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Removal of Eosin Y Dye by Biosorption Using Chitin-Alginate Beads From Peneaus Monodon Shells.

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ABSTRACT

This study aims for a biosorption treatment of eosin Y an anionic standard dye using chitin-alginate beads obtained from shrimp shells. Chitin was made into beads using sodium alginate and batch adsorption of a standard dye eosin Y was carried out. Parameters such as contact time, dye concentration and pH were optimized. The adsorption isotherm and kinetic studies states that it follows Langmuir isotherm and pseudo second order kinetics. Physical and chemical characterization was also done with FTIR and TGA. From TGA it was observed that the thermal stability is up to 260°C and decomposition starts with higher temperatures. The efficient removal of eosin Y from the aqueous solution was 83% with the optimized parameters. From this work it is inferred that chitin a polymer from waste shrimp shells can be used as biosorbent for treating the dye waste water from the dyeing units of textile industry.

Keywords: Chitin-Alginate, Eosin Y, Adsorption, Optimization

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INTRODUCTION

The art of applying color to fabric was known to mankind in 3500 BC and since then the use of synthetic dyes have provided a wide range of colorfast, bright hues. It is estimated that over 7×10^5 tons of synthetic dyes are annually produced worldwide and over 10,000 different dyes and pigments are used industrially [1]. Up to 200,000 tons of these dyes are lost to effluents every year during dyeing and finishing operations in the textile industries. This accounts to 17 to 20 percent of industrial water pollution as estimated by the World Bank [2]. There are over 7000 large-scale textile printing and dyeing industries in India concentrated mainly in Gujarat, Maharashtra, Rajasthan and Tamil Nadu states. They are water-intensive industries requiring a large volume of freshwater at various steps of processing and therefore, the volume of wastewater produced too is equally large [3]. 72 toxic chemicals have been identified in water solely from textile dyeing, out of which, 30 cannot be removed. About 40 percent of colorants that are used globally contain organically bound chlorine, a known carcinogen. Their toxic nature has become a cause of grave concern to environmentalists. Also, this represents an appalling environmental problem for the clothing and textile manufacturers [4].

Eosin Y is a pink, water soluble, heterocyclic acid dye, containing bromine atoms displaying yellow-green fluorescence [5]. Due to its vivid color, the dye is commonly used in the fields of dyeing, printing, leather and also for printing inks and fluorescent pigments, etc. The toxic nature of the dye is still not quantified enough, but its prevalence in the living systems is proved to be harmful. Thus, there is a need for introducing an efficient method for the removal or recovery of eosin generated from industrial waste solutions [6]. Biological methods are also ineffective in degrading Eosin Y due to its stability to oxidizing agents, heat, light and complex aromatic structure [7]. Thus, the safe removal of such a harmful dye is the prime aim of our present research and this could be accomplished by using chitin. It is the major component of crustacean shells, cuticles of insects, fungal cell walls, yeast, green algae [8, 9, 10] and is found in enormous amount which can be easily obtained by simple extraction [11].

MATERIALS AND METHOD

Preparation of Adsorbent (Chitin Beads) and Standard Eosin Y Dye

1g of sodium alginate was dissolved with 100ml of distilled water by continuous stirring at warm temperature. To this solution 2g of chitin powder was added and stirred until a gel formation occurs. The chitin alginate solution was introduced as droplets into calcium chloride solution (5%) through a sterilized dropper and uniform sized beads were formed. The bead size was measured by volume displacement method. The chitin beads were washed with distilled water and stored in refrigerator. 1% stock solution of eosin Y dye was prepared by dissolving 0.1g of eosin Y powder in 100ml of distilled water. From the stock the working solution of 0.01%, 0.02%....0.1% was prepared. The absorbance was recorded at 540nm and a standard graph was plotted.

Optimization Process

The effect of various parameters like contact time from 10min to 120min, concentration of eosin Y (0.1g/L to 1 g/L), initial pH (2 to 8) were optimized for the process of adsorption.

