, plastics and leather [1]. Colored industrial effluent contains many varieties of synthetic dyes including azo dyes which are mostly toxic and mutagenic, and even carcinogenic in nature. Congo Red is an azo dye which is used in textile, paper and pulp, leather industries etc. Congo redis a benzidine based anionic diazo dye. These dyes have been known to cause an allergic reaction and to be metabolized to benzidine, a human carcinogen. Synthetic dyes such as Congo red are very difficult to remove because of their complex aromatic structure, which provides them physico-chemical, thermal and optical stability [2]. Although contaminated waste water may be treated with conventional physical–chemical methods like reverse osmosis, ion exchange, chemical precipitation or lime coagulation and oxidation, the application of these techniques has been restricted due to high energy consumptions or expensive synthetic resins and chemicals [3]. Moreover, these methods generate large amount of toxic sludge and are ineffective at lower concentrations of dye. Adsorption is the most widely used technique for the removal of dyes [4]. It has become popular because of its simplicity, low cost and the availability of wide range of adsorbents. Activated carbon is the most widely used adsorbent throughout the world [5]. Activated carbon has very high capacity for adsorbing dyes because of their structural characteristics and porosity. But, activated carbon has several dis advantages like it is non-selective and higher the quality, higher the cost. Also, regeneration of activated carbon using chemical and thermal procedure is quite expensive, difficult and will result in loss of adsorbent. So it is very important to find alternatives for activated carbon. Chitosan used in the present work is a natural hetero polymer. It is composed of N-glucosamine and N-acetyl glucosamine residues [6]. Chitosan is obtained by deacetylation of Chitin. It is available as flakes and powder. The regeneration of chitosan powder is difficult. Chitosan beads modified with a cationic surfactant CTABsurfactant (Cetyl Trimethyl Ammonium Bromide) has shown very high adsorption capacity for anionic dye [7]. But the time required for preparation of beads was more than twenty four hours which made the process less

attractive. . In the present work, chitosan beads were prepared and modified with CTAB in a simpler way. Beads were formed in less than thirty minutes. The adsorbent was used for the removal of dye Congo Red (CR). Batch studies were conducted to study the effect of CTAB concentration, contact time, agitation speed, adsorbent dosage, pH and initial dye concentration on dye removal. Batch equilibrium data were analyzed using Langmuir and Freundlich isotherm model. Batch kinetic data were analyzed using Pseudo first order kinetic model and pseudo second order kinetic model.

II. MATERIALS AND METHODS

2.1. Materials

Adsorbent: chitosan (90% de acetylated was purchased from Marine Biotech Ltd, Kerala.

Dye: Congo Red (S.D.FineChem Ltd) was purchased locally. Reagents and chemicals: Acetic acid (Fisher Scientific), NaOH (Fisher Scientific), CTAB (S.D.Fine Chem Ltd), Acetone (Qualigens) and HCl (RFCL Ltd) were purchased locally.

2.2. Preparation of Chitosan Beads (CB)

Chitosan beads were prepared by dissolving 2 gm chitosan in 60 ml of 5% (v/v) acetic acid. The solution was stirred in magnetic stirrer for 20 minutes. Solution after stirring was added drop wise to 5oo ml of 0.5 M NaOH using a syringe. Beads were formed due to neutralization reaction between NaOH and acetic acid. Beads were washed with distilled water and stored in distilled water until used.

2.3. Preparation of Chitosan Beads Impregnated with CTAB (CB-CTAB)

1% (wt/v) CTAB solution was prepared by dissolving 1 gm CTAB in 100 ml distilled water. 0.01%, 0.02%, 0.03% and 0.04% CTAB chitosan beads were prepared by dissolving required amount of CTAB solution to 2 gm chitosan. The volume was made up to 60 ml using 5% (v/v) acetic acid. The solution was stirred in a magnetic stirrer for twenty minutes. After stirring, solution was addeddrop wise to 500 ml NaOH using syringe. Beads were washed thoroughly with distilled water and stored in distilled under used.

