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An Unmitigated Study on Adsorption Behavior of Acid Black Dye on Titanium Coated Chitosan Beads.

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ABSTRACT

Photo catalysis using TiO_2 is one of the effective methods for dye decolourization, in addition the sequestration of these photo catalysed dyes using biopolymer are recent method of interest for complete removal of dyes from the waste water. In this preliminary attempt the chitosan was extracted from prawn shell wastes and utilized for biosorption of azo dyes. This polymer was encapsulated over glass beads after amended with TiO_2. The encapsulated glass beads were packed in a glass column and azo dye decolorizationwas carried out and determined colorimetrically using UV-Visible spectrophotometer. The characterization of glass beads with TiO_2 amended chitosan and azo dye adsorbed TiO_2 amended chitosan was evaluated using Field Emission Scanning Electron Microscopy(FESEM) and Fourier Transform Infra Red spectroscopy (FTIR). The adsorption kinetics models and Langmuir, Freundlich and Temkin equilibrium isotherm models were also ascertained.

Keywords: Chitosan, Chitosan TiO_2, decolorization, Acid Black, Adsorption, Kinetics.

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INTRODUCTION

Chitin is the second most important natural polymer in the world. The main sources exploited are two marine crustaceans, shrimp and crabs [1, 2]. Dyes play a significant role as pollutants when they are disposed into precious water resources without proper treatment[3]. Azo dyes are major constituents of the dyes which xenobiotic and resist degradation. As a part of purification, adsorption attracts a foremost role in dye removal. The developing exigency for efficient and low-cost treatment methods and the value of adsorption has resulted in identifying the low-cost alternative adsorbents (LCAs) [4].

There is a need to identify substitute treatments that for removing dyes from large volumes of effluents in low cost, such as biological or combination systems. This article analysis the effective technologies in converting chitosan into effective, energy and cost effective alternative for dye removal and decolorization applicable on large scale.

EXPERIMENTAL

Preparation of Chitosan

The adsorbent materials used in this study was Chitosan. The shell waste of prawn have been collected from the Royapuram fishing harbor (13.1256° N, 80.2976° E) and cleaned using distilled water and dried under sunlight. The dried shell was and cleaned them using distilled water and dried them. In 4% NaOH the samples was boiled and allowed to cool for 30 minutes at room temperature [5] [6]. For demineralization 1% HCl was used four times its quantity and the samples were allowed to soak for 24 h to remove the minerals (mainly calcium carbonate) [7].

The demineralized shrimp shell samples were then treated for one hour with 50 ml of a 2% NaOH solution to decompose the albumen into water soluble amino-acids. The remaining chitin is washed with deionized water, which is then drained off. The chitin was further converted into chitosan by the process of deacetylation [8]. The filtered chitosan is kept in a muffler furnace at 150°C until it becomes fully dried.

Preparation of bio- polymer and encapsulation over glass beads

The washed glass beads were soaked in Potassium di chromate solution and washed with water was dipped in a bio-polymer for encapsulation and the encapsulated glass beads are taken in a Petri plate for drying purpose and this encapsulate glass beads is dried in a room temperature.[9]

Chitosan –Titanium dioxide polymer (CH-TiO_2)

1 gram of TiO_2 powder and mix with the bio-polymer and it is stirred until it becomes homogenous [10].

Preparation of 1 ppm Dye Solution

Preparation of Dye solution is carried out by mixing 1 mg of azo dye namely “Acid Black” powder with 1 litre of distilled water.

Dye decolorization

For dye decolorization, two burette and fill that with the encapsulated glass beads. In 1st burette, the encapsulated chitosan-TiO_2 glass beads and in 2nd burette we fill the glass beads which was not encapsulated. After filling the burette with a certain height (25cms), the burettes were filled with the dye solution (Acid Black) and studied the decolorization of dye by taking samples in some fixed interval and checked the decolorization by using Varian Cary UV-Vis Spectrophotometer [11][12].

Mathematical modeling study

Adsorption Isotherm design

If the adsorbent and adsorbate are contacted long enough, an equilibrium will be established between the amount of adsorbate adsorbed and the amount of adsorbate in solution. The equilibrium relationship is described by **adsorption isotherms** [13] [14] [15].