Adsorption Process and its Characterization

Batch adsorption process was carried out with the optimized parameters. The amount of dye adsorbed per unit mass was calculated as

$$Q_e = (C_i - C_e)V/m$$

Where C_i and C_e are the initial and equilibrium concentration (mg/L), m is the mass of the adsorbent (g) and V is the volume of the solution (mL).

Percent dye removal (DR) was calculated using the equation

$$\% DR = (C_i - C_e) / C_i * 100$$

The sample was dried completely in desiccator before FTIR. Chitin-eosin Y dye disks was prepared with KBr and analyzed using ASCII PEDS 1.60 instrument in the standard range of 4000 to 400 cm^{-1} .

TGA was also carried out using 6.9370 mg of sample in TGA Q50 V20.13 Build 39 instrument to check for the sample mass with respect to time and temperature in the range of 50°C to 800°C.

Adsorption Isotherms and Adsorption Kinetics

The two adsorption isotherms, Langmuir isotherm [12] and Freundlich isotherm [13] along with separation factor validating Langmuir were determined. Pseudo-first order, second order kinetic [14] and intraparticle diffusion models were studied to analyze the controlling mechanisms and the chemical reactions of eosin Y dye adsorption on chitin beads.

RESULTS AND DISCUSSION

The chitin beads formed were of uniform size measuring 0.22cm radius and the beads before and after adsorption as shown in fig. 1 and fig. 2.



Fig 1: Chitin-Alginate beads



Fig 2: Eosin Y dye adsorbed on chitin-alginate beads

Fourier Transform Infrared (FTIR) of Chitin-Eosin Y

Fig 3 shows FTIR of chitin-eosin Y. The peaks at 3484.74 cm^{-1} and 1623.77 cm^{-1} can be attributed to -NH vibrations and -azo group, while the peak at 2887.88 cm^{-1} illustrates the asymmetric stretching of -CH. The peak at 1118.51 cm^{-1} indicates the aliphatic secondary amine, while the peak at 1658.04 cm^{-1} indicates the formation of aliphatic amines confirming the adsorption of eosin Y with chitin.