2.4. Batch Experiments

Batch experiments were carried out in orbitek shaker. To study the effect of CTAB concentration, 0.5 gm. of beads were added to 50 ml of 10 ppm solution and agitated in shaker for four hours. Concentration of CTAB in beads were varied from 0.01% to 0.04%. The effect of contact time was studied by adding 0.5 gm. beads to 50 ml of 10 ppm dye solution and agitating at 160 rpm. The sample was analyzed for dye concentration after every one hour for seven hours. To study the effect of agitation speed, 0.5 gm. of beads were added to 50 ml of dye solution and agitated at different speed (120 rpm to 200 rpm) for four hours. To study the effect of adsorbent dosage, amount of chitosan was varied from 0.25gm to 1.5 gm and agitated at 160 rpm for four hours. To study the effect of pH, pH of the solution was varied from 4 to 9 using 0.1 N HCl and 0.1 N NaOH. The absorbance of dye solution was measured at 497 nm using uv-visible spectrophotometer SL 159 and concentration of dye was determined using calibration chart.

The amount of dye adsorbed was determined using the following mass balance equation;

$$q_e = \frac{C_o - C_e}{W} V \quad (1)$$

Where, q_e is the adsorption capacity mg/gm; C_o is the initial dye concentration, ppm; C_e is the equilibrium dye concentration, ppm; V is the volume of dye solution, ml and W is the dry weight of adsorbent, gm.

III. RESULTS AND DISCUSSION

3.1. Characterization of the Adsorbent

The FTIR analysis of chitosan beads before and after modification with CTAB is shown in figure 1. The spectrum of chitosan beads CB were characterized by bands at 1559.26 cm^{-1} (-N-H- bend of primary amines), the adsorption sites and 1318.98 cm^{-1} (-C-O- stretch of alcohol). The spectrum of chitosan beads impregnated with CTAB are characterized by bands at 1558.10 cm^{-1} (-N-H- bend of primary amines), the adsorption sites 1300.84 cm^{-1} (-C-O- stretch of alcohol), 1652.82 cm^{-1} (-N-H- bend of primary amines), 1241.59 cm^{-1}(-C-H- Wag of alkyl halide), 846.04 cm^{-1} (-N-H Wag of primary and secondary amines) and 429.19 cm^{-1} (-C-Br stretch of alkyl halide), responsible for hydrophobic interaction. The difference in composition of beads confirms that CTAB has been successfully impregnated to the beads.

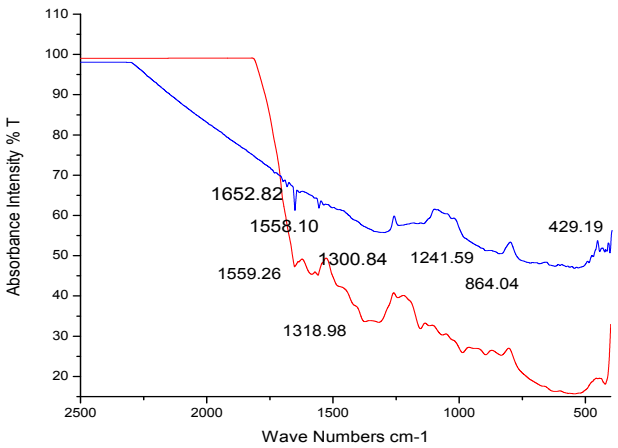

Figure 1. FTIR analysis of chitosan beads

3.2. Effect of CTAB Concentration

Graphical representation of effect of CTAB concentration is given in figure 2. It can be seen that as the concentration of CTAB increased from 0.01% to 0.02%, value of q_t increased. Further increase in CTAB concentration resulted in a decrease in qtvalues. The increase in adsorption capacity with increase in CTAB concentration is due to the increased hydrophobic interaction between the hydrophobic moieties of CTAB and the hydrophobic moieties of dye. The increased positive charge due to the positively charged head group of CTAB might also have contributed to the increased adsorption capacity. Above 0.02 % CTAB concentration, foam formation occurred. The beads formed were less rigid and adsorption capacity was lesser. But the adsorption capacity of beads with CTAB was higher compared to the beads without CTAB. So 0.02 % CTAB concentration was taken as the optimum concentration for adsorption.