Langmuir Isotherm

The Langmuir model is based on the assumption that the maximum adsorption occurs when a saturated monolayer of solute molecules is present on the adsorbent surface, the energy of adsorption is constant and there is no migration of adsorbate molecules in the surface plane.

The Langmuir equation may be written as:

$$Q_e = \frac{Q_{max} K_L C}{1 + K_L C}$$

The Langmuir equation can be expressed in its linear form as:

$$\frac{c_e}{Q_e} = \frac{1}{Q_m K_L} + \frac{c_e}{Q_m}$$

Where Q_{max} (mg/g) and K_L (L/mg) are the Langmuir constants, representing the maximum adsorption capacity for the solid phase loading and the energy constant related to the heat of adsorption respectively. The values of Q_m and K_L can be evaluated from the intercept and the slope of the linear plot of experimental data.

Freundlich Isotherm.

The Freundlich isotherm model is an empirical relationship defining the adsorption of solutes from a liquid to a solid surface and assumes that dissimilar sites with adsorption energies are involved. Freundlich adsorption isotherm is the relationship between the amounts of ligand adsorbed per unit mass of adsorbent, q_e, and the concentration of the nickel at equilibrium, C_e.

$$Q_e = k_f C_e^{1/n}$$

The logarithmic form of the equation becomes,

$$\mathbf{Log\ q_e = log\ k_f + (1/n)\ log\ Ce}$$

Where K_f& n are the Freundlich constants, the characteristics of the system.K_f and n are the indicators of the adsorption capacity and adsorption intensity, respectively. The ability of Freundlich model to fit the experimental data was examined. For this case, the plot of log Ce vs. log qe was employed to generate the intercept value of $K_f$and the slope of n.

Temkin isotherm.

The Temkin isotherm has been used in the following form:

$$\mathbf{q_e = (RT/b)\ log\ (A\ c_e)}$$

A linear form of the Temkin isotherm can be expressed as:

$$\mathbf{q_e = (RT/b)\ log\ A + (RT/b)\ log\ c_e}$$

$$q_e = B \log A + B \log c_e$$

The adsorption data can be analyzed according to Therefore a plot of q_e versus $\log C_e$ enables one to determine the constants A and B.

Adsorption kinetics

To observe the adsorption kinetics on Chitosan coated with Titanium oxide, the pseudo-first-order and pseudo-second-order models was used to fit the experimental data [16] [17] [18].

The **first order equation** of Lagergren is generally expressed as follows.

$$dq/dt = k1\ (qe - qt)$$

whereq$_e$ is the amount of dye adsorbed at equilibrium (mg/g), q_t is the amount of dye adsorbed at time t (min^{-1}), and k_1 is the rate constant of pseudo-first-order adsorption. If it supposed that q=0 at t=0, then:

$$\log (q_e - q_t) = \log qe - k_1 t$$

The **pseudo-second-order** kinetic rate equation is expressed as follows.

$$dqt/dt = k_2\ (qe - qt)\ 2$$

Where K_2 is the rate constant of **pseudo-second-order** reaction (g/mg/min). The integrated form of Equation when (t=0 →t and qt=0→ 0qe) the following expression is obtained:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

Where qe, qt are the amounts of adsorbent at equilibrium and at time t (mmol g^{-1}), k_1 is the rate constant of pseudo-first order kinetics equation (min^{-1}), and K_2 is the pseudo-second order rate constant (g $mmol^{-1}$ min^{-1}).

Characterization of Chitosan –Titanium dioxide polymer (CH-TiO_2)

Field Emission Scanning Electron Microscope (FESEM) [19] [20]

FESEM is a type of electron microscope that uses a focused beam of high-energy electrons in producing a variety of signals at the surface of a solid specimen. The carefully chosen effective samples were placed in module and observed in SUPRA 55, CARL ZEISS Germany, and micrographs were taken at different magnification.

Fourier Transform Infrared Spectroscopy [21] [22]

Fourier Transform Infrared spectroscopy is a valuable tool in determining specific functional groups or chemical bonds that exist in a material after pelletizing with KBr crystals and analysed in FTIR (BRUKER).

