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Adsorption Studies on The Removal of Reactive Red Dye from Aqueous Solution Using ECH Crosslinked Chitosan Beads

M. Nagapadma*, Keerthi K Pai, Chetana M, Madhu Shree

Department of Chemical Engineering, MVJ College of Engineering, Bangalore, Karnataka India

**Corresponding Author: Nagapadma.M*

Abstract: **The increase in the use of dyes in industries has caused major problems in the treatment of the industrial effluent. The need to create economically and ecologically sound solutions to this problem has been investigated here. 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 batch operations. The extent of adsorption was tested against parameters of time, adsorbent dosage, initial dye concentration, rpm and pH. 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. A higher initial concentration of dye and pH of 3 was found to be favorable for adsorption. Complete removal of dye was achieved at 3 hours for a dye solution of 100ppm at pH 3. Kinetic rate studies established that the pseudo-second order kinetics was most suited to the adsorption of reactive red onto chitosan beads The Freundlich isotherm was in agreement with the experimental data.**

Keywords: **Adsorption, Kinetics, Isotherms, Chitosan, Reactive Red Dye.**

I. INTRODUCTION

Dyes are colored substances that have an affinity to the substrates on which they are applied. 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 of pH, time, Initial dye concentration, adsorbent dosage, agitation speed and equilibrium isotherm of congo red on chitosan beds were investigated.

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.

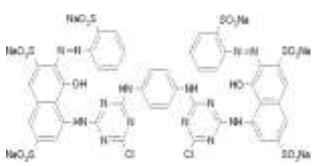


Figure 1. Reactive red dye

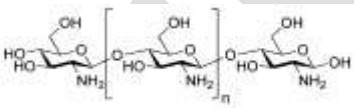


Figure 2. Chitosan

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.

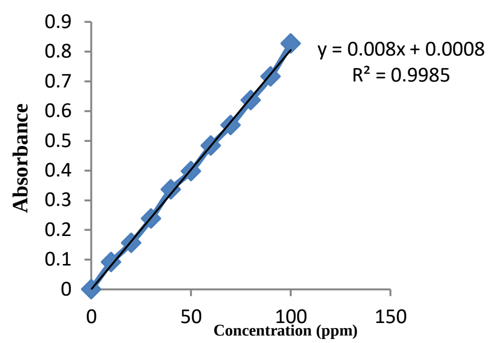
Epichlorohydrin or ECH is a widely known cross linking agent. The procedure for cross linking is as follows: The wet, non-cross linked chitosan beads are weighed in an electronic balance. These beads are suspended in 0.5 M NaOH solutions and ECH is added in the ratio 1:2 by weight. The beads in solution 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 known quantity of adsorbent is added to dye solution of known strength in a conical flask. This is then placed in a shaker for a specific period of time and then adsorbent is sieved out. The filtrate is analysed in the UV Spectrophotometer at the maximum wavelength for specific dye. The absorbance values are noted and corresponding concentrations are determined from the calibration chart.

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 Batch Kinetic Studies

3.1.1 Effect of agitation period

The batch adsorption of dye onto both normal and cross linked chitosan beads has been carried out by varying agitation time. The plot of adsorption capacity vs time shows that adsorption rate increases as time increases and it reached equilibrium adsorption at 180 minutes after which adsorption capacity remains constant.. Hence it can be concluded that the optimum time for adsorption of Reactive Red onto chitosan beads is 3 hours. Further it is seen that the ECH cross linked chitosan show a significant increase in efficiency than the normal beads**.**

