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Packed Bed Column Studies for the Removal Of Reactive Red Dye Using ECH Cross linked Chitosan Beads

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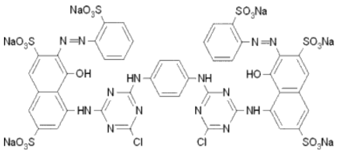
ABSTRACT

Dyes are coloured substances that have an affinity to the substrates on which they are applied. The dye is generally applied in an aqueous solution, and requires a mordant to improve the fastness of the dye on the fiber.Reactive dyes are a class of highly coloured organic substances, primarily used for tinting textiles. They attach themselves to their substrates by a chemical reaction that forms a covalent bond between the molecule of dye and that of the fibre Bio-adsorbent chitosan has shown very promising characteristics in this field. A comparative study of adsorption of aqueous Reactive red dye solution on non-cross linked chitosan beads and ECH cross linked chitosan beads was conducted using fixed bed continuous column. Cross linked beads were found to be more efficient than normal beads. ECH cross linked chitosan beads are visibly more rigid than chitosan beads and they have high stability in acidic medium compared to chitosan beads which disintegrate in acidic medium. Continuous operation of fixed bed with ECH cross linked chitosan beads shows good promise with an efficiency of 60.635% for a bed height of 2.5cm and flow rate of 4ml/min Data from column studies were fitted to three well established column models, Thomas model and Yoon-Nelson model. The experimental data were in good agreement with theoretical results. The study revealed the applicability of chitosan in fixed bed column for.removal of Reactive Red.
Keywords: Adsorption, Fixed Bed Column Studies,Chitosan, Reactive Red Dye.

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I. INTRODUCTION

Water pollution is a major problem faced by the world today. They are used in several industries like textiles, paper, plastics, leather, cosmetics, food and pharmaceuticals as they offer a vast range of new colors, and they imparted better properties to the dyed materials. Dyes have wide range of applications several industries including textiles, paper, plastics, leather, cosmetics, food and pharmaceuticals. There are more than 100,000 commercially available dyes. Synthetic dyes have quickly replaced the traditional natural dyes as they cost less, they offered a vast range of new colors, and they imparted better properties to the dyed materials. . The dyes are toxic in nature and also possess carcinogenic properties.

Conventional methods for removing dyes include coagulation and flocculation, oxidation or ozonation and membrane separation. However, these methods are not widely used due to their high cost and economic disadvantage. In contrast, adsorption techniques are by far the most versatile and widely used for treatment of waste water. Some of the common adsorbents used are activated carbon, alumina, silica gels etc. In recent years, most studies have been focused on the on the development of cheap and effective new bio-adsorbents. Azlan Kamari et al [1] showed that chitosan and chitosan-EGDE beads were favourable absorbers for removing Acid Red 37 and Acid Blue 25 from aqueous solution and could be employed as low-cost alternatives for the removal of acid dyes in wastewater treatment. *M.S. Chiou, H.Y. et al* [2] found that cross linking agent epichlorohydrin was proved to give higher adsorption of 1800g/kg for RR189 compared to other cross linking agents like glutaraldehyde. Rigidity of beads was improved by using Sodium tripolyphosphate. Sudipta Chatterjee et al [3] impregnated chitosan beads with surfactant (CTAB) and found that significantly increased adsorption capacity from 178.32 (0 wt% CTAB) to 373.29 mg/g (0.05 wt% CTAB) for adsorption of congo red (CR) from an initial concentration of 1000 mg/l. Chia-Yun Chen et al[4] studied biosorption of azo dyes from aqueous solution on the template crosslinked-chitosan nanoparticles and found that the maximum monolayer adsorption capacities of the RB5 dye on the ECH-RB5 nanoparticles and the 3R dye on the ECH-3R nanoparticles were greater than those of other adsorbents reported in related studies. Nitrate removal from aqueous solutions by cross-linked chitosan beads conditioned with sodium bisulfate showed that the maximum adsorption capacity was 104.0 mg $g^{-1}$for the conditioned cross-linked chitosan beads at pH 5, while it was 90.7 mg $g^{-1}$for normal chitosan beads [5].

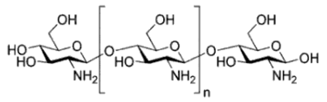
According to *Liu. et al.*, Chitosan is good adsorbent for metal ions and dyes. However chitosan disintegrates in acidic medium which can be avoided by cross linking with ECH or glutaraldehyde [6] . The good adsorption capacity of chitosan is due to its high content of amino and hydroxyl functional groups. To improve acid stability, mechanical strength, pore size, hydrophilicity and biocompability chemical modification methods, such as chemical cross-linking of the surface of the chitosan beads with cross-linking agents, have been performed by M.S. Chiou, H.Y. Liet al [2].