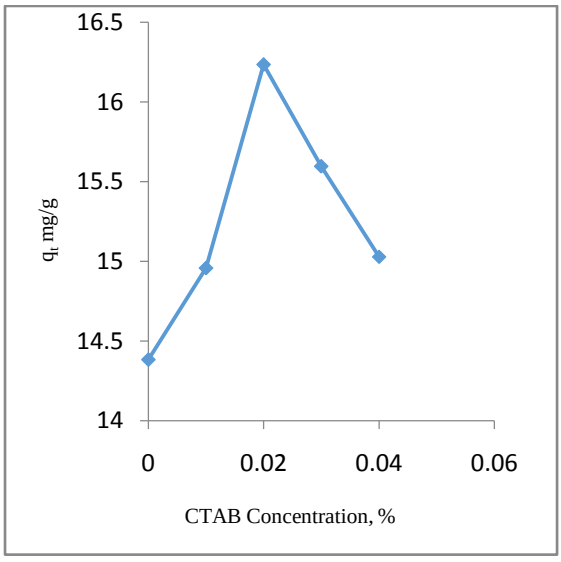

Figure 2: Effect of CTAB Concentration onAdsorption Capacity

3.3. Effect of Contact Time

Effect of contact time on dye removal is shown in figure 3. It can be seen that, there was a rapid increase in adsorption capacity as the contact time increased from 0 to 4 hours for both chitosan beads and chitosan beads modified with CTAB. After 4 hours, there was no considerable increase in adsorption capacity for both chitosan beads and chitosan beads impregnated with CTAB. Equilibrium reached after 4 hours and 4 hours was taken as the optimum time for dye removal for Congo Red.

3.4. Effect of Agitation Speed

The effect of agitation speed on dye removal is shown in figure 4. As agitation speed increased from 120 rpm to 160 rpm, there was a significant increase in adsorption capacity. Further increase in agitation speed did not have significant effect on dye removal. Lower adsorption capacity at lower speed was due to thepoor interaction between adsorbate and adsorbent. As the speed reached 160 rpm, there was sufficient increase in adsorption capacity. As the speed was increased above 160 rpm, adsorption capacity did not vary significantly. Thus, 160 rpm is the optimum agitation speed for dye removal.