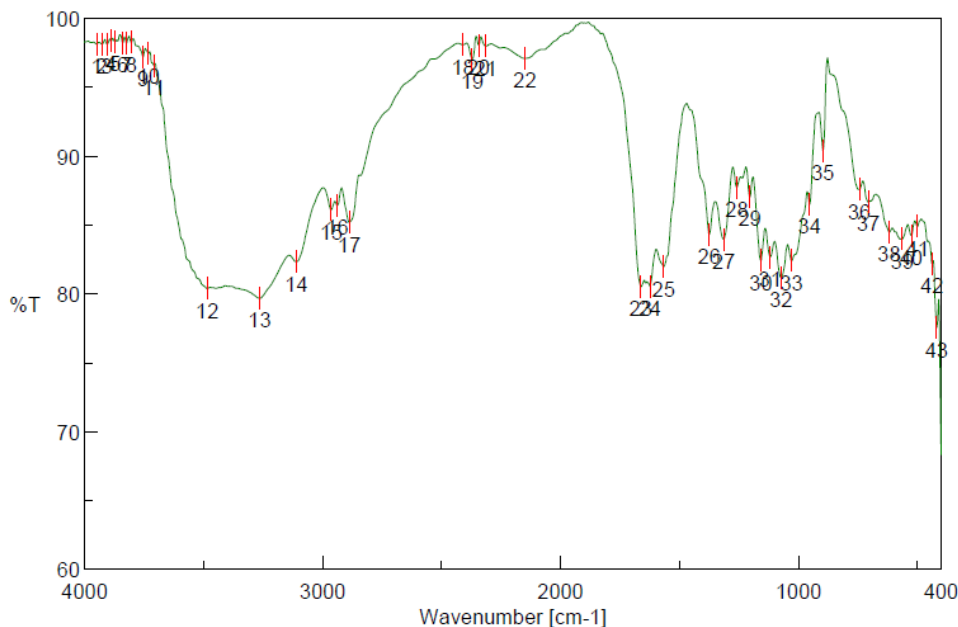


Fig 3: FTIR of Chitin-Eosin Y

Thermal Gravimetric Analysis (TGA) of Chitin-Eosin Y

The weight loss of chitin-eosin Y in the range of 25°C to 140°C was around 8% due to water evaporation. The second stage from 140°C to 260°C showed a loss of 4% due to dehydration and depolymerization. Further decrease in weight of 45% was observed in the 260°C to 385°C which attributes to the residual decomposition. The final residue obtained was 0.879mg at 800°C (fig. 4). A similar trend was observed by Anna Puchalska [15] using chitosan blended with hydroxyapatite, nanoclay and nanosilver.

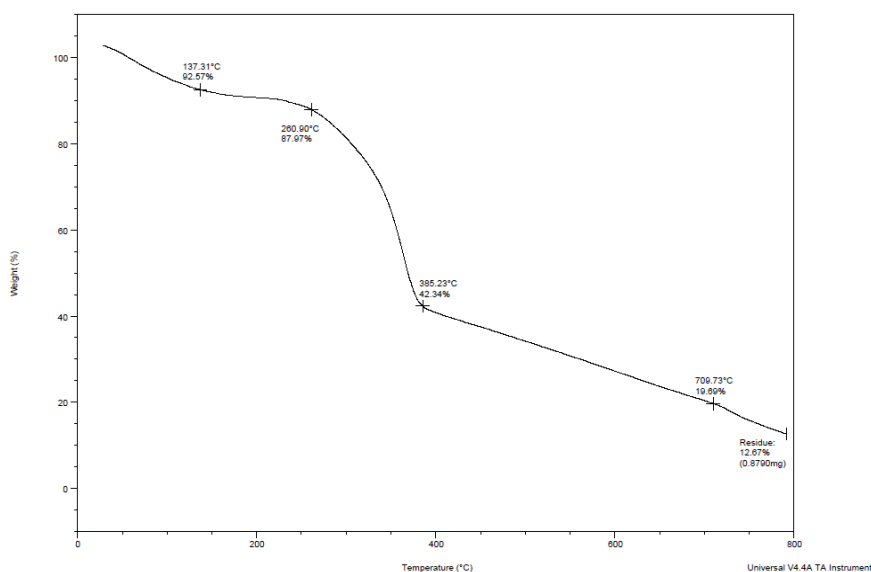


Fig 4: TGA of Chitin-Eosin Y

Effect of pH on the adsorption process

In acidic pH 3 a maximum adsorption of 83% was obtained, on the contrary at higher pH 5.5 adsorption decreased drastically (fig. 5). This can be due to the fact that at low pH, the amine group on chitin is protonated and it exerts an electrostatic pull on anionic eosin dye. However at higher pH more OH⁻ is formed and it competes with the anionic dye to bind to the adsorption site onto the adsorbent [5, 16].