The adsorption capacity of chitosan can be improved by , several chemical modifications such as cross-linking, insertion of new functional groups, or conditioning of chitosan beads or resins [6]. The present study concentrates on adsorption Reactive dye by chemically modified chitosan beads. Epichlorohydrin (ECH) was selected as a cross-linking agent because ECH does not interact with cationic amine groups of chitosan during cross-linking. It is an organochlorine compound. Being a highly reactive compound it easily gets linked to chitosan. This cross linking improves the mechanical strength of polymer chains. The effect flow rate,bed height and breakthrough curved are studied.

II. MATERIALS AND METHODS

2.1 Chemicals and Preliminary Characteristics of Adsorbent

Chitosan (90% deactivated , Indian marine sea foods limited) and Reactive red (Industrial grade) was used without further purification. The chemical structure of Reactive red is shown in the figure. The other reagents used in this study were of pure analytical grade. De-ionized water prepared by passing distilled water through a de-ionizing column.



2.2 Dye Solution Preparations

Stock solution of 100 ppm Reactive red dye solution is made by adding deionized water up to the mark in the standard flask to 0.1 gm of dye.. Dye solutions of different concentrations are required for the study and can be prepared by diluting the stock solution. Dye concentration was determined by using absorbance values measured before and after the treatment at 578nm with Elico India Limited (Sl 159) UV visible spectrophotometer.

2.3 Preparation of Chitosan Beads And ECH Cross Linking

Chitosan beads were prepared by dissolving 2g of chitosan powder in 60ml of 5% acetic acid solution in a beaker. Chitosan mixture is added drop wise into the 0.5M NaOH solution through a syringe .The beads are then washed in distilled water and then stored in distilled water to prevent the drying of the beads.

Epichlorohydrin or ECH is a widely known cross linking agent. The procedure for cross linking is as follows: The wet, non-cross linked chitosan beads are weighed in an electronic balance. These beads are suspended in 0.5 M NaOH solutions and ECH is added in the ratio 1:2 by weight. The beads in solution are agitated for a period of 3 hours at a temperature of 30-35^{o}C. The beads obtained now are more rigid in nature and also have resistance to acid attack. The cross linked beads are washed in distilled water and stored in it till further use.

2.4 Experimental Methodology

A column is fitted with a mesh on which the adsorbent is fixed. There is a continuous input of dye solution at the top of the column. A flow controller is fitted to regulate the flow rate of dye solution. The liquid passes through the bed of adsorbent and exits the column at the bottom. Absorbance of the dye solution is noted at regular intervals.

2.5 Calibration of Reactive Red dye

The Reactive red dye sample is calibrated using absorbance values obtained for different concentrations. The calibration chart helps to identify respective colour removal capacities of various adsorbents. Figure 1 showing the graphical representation of calibration of Reactive Red dye.

The amount of Reactive Red dye adsorbed (q_e) i.e adsorption capacity was determined by using the following equation:

$$q_e = V(C_0 - C_e)/m$$

Where C_0 and C_e represent initial and equilibrium Reactive Red dye concentrations (μmol/L), V is the volume of Reactive Red dye solution (L) and m is the amount (g) of chitosan.

III. RESULTS AND DISCUSSIONS

3.1 Continuous Column Studies

Data from lab scale experiments can be used as the basis for the design of full scale column operations. Many models have been proposed for the evaluation of efficiency and applicability of column models for operations at industrial level. To design a column adsorption operation, prediction of break through curve and adsorbent capacity for the required adsorbate under given set of operating conditions is necessary. In the present work, adsorption data from fixed bed column studies were analyzed using Thomas model and Yoon-Nelson model. Thomas model is based on the mass transfer model which assumes that dye migrates from the solution to the film around the particle and diffuses through the liquid film to the surface of adsorbent. This is followed by intraparticle diffusion and adsorption on active site. Linear form of Thomas model for adsorption is

Where, C_o is initial dye concentration, ppm; C_t is effluent dye concentration at time t; ppm K_{TH} is Thomas model constant, L/min.mg; qe is prediction adsorption capacity, mg/gm. x is mass of adsorbent, gm; Q is inlet flow concentration, ml/min. The value of K_{TH} and qe are determined from slope and intercept of a plot of ln (C_0/C_t -1) versus t.

The main aim of Yoon-Nelson model is to predict the time of column run before regeneration or replacement of column becomes necessary. The model is a very simple way to represent the break through curve. The major advantage of using this model is that it requires no detailed data concerning the type of adsorbent, characteristics of adsorbate and physical properties of adsorbent bed. This model assumes that, the rate of decrease in the probability of adsorption for each adsorbate molecule is proportional to the probability of adsorbate adsorption and the probability of adsorbate breakthrough on the adsorbent. According to this model, the amount of dye adsorbed in a fixed bed is half of the total dye entering the adsorbent bed within time period 2τ, where τ is the time required for 50 % break through. Linear form of Yoon-Nelson model is give

Where, C_0 is initial dye concentration, ppm; C_t is dye concentration at time t, ppm; t is flow time, min.; τ is time required for 50 % breakthrough, min; K_{YN} is Yoon-Nelson rate constant, 1/min. The values of K_{YN} and τ are determined from the slope and intercept of ln (Ct/ (C0-Ct)) versus t.