RESULT AND DISCUSSION

Effect of pH

Solutions of dye (acid black) with different pH was prepared, the effect of pH variation from 4.0 - 9.0 was studied by adjusting the pH of dye solution using 0.1N HCl or NaOH and it was shown that %removal of dye was maximum at pH 8. The initial and final concentration was observed by using UV spectroscopy. The Graph was drawn between pH and % removal of the dye on CT glass beads.

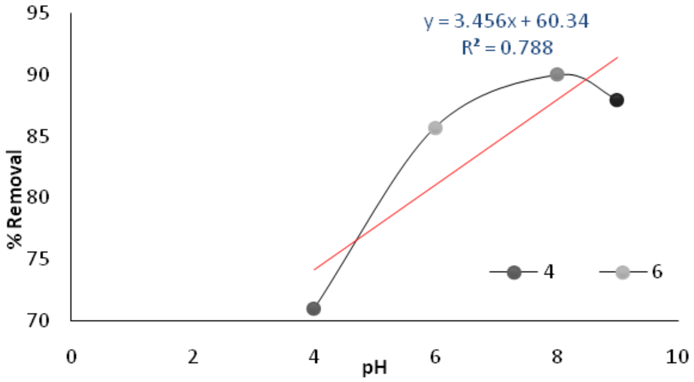


Figure 1: Variation of % Removal at different pH at 100ppm

Effect of contact time

The effect of contact time for dye adsorption on CT glass beads is shown in figure -2 and it was observed that in the 1st hour the % removal was very high. After 4th hour equilibrium attains so there is negligible % of removal.

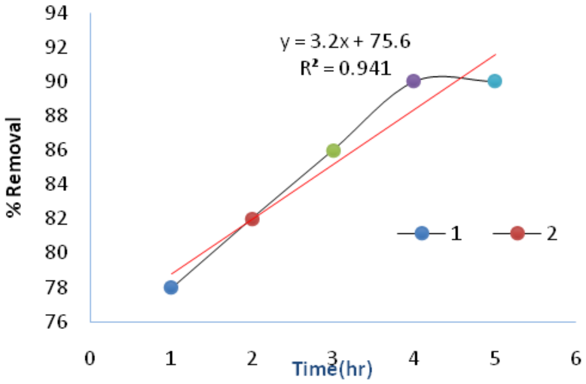


Figure 2: % Removal of dye at different time interval

From the above figure which is plot between time and % removal, shows that equilibrium attains at 4th hour and after that there is no change in the percentage removal.

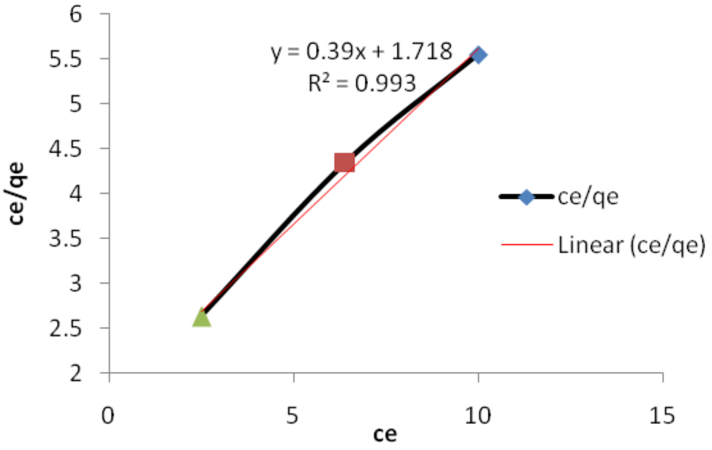


Figure 3: Langmuir equilibrium isotherm model for the adsorption of dyes on Chitosan Titanium (CT) beads at pH 8.

The Langmuir isotherm model was chosen for the estimation of maximum adsorption capacity corresponding to complete monolayer coverage on the glass beads surface and it is observed that adsorption capacity is more in Chitosan –Titanium dioxide (CT) glass bead as the valve of K_l is higher for CT which is shown in table 1.

Table 1 Linear Langmuir isotherm parameters

Bio Polymer	q_m	K_l	R^2
CT	2.60	0.2202	0.9939

Freundlich Isotherm.

The Freundlich model was chosen to estimate the adsorption intensity of the adsorbate on the adsorbent surface.