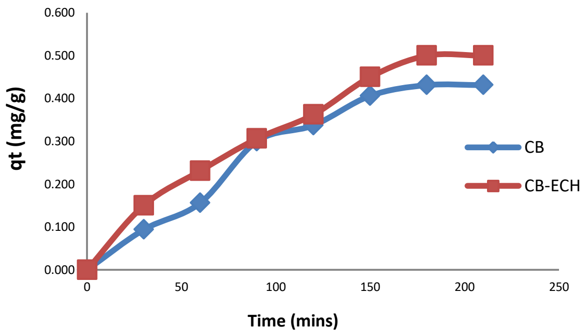
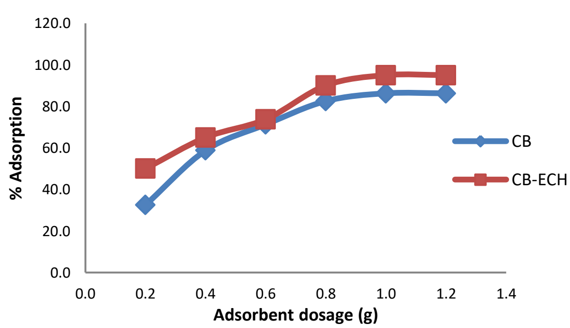


Figure: Effect of time on adsorption of dye (1g dosage)

3.1.2 Effect of Adsorbent Dosage

To study the effect of amount of adsorbent on the removal of dye, the dosage was varied from 0.2g to1.4g. The equilibrium value of amount adsorbed was found to increase from 0.2g to 1.0g of chitosan beads for 50ml of dye solution. Beyond 1g, there was no further increase in the amount adsorbed. Therefore the optimum dosage is 1g of adsorbent per 50ml of dye solution.Here, it is again observed that the ECH cross linking improves the efficiency of the adsorbent and a higher percentage removal is observed than that for normal beads.



3.1.3 Effect of Initial Dye Concentration

The extent of adsorption was observed with change in the initial concentration of dye. As seen in Fig.8 and Fig.9 it is evident that the amount of dye removed increases with increase in initial dye concentration and shows a maximum removal at the 100 ppm mark. The rate of adsorption increases steadily with time for solutions of higher concentrations while the increase is almost negligible at lower concentrations. This gives rise to the conclusion that lesser time and smaller adsorbent dosage may suffice for low concentrations, while 100ppm initial concentration is optimum for a period of 3 hours and an adsorbent dosage of 1g/50ml of solution.ECH cross linked beads again show a higher percent removal of dye as compared to normal beads.

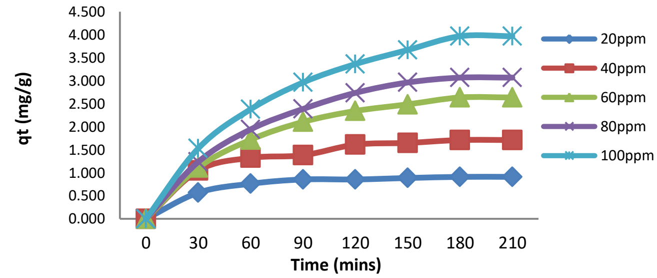


Figure: Effect of initial dye concentration on adsorption of dye onto chitosan beads

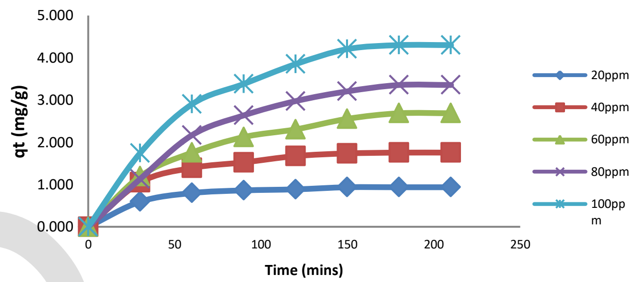


Figure: Effect of initial dye concentration on adsorption of dye onto ECH cross linked chitosan beads

3.1.4 Effect Of pH

The effects of initial pH of dye solution were observed by varying the pH between 2 and 6. Maximum efficiency was observed for cross linked beads at pH 3. It is important to note that the stability of normal beads is very poor in acidic medium and hence show poor efficiency. The beads were found to disintegrate in the lower pH solutions and disappear after some time. ECH cross linked beads are resistant to acidic medium and show an efficiency of 100% at the optimum conditions. As the pH increases and as the solution becomes more basic it is observed that the adsorption capacity of the chitosan beads decrease. This phenomenon can be exploited in research of regeneration of the beads.