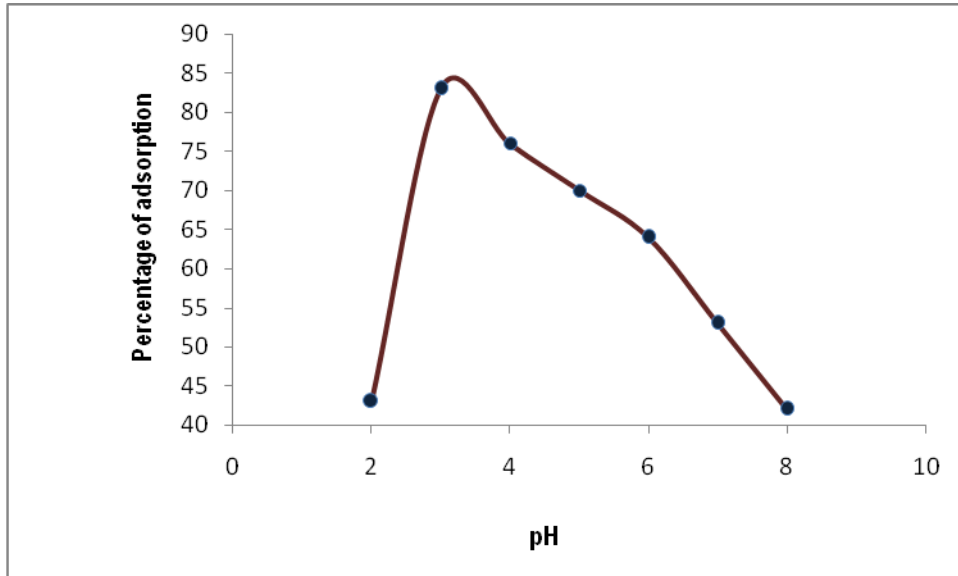


Fig 5: Effect of pH on the adsorption process

Effect of dye concentration

The percentage of adsorption of eosin Y by chitin beads is plotted as a function of dye concentration in fig. 6 and the maximum adsorption of 83% was observed at 700mg/L. The adsorption increases with the increase in the initial dye concentration and above 700mg/L there is a decline in the curve which attributes to the fact that the saturation of adsorption site has occurred and a decrease in the available surface area of the adsorbent [17, 18].

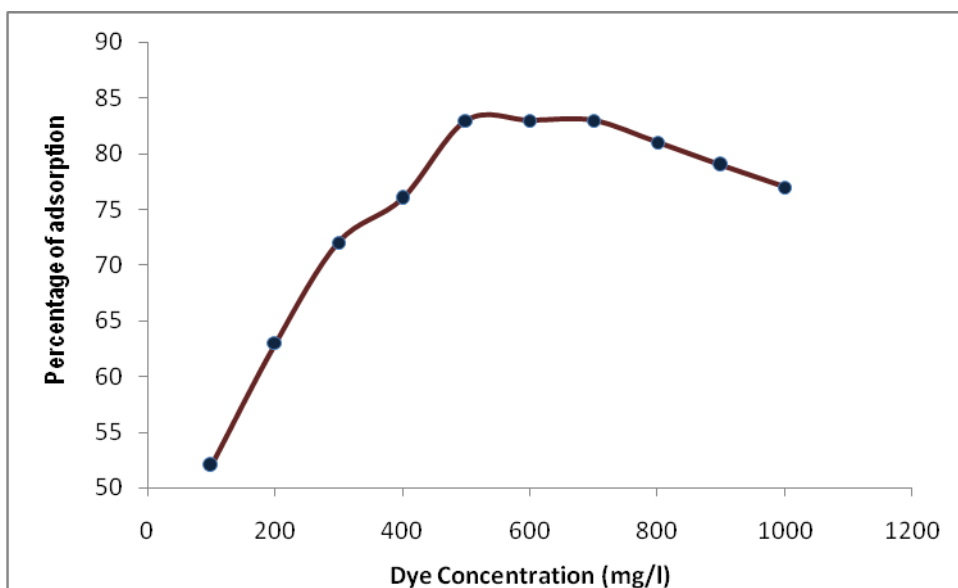


Fig 6: Effect of dye concentration

Effect of contact time

The optimum contact time for the dye to be adsorbed by chitin beads is 90min. From the graph (fig. 7), it is clear that the extent of adsorption is rapid in the initial stages and becomes slow in later stages till saturation is allowed. The final dye concentration did not vary significantly after 90 min from the start of adsorption process. This shows that equilibrium can be assumed to be achieved after 90 min. It is basically due to saturation of the active site which does not allow further adsorption to take place. A similar adsorption pattern was reported by Nandhakumar et al. [19] where the maximum adsorption of eosin Y was at 100min.