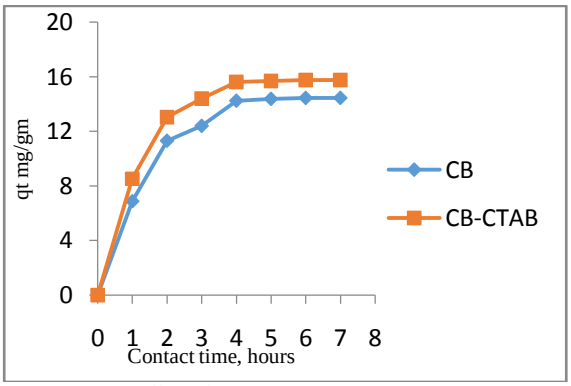

Figure 3: Effect of Contact Time on Adsorption Capacity

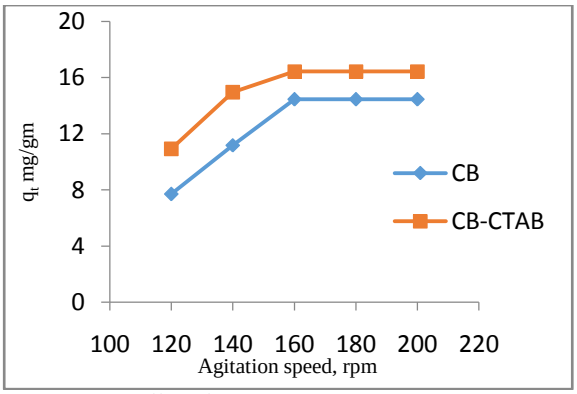

Figure 4: Effect of Agitation Speed on Adsorption Capacity

3.5. Effect of Adsorbent Dosage

The effect of adsorbent dosage on percentage dye removal is shown in figure 5. With increase in adsorbent dosage from 0.25 gram to 1.25 gram, removal of Congo Red using chitosan beads increased from 40.39 % to 89.68 %. Further increase in adsorbent dosage did not give increased dye removal. For beads impregnated with CTAB, percentage removal of Congo Red increased from 49.25 % to 90.57 %. From above table, it can be seen that 1.5 gram chitosan and 0.75 gram chitosan beads impregnated with CTAB were showing 90 % dye removal. Thus modification of chitosan with CTAB resulted in less adsorbent requirement.

3.6. Effect of Initial Dye Concentration

Effect of initial dye concentration on adsorption capacity is shown in figure 6. The adsorption capacity increased with increase in dye concentration. This was because, concentration difference was the driving force for adsorption and higher concentration, driving force increased. At every concentration, CTAB modified beads had higher adsorption capacity. Also, the adsorption capacity of CTAB impregnated beads increased with increase in adsorption capacity. At higher concentration, adsorption capacities of CTAB beads were almost 20 % greater as compared to beads without CTAB. That at higher dye concentration, hydrophobic interaction between dye and CTAB was higher.