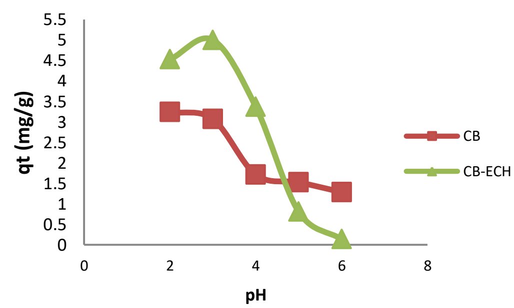


Figure: Effect of pH

3.1.5 Effect of Agitation Speed

Adsorption of reactive red dye onto chitosan beads was also studied with varying speeds of rotation in the range 120-

200rpm. At the lower and upper limits of this range, adsorption was found to be very less. The optimum rpm was determined as 160 rpm as shown in Fig. 11 .It can be concluded that at low rpm there is not enough interaction between the adsorbent and adsorbate while at high speeds, most of the solution is thrown outwards against the wall of the flask due to centrifugal force and the adsorbent is collected at the centre. In both scenarios the amount of dye adsorbed is very low compared to medium speeds. Here there is only a slight increase in % adsorption on ECH cross linked chitosan beads.

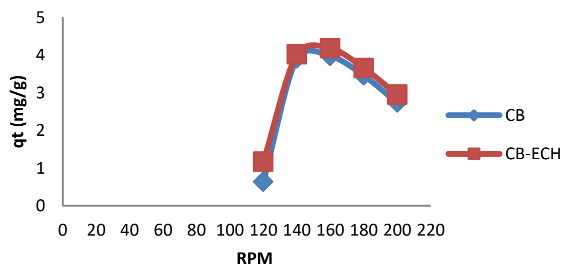


Figure: Effect of RPM on amount of dye adsorbed.

3.2 Equilibrium Adsorption Isotherms

The adsorption isotherms describe the equilibrium relationship between the amount of material adsorbed and the amount of adsorbent used. The Freundlich isotherm is mathematically expressed as: $\frac{x}{m} = k * C_e^{\frac{1}{n}}$

Where x is the amount of solute adsorbed, m is the mass of adsorbent, C_e is the equilibrium concentration of the solute, k and n are Freundlich constants. The constant k is related to the extent of degree of adsorption while n estimates the intensity of adsorption. Frendlich constants were determined from the graphs plotted for log(x/m) in ordinate and logc in abscissa. Freundlich constants evaluated for normal and cross linked chitosan beads for which equilibrium data is taken from effect of initial concentration on dyes. The results are shown in the figure14 & 15. The calculated results of Freundlich isotherm constants for both normal and cross linked chitosan beads are given in table 4&5.It is found that the adsorption of reactive dye on chitosan and ECH-crosslinked chitosan beads were correlated well(R >0.90).

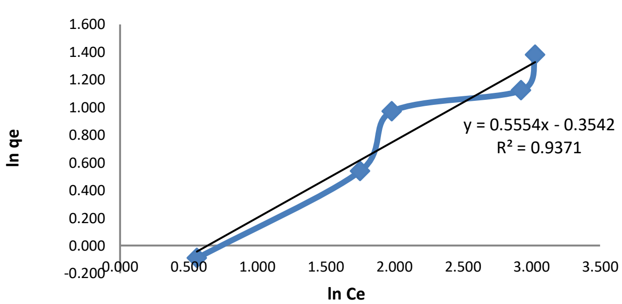


Figure: Freundlich isotherm for chitosan beads

Table 1: Freundlich constants for chitosan beads

Co	Ce	qe
20	1.750	0.913
40	5.750	1.713
60	7.250	2.638
80	18.625	3.069
100	20.625	3.969