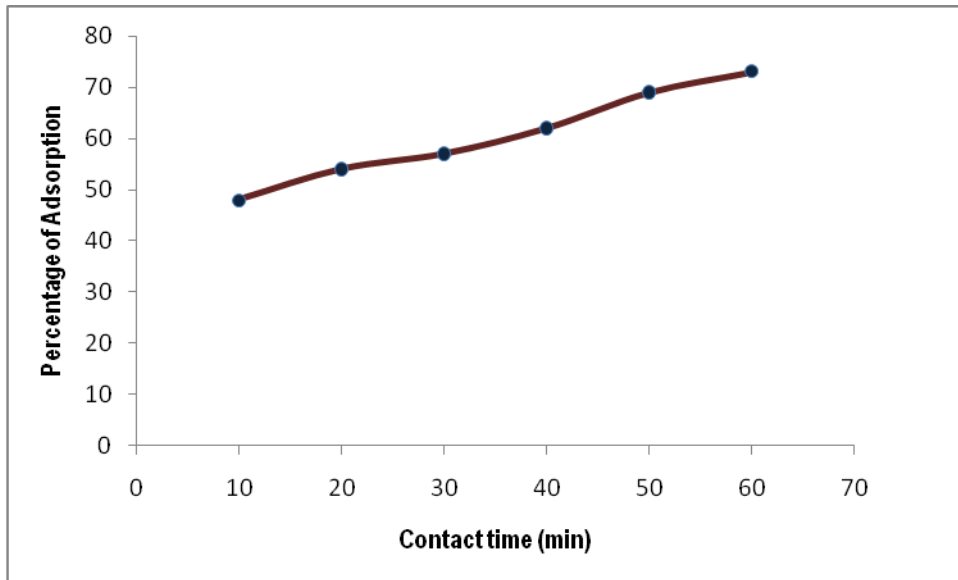


Fig 7: Effect of contact time

Langmuir isotherm

For Langmuir isotherm calculation a graph is drawn with C_e/Q_e vs. C_e . From the graph (fig. 8) it is inferred that $R^2 = 0.98$ indicating adsorption of eosin Y dye on chitin beads fits Langmuir isotherm and also the process is favorable. Sudipta Chatterjee et al. [20] stated irreversibility and best fit in Langmuir equilibrium of eosin Y adsorption with chitosan hydro beads.