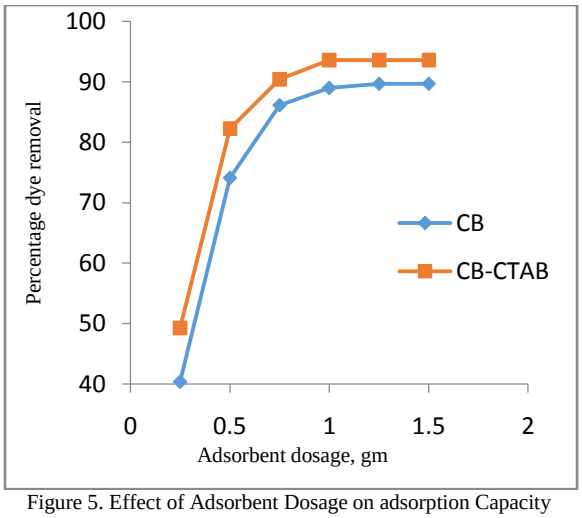

Figure 5. Effect of Adsorbent Dosage on adsorption Capacity

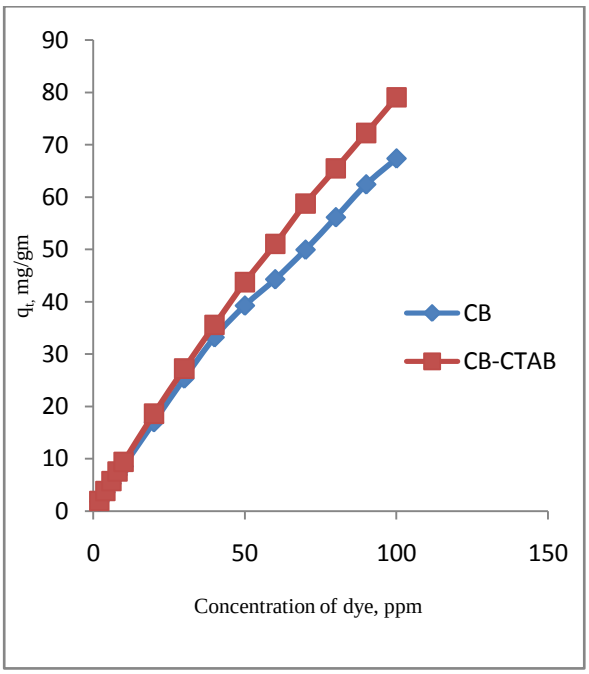

Figure 6: Effect of Initial Dye Concentration on Adsorption Capacity

3.7. Effect of pH

Figure 7 shows the effect of pH on dye removal. Higher adsorption capacity was attained at lower pH. With increase in pH, adsorption capacity decreased considerably. At every pH, CTAB modified beads were showing higher adsorption. Higher adsorption capacity at lower pH is due to the increased number of protonated amino groups. At very high pH, more OH groups will be available and results in repulsion between adsorbent and negatively charged dye molecules. This principle is used for regeneration of column after adsorption.

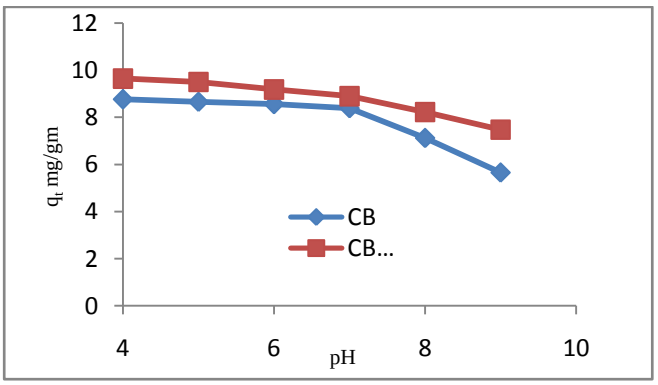

Figure 7: Effect of pH on Adsorption Capacity

3.8. Equilibrium Adsorption Isotherm

Equilibrium adsorption isotherm model is fundamental in describing the interactive behavior between adsorbent and adsorbate. The distribution of the adsorbate between the adsorbent and the liquid phase is a measure of the position of equilibrium in the adsorption process and is expressed by isotherm

models. In the present study, equilibrium data were analyzed using Langmuir and Freundlich isotherm models. Langmuir isotherm model assumes monolayer adsorption of adsorbate on a homogeneous surface of adsorbent. It is valid for adsorption onto a surface with a finite number of identical adsorption sites of uniform energies of adsorption with no transmigration of adsorbate in the plane of the surface. The linearized form of Langmuir model is;

$$\frac{C_e}{q_e} = \frac{1}{K_L} + a_L \frac{C_e}{K_L} \qquad (2)$$

Where, C_e is the equilibrium dye concentration, ppm; q_e is equilibrium dye concentration on the adsorbent, mg/gm; a_l, is Langmuir constant, 1/mg; K_L is Langmuir constant, 1/gm.

a_L and k_L are determined from the slope and intercept of the plot of C_e/q_e versus C_e

The maximum adsorption capacity Q_o(mg/gm) is given as

$Q_o = K_L/a_L$

The most important feature of Langmuir isotherm can be expressed in terms of a dimensionless constant, R_L which is givenby the following equation;

$$R_L = \frac{1}{1 + a_L C_o} \quad (3)$$

R_L values in the range 0 to 1 indicate favorable adsorption. It is suggested that the adsorption is unfavorable if R_L is greater than 1.

Freundlich model is usually adopted for heterogeneous adsorption. It is an empirical equation which describes the surface heterogeneity of the adsorbent. This model considers multi-layer adsorption with a heterogeneous energetic distribution of active sites which is accompanied by interaction between adsorbed molecules.