n	k_f	R^2
1.802	0.702	0.937

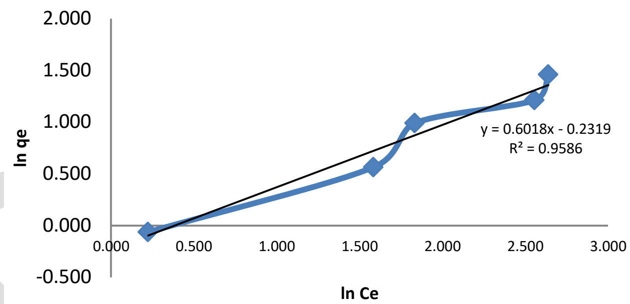


Figure: Freundlich isotherm for ECH cross linked beads

Table 2: Freundlich constants for ECH-crosslinked chitosan beads

Co	Ce	qe
20	1.250	0.938
40	4.875	1.756
60	6.250	2.688
80	12.875	3.356
100	14.000	4.300

n	k_f	R^2
1.664	0.794	0.958

The Langmuir isotherm is developed based on the assumption that a mono layer of adsorbate specieswill be forming onto the surface of the adsorbent. It has also been assumed that the surface sites are completely energetically homogeneous. The study of Langmuir isotherm is essential in assessing the adsorption efficiency of the adThe Langmuir isotherm is developed based on the assumption that a mono layer of adsorbate specieswill be forming onto the surface of the adsorbent. It has also been assumed that the surface sites are completely energetically homogeneous. The study of Langmuir isotherm is essential in assessing the adsorption efficiency of the adsorbentsorbent.

$$q_e = K_L C_e/(1+a_L C_e)$$

Where q_e is the amount of dye adsorbed per unit weight of adsorbent. C_e is the concentration of dye remaining in solution at equilibrium. K_L and a_L are the Langmuir constant. The slopes and y intercepts of plots of C_e/q_e versus C_e gives a straight line of slope a_L/K_L and y intercept $1/K_L$. The results are shown in figure 16 & 17.As observed by the plots of Langmuir isotherm, the regression coefficients are lower than 0.99 and are therefore it can be concluded that adsorption is not in agreement with the Langmuir Isotherm according to the experimental data.

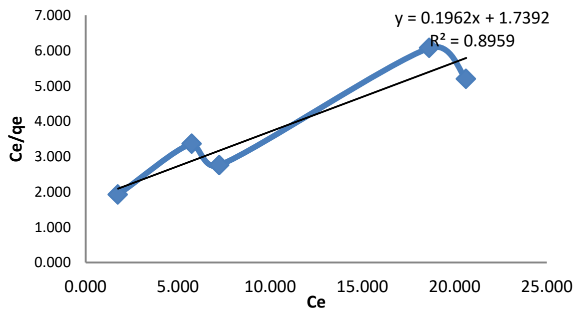


Figure: Langmuir isotherm for chitosan beads

Table 3: Langmuir constants for chitosan beads

Co	Ce	qe
20	1.250	0.938
40	4.875	1.756
60	6.250	2.688
80	12.875	3.356
100	14.000	4.300

k_l	a_l	R^2
0.679	0.106	0.804

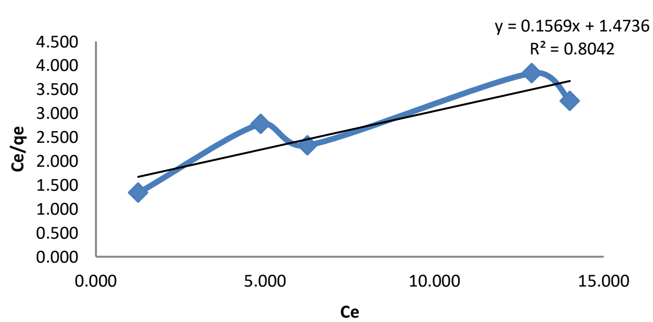


Figure: Langmuir adsorption isotherm for ECH cross linked chitosan

Table4: Langmuir constants for ECH cross linked chitosan beads

Co	Ce	qe
20	1.750	0.913
40	5.750	1.713
60	7.250	2.638
80	18.625	3.069
100	20.625	3.969