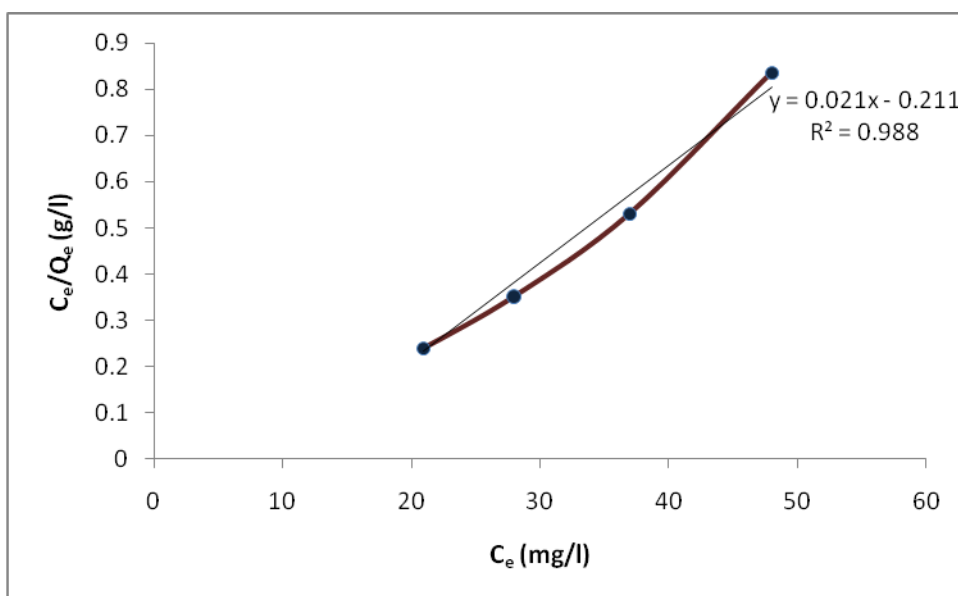


Fig 8: Langmuir Isotherm

Separation factor

R_L values within the range $0 < R_L < 1$ indicate favorable adsorption, $R_L > 1$ is unfavorable, $R_L = 1$ is linear, $R_L = 0$ is irreversible. R_L values in this study is in the range of 0.01 to 0.09 (fig. 9) indicating favorable Langmuir adsorption isotherm. This is comparatively high than that of teak leaf litter powder adsorption [21]

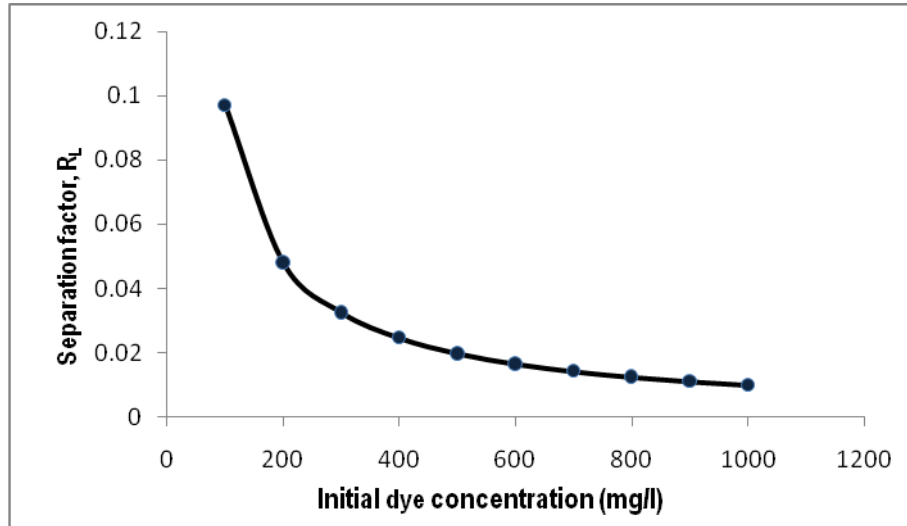


Fig 9: Separation Factor

Freundlich isotherm

Freundlich isotherm was calculated using the linearized form the equation

$$\log q_e = \log K_f + 1/n \log C_e$$

Where K_f is the Freundlich's constant. The n value should be between 1 and 10 for Freundlich to be favorable. From fig. 10, $n = 0.33$ which is below 1 signifying adsorption of eosin Y dye on chitin beads fits Langmuir isotherm similar to that of teak sawdust [22].