The linear form of Freundlich equation is;

$$\ln q_e = \ln K_F + \frac{\ln C_e}{n} \quad (4)$$

Where, K_F is Freundlich constant, 1/gm; n is Freundlich constant;q_e is equilibrium adsorption capacity, mg/gm;C_e is equilibrium dye concentration, ppm

K_F is related to extend of adsorption 1/n is related to the adsorption intensity and varies with the heterogeneity of the material. n represents the mutual interaction of the adsorbed species. Usually, the experimental values of n are greater than unity which means that the forces of interaction between adsorbedmolecules are repulsive. If the value of n is close to zero, it implies that the system more heterogeneous. The values of 1/n and K_F are calculated from the slope and intercept of the plot of ln q_e versus ln C_e.

Equilibrium adsorption data analyzed by Langmuir model is shown in figures 8 and 9. The values of Langmuir constant and maximum adsorption capacity determined by model are given in table 1.

The maximum adsorption capacity calculate from Langmuir model for chitosan beads impregnated with CTAB is almost 20 % higher as compared to chitosan beads.

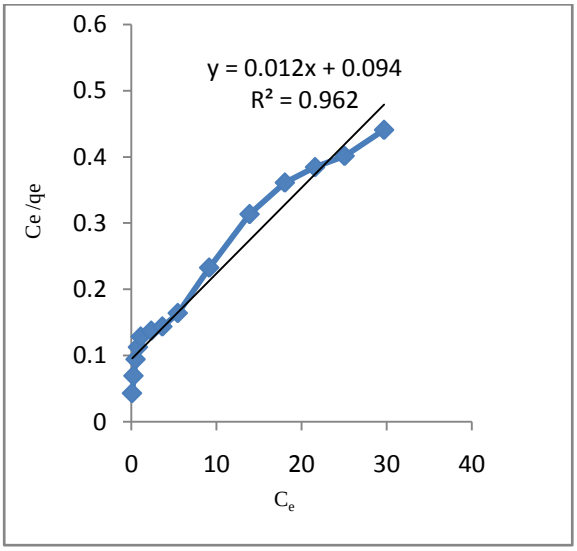

Figure 8: Langmuir Plot for CB

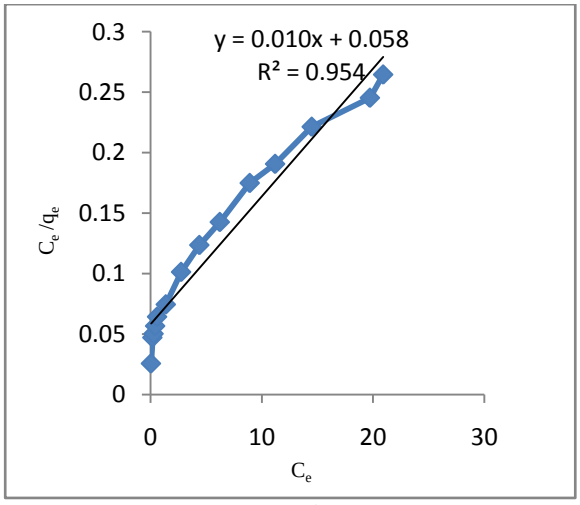

Figure 9: Langmuir Plot for CB-CTAB

Table 1: Langmuir Constants for Congo Red

Bead	K_L(1/mg)	a_L (1/gm)	Q_0(mg/gm)	R^2
CB	10.61	0.13	77.55	0.96
CB-CTAB	17.18	0.18	94.39	0.95

Freundlich model for Congo Red using chitosan beads and chitosan beads impregnated with CTAB are shown in the figures 10 and 11.The values of Freundlich constants are presented table 2.