ECH Cross linked Chitosan beads modified were packed in a column with a diameter of 4.5cm and a height of 30cm was used. A steel mesh was inserted in the column and ECH cross linked chitosan beads were used as adsorbent. The initial concentration of dye was 100ppm and pH 3 was maintained The dye solution to be treated was stored in an overhead tank. The solution was made to flow under gravity. Control valves were used at the inlet and outlet to control the flow rate. Effect of flow rate, bed height and were investigated.

3.1.1 Effect of Bed Height

The breakthrough curves for variations of bed heights from 1cm to 3.5cm ata flow rate of 4 ml/min is shown in Fig. 24 It is observed that the amount of dye adsorbed increased in the range of 1cm to 3cm and then decreased. A bed height of 2.5cm showed the optimum adsorption.

3.1.2 Effect of Flow Rate

The effect of flow rate on column adsorption was studied by varying the flow rate of input in the range 3 to 7 ml/min with a fixed bed height of 2.5cm. The breakthrough curve obtained is shown in Fig. 25. The adsorption was found to be higher at lower flow rates while the extent of adsorption decreased with an increase in flow rate. A flow rate of 4ml/min was observed to be most suitable.

Table 12 summarizes the breakthrough analysis for effect of bed height and effect of flow rate on the extent of adsorption in fixed bed continuous column.

Co (mg/l)	H (cm)	Q (ml/min)	t_b (min)	V_b (ml)	q_{total}	q_e	W_{total}	R %
100	2.50	4	40	160	43.650	2.461	72	60.625
100	2.50	3	100	300	31.185	1.758	54	57.750
100	2.50	6	150	900	39.420	2.223	108	36.500
100	2.50	7	140	980	31.973	1.803	126	25.375
100	1.00	4	190	760	27.700	3.905	80	34.625
100	2.00	4	260	1040	68.850	4.853	120	57.375
100	3.50	4	30	120	29.430	1.185	72	40.875

3.1.3 Modelling of Fixed Bed Columns

It is necessary to fit the adsorption data using established models and subsequently determine the associated parameters associated with the models to establish the extent of their influence on adsorption. This data is of great importance for the optimization of the fixed bed continuous column.

3.2. THOMAS MODEL

The Thomas model assumes plug flow behavior in the bed and uses Langmuir isotherm for equilibrium and second order reversible kinetics. This model is suitable for processes where the resistance to internal and external diffusion is negligible. The linearized form of the Thomas model can be expressed as:

where, q_o (mg/g) is the equilibrium blue dye uptake per gram of adsorbent, Q (ml/min) is the flow rate, w (g) is the mass of adsorbent, k_{Th} (ml/min.mg) is the Thomas rate constant.

The column data was fitted to the Thomas model to determine the related constants using linear regression. The results are listed in Table 13. The values of regression coefficient were in the range of 0.88 to 0.972. Hence the Thomas model was suitable for the fixed bed continuous column where adsorption was not limited by resistance to internal and external diffusion.

Co (mg/l)	H (cm)	Q (ml/min)	K_{TH} ml/mg min)	q_o (mg/g) (theoretical)	R^2
100	2.5	4	0.00004	6.451	0.934
100	2.5	3	0.00005	4.046	0.972
100	2.5	6	0.00003	5.582	0.941
100	2.5	7	0.00008	0.474	0.880

3.3. YOON-NELSON MODEL

This model was developed based on the assumption that rate of decrease in the adsorption of adsorbate is proportional to the breakthrough of the adsorbate on the adsorbent. The linearized form of the Yoon-Nelson model is represented as below:

where, k_{YN} is the rate velocity constant, *T* (min) is the breakthrough time.

Co (mg/l)	H (cm)	Q (ml/min)	k_{YN} (l/mg min)	T (min)	R^2
100	2.5	4	0.004	286	0.934
100	2.5	3	0.005	239.2	0.972
100	2.5	6	0.003	32	0.88
100	2.5	7	0.008	61.875	0.941

The regression coefficients obtained from the linear regression method range from 0.88 to 0.972 as in the Thomas model. Therefore both models can be suitably used to optimize the fixed bed continuous column.

IV. CONCLUSION

In the present work, removal of Reactive Red in fixed bed column was investigated. ECH crosslinked chitosan beads were used as adsorbent. A polyethylene column with a diameter of 4.5cm and a height of 30cm was used. Effect of inlet flow rate, bed height on break through curve was studied. Continuous operation of fixed bed with ECH cross linked chitosan beads shows good promise with an efficiency of 60.635% for a bed height of 2.5cm and flow rate of 4ml/min. Fixed bed column was modeled using Thomas model, l and YoonNelson model. The experimental data were in good agreement with theoretical results. The study revealed that ECH crosslimked chitosan beads packed in column can be used as effective adsorbent for removal of azo dyes.

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