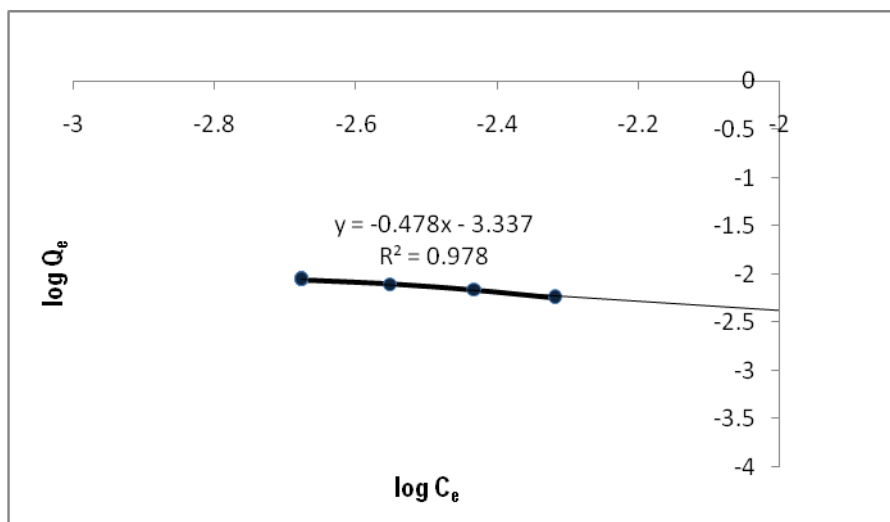


Fig 10: Freundlich Isotherms

Adsorption kinetics

A graph of $\log (q_e - q_t)$ against t was plotted to determine the pseudo-first order kinetics rate constant k_{ad} , and correlation coefficient, R^2 , as shown in fig. 11. R^2 value was found to be 0.906 and rate constant was 0.4899 min^{-1} . Fig. 12 shows pseudo-second order kinetics correlation coefficient, R^2 value which was 0.914 and the rate constant was 0.740 g min/mg . The correlation coefficient and rate constant obtained from the pseudo-second order plot (R^2 and K_2) was found to be better than that of pseudo-first order plot (R^2 and K_1) showing that application of pseudo-second order plot was the best for adsorption of eosin Y dye on chitin beads. Xiao-Yi Huang et al. [23] studied a similar adsorption pattern with ethylene diamine modified chitosan proving that the rate limiting step is the adsorption mechanism and not the mass transfer [24].