k_l	a_l	R^2
0.575	0.113	0.895

IV. CONCLUSION

Normal Chitosan beads and ECH-crosslinked beads were sucessfully able to adsorb Reactive dye from aqueous solutions. ECH cross linked beads show significantly higher adsorption capacity at optimum conditions than non-cross linked beads. The adsorption capacity increases largely with decreasing pH of the dye solution. The highest percent removal of anionic dye achieved at pH 3, in contact time of 3hrs, by adsorbent dose of 1g/50ml solution used and 100mg/L of initial dye concentration.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.Freundlich isotherm is best suited for the adsorption of Reactive red dye by Chitosan and cross-linked chitosan beads as indicated by experimental data. It can be concluded that the high adsorption capacity of the Chitosan and cross-linked chitosan beads could be a feasible medium for the removal of reactive dye from wastewater and potentially an alternative for the decolorization of wastewater.

REFERENCES

[1]. "Chitosan and chemically modified chitosan beads for acid dyes sorption", AZLAN Kamari , WAN SAIME Wan Ngah , Journal of Environmental Sciences 21(2009) 296–302
[2]. " Adsorption behaviour of reactive dye in aqueous solution on chemical cross linked chitosan beads", M.S. Chiou, H.Y. Li, Chemosphere 50 1095-1105, 2003.
[3]. "Influence of impregnation of chitosan beads with cetyl trimethyl ammonium bromide on their structure and adsorption of congo red from aqueous solutions", Sudipta Chatterjee , Min W. Lee , Seung H. Woo, Chemical Engineering Journal 155 (2009) 254–259
[4]. " Competitive biosorption of azo dyes from aqueous solution on the templated crosslinked-chitosan nanoparticles", Chia-Yun Chen, Jen-Chao Chang, Arh-Hwang Chen Journal of Hazardous Materials185 (2011) 430–441
[5]. "Nitrate removal from aqueous solutions by cross-linked chitosan beads conditioned with sodium bisulfate" , Sudipta Chatterjee , Dae S. Lee, Min W. Lee, Seung H. Woo, Journal of Hazardous Materials 166 (2009) 508–513
[6]. "Adsorption of heavy metal ions, dyes and protiens by chitosan and its derivatives-A review", Liu. et al. J. Ocean Univ. China (Oceanic and coastal sea research) 2013 12: 500-508,
[7]. "Adsorption of methyl orange onto chitosan from aqueous solution",T.K.Saha et al.J. Water Resource and Protection,2010,2,898-906 .
[8]. "Adsorption of reactive azo dyes on chitosan/oil palm ash composites adsorbent :batch and continuous studies " Masitah Binti Hasan University Sains Malaysia (2008).
[9]. "Euilibrium Studies on the removal of Methyl Orange from Aqueous Solution by Adsorption on to Bioploymer"Gurusamy Annadurai et al.Drug Invention Today2012,4(11),590-593.,
[10]. "Studies of Chitosan at Different pH's in the Removal of Common Chlorinated Organics from Wastewater "Jih-Hsing Changa,, Ching-Lung Chena, Amanda V. Ellis b, and Cheng-Hung Tungc,

International Journal of Applied Science and Engineering ,2012. 10, 4: 293-306.

[11]. "Kinetic Model for the Removal of Methyl Orange (Dye) From Aqueous Solution Using Avocado Pear "A.K Asiagwu,, P.E Omuku, & C.O Alisa, Journal of Chemical, Biological and Physical Sciences, Vol. 3, No. 1, 48-57.