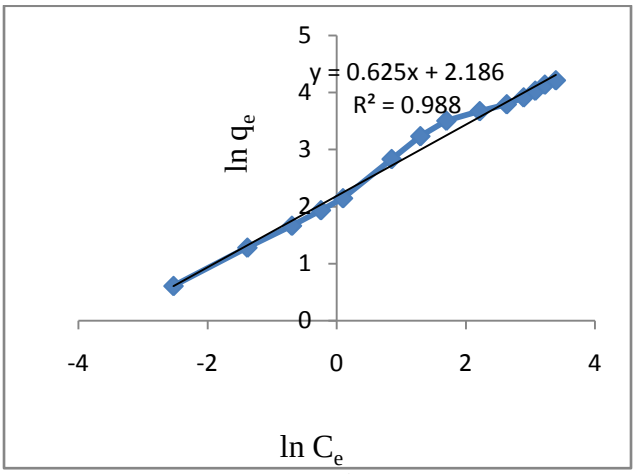

Figure 10: Freundlich Plot for CB

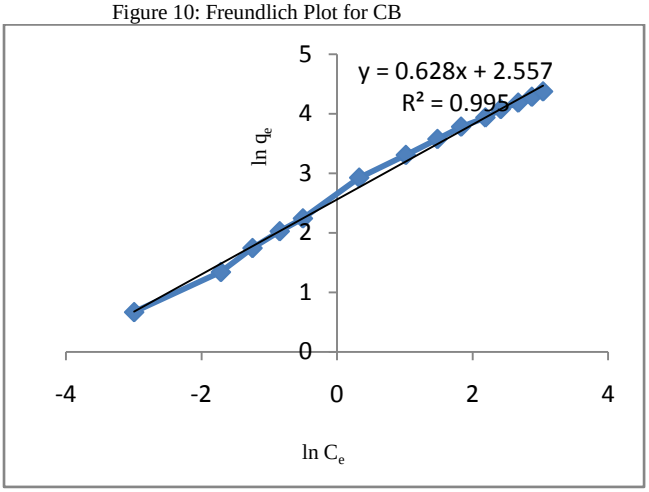

Figure 11: Freundlich Plot for CB-CTAB

Table 2: Freundlich Constants for CR

Bead	N	K_F (1/gm)	R^2
CB	1.53	8.90	0.98
CB-CTAB	1.59	12.90	0.99

The value of K_F which represents extend of adsorption is higher for chitosan beads impregnated with CTAB. Value of R^2 represents the deviation of system from model. On analyzing the values of R^2, it can be confirmed that the model is best fitted to Freundlich model.

3.9. Kinetics of Adsorption

Studying kinetics of adsorption is very important for designing adsorption systems and is required for selecting optimum operating conditions for batch adsorption study. To investigate the adsorption kinetics of Congo Red on chitosan beads and chitosan beads impregnated with CTAB, pseudo first order and pseudo second order models were used in this study.

The linear form of pseudo first order rate equation is;

$$\log(q_e - q_t) = \log q_{e(cal)} - \frac{k_1 t}{2.303} \qquad (5)$$

Where, $q_e$is the mount of dye adsorbed at equilibrium, mg/gm; qt is the mount of dye adsorbed at time t, mg/gm; k_1 is the rate constant, 1/min; $q_{e\,(cal)}$ is the calculated adsorption capacity, mg/gm.

The values of k_1 and $q_{e\,(cal)}$ were obtained from the slope and intercept of log (q_e-q_t) versus t.

The linearized form of pseudo second order rate equation is given as;

$$\frac{t}{q_t} = \frac{1}{h} + \frac{t}{q_{e(cal)}} \qquad (6)$$

Where, q_t is the amount of dye adsorbed at time t, mg/gm.; h is the initial adsorption rate, (mg/gm.min).

The value of $q_{e\,(cal)}$ and h are obtained from the slope and intercept of t/q_t versus t

The value of pseudo second order rate constant is given by the following equation;

$$h = k_2 q_{e\,(cal)}{}^2 \qquad (7)$$

Where, k_2 is Pseudo second order rate constant, g/mg.min.

The pseudo first order and pseudo second order kinetic constants determined from batch kinetic studies are given in the following tables. The corresponding kinetic plots are also shown in figures 12 and 13.