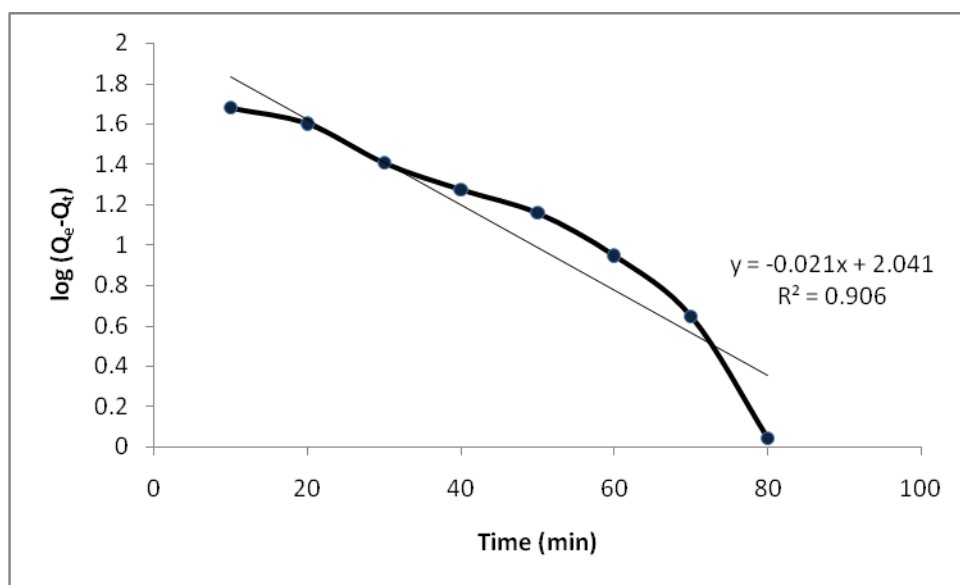


Fig 11: Pseudo-First Order Kinetics

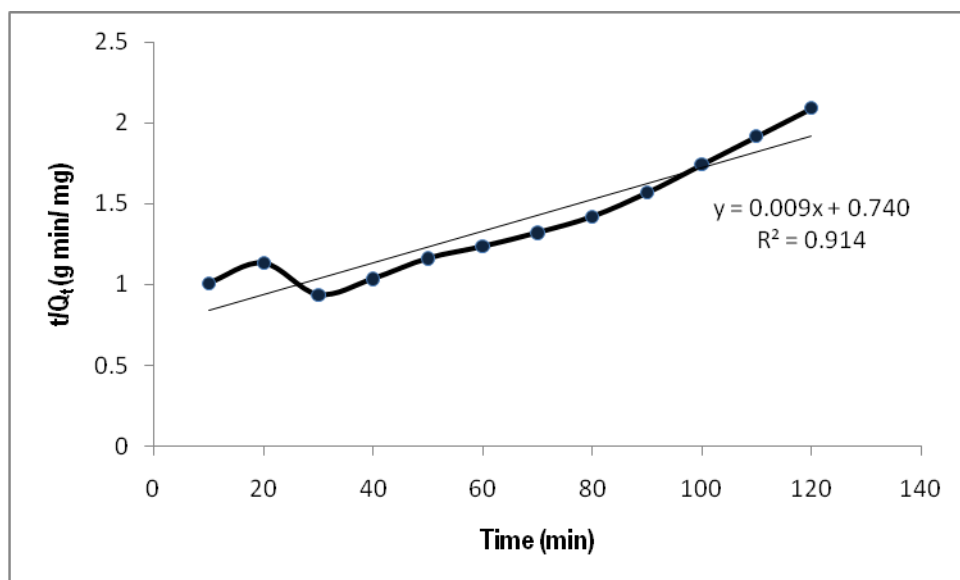


Fig 12: Pseudo-Second Order Kinetics

Intraparticle diffusion

In the intraparticle diffusion graph (fig.13) the slope of linear portion gives rate constant of diffusion $K_i = 6.434 \text{ mg/g min}^{1/2}$. The linear portion of the plot shows that intraparticle diffusion of dye has taken place

and it is multistage process with external surface adsorption as the first stage followed by intraparticle diffusion and finally equilibrium as the third stage [25]. When the intercept value is larger, it denotes that there is a larger boundary layer. Here, since the intercept value is low, there is no boundary layer formation.

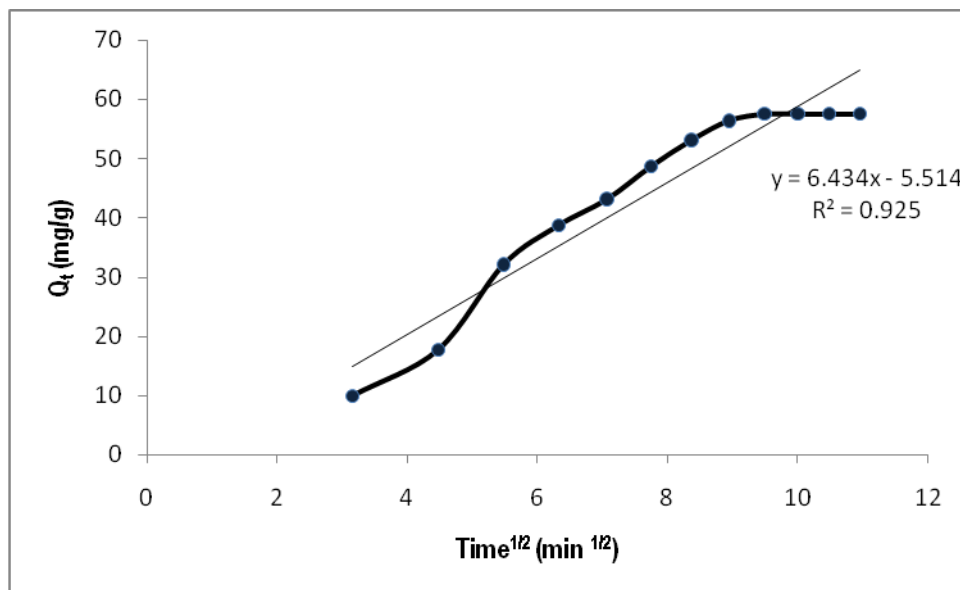


Fig 13: Intraparticle Diffusion

CONCLUSION

The present study proves that with optimized pH 3, initial dye concentration of 700mg/l and contact time of 90 min 83% eosin Y dye can be removed from aqueous solution. Hence chitin-alginate beads can act as better adsorbent for the removal of standard anionic dyes from the textile effluent and protect the aquatic environment.

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