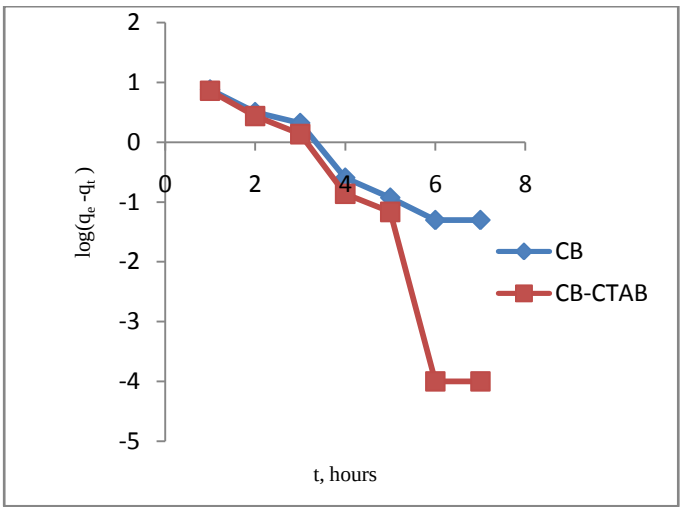

Figure 12: Pseudo First Order Plot

Table 3: Pseudo First Order Rate Constants for CR

Bead	K_1 (1/hour)	$q_{e(cal)}$, (mg/gm)	R^2
CB	0.93	19.29	0.94
CB-CTAB	2.03	202.72	0.89

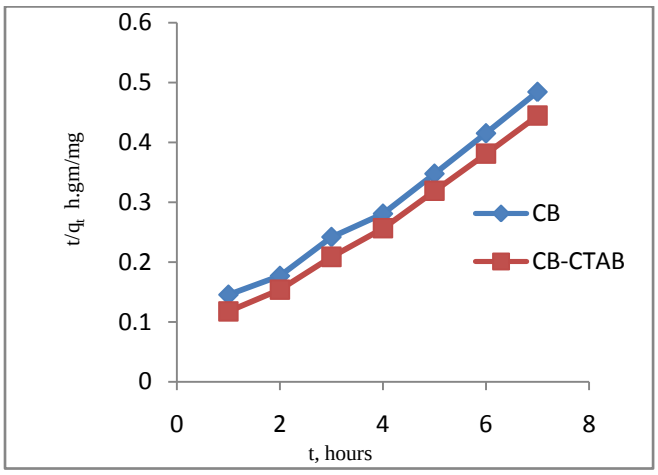

Figure 13: Pseudo Second Order Plot for CR

Table 4: Pseudo Second Order Rate Constants for CR

Bead	K_2 (gm/mg.hr)	$q_{e(cal)}$, (mg/gm)	h (mg/gm.hr)	R^2
CB	0.04	17.51	14.22	0.98
CB-CTAB	0.05	19.15	20.96	0.99

The value of R^2 indicates that adsorption of Congo Red on chitosan beads and chitosan beads impregnated with CTAB follows pseudo second order kinetics. The value of pseudo second order rate constant is higher for beads modified with CTAB. Thus, mass transfer is higher for modified beads. The values of h calculated from pseudo second order kinetics which represents the initial mass transfer rate is also very high for CTAB modifiedbeads.

IV. CONCLUSION

In the present work, experiments were carried out to study azo dye removal from aqueous solutions using chitosan beads and chitosan beads impregnated with CTAB. Results indicate that the adsorption capacity increased on modifying chitosan beads with CTAB. 0.02 % CTAB concentration has shown highest adsorption capacity. Studies were carried out inbatch mode to study the effect of contact time, agitation speed, adsorbent dosage, initial dye concentration and pH. The results showed that at every conditions, CTABimpregnated beads had higher adsorption capacity than chitosan beads. Equilibrium was reached after 4 hours. Adsorption capacity increased with increase in initial dye concentration and percentage dye removal decreased with increase in concentration of dye. Adsorption was higher at lower pH. Equilibrium isotherm data were described well with Freundlich isotherm model. Adsorption followed pseudo second order kinetics.

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