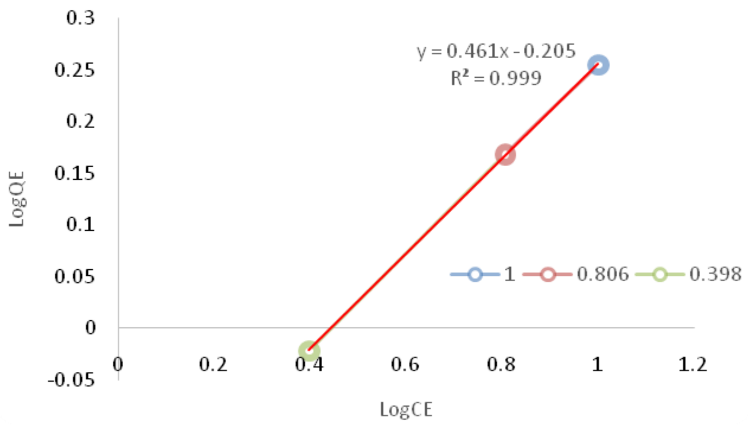


Figure 4: Freundlich equilibrium isotherm model for the adsorption of the dyes on Chitosan Titanium (CT) glass beads at pH 8.

The experimental data from the batch adsorption study the dye removal is plotted logarithmically using the linear Freundlich isotherm equation. It is observed that the value of K_f is more in CT as compared to C which is shown in Table 2.

Table 2: Freundlich isotherm parameters

Bio polymer	1/n	K_f	r^2
CT	0.461	0.623	0.999

Temkin isotherm.

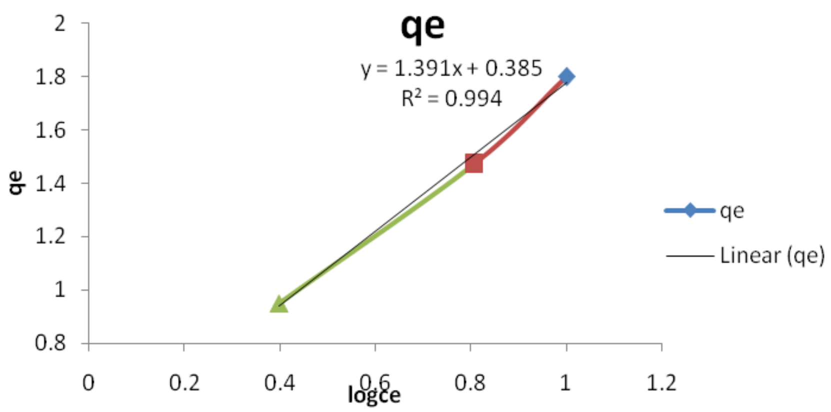


Figure 5: Temkin equilibrium isotherm model for the adsorption of the dyes on Chitosan Titanium (CT) glass beads at pH 8.

Table 3: Temkin isotherm parameters

Biopolymer	K_T	B_T	r^2
(CT)	1.89	1.3915	0.9949

Adsorption kinetics

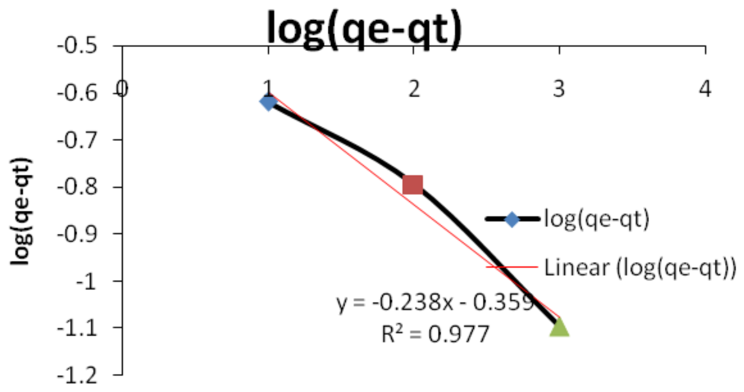


Figure 6: Kinetic models for the adsorption of dye on Chitosan Titanium (CT) glass beads

Table 4: Kinetic models for the adsorption of dye on Chitosan Titanium (CT) glass beads.

Time (hr)	q_t	t/q_t
1	1.56	0.64
2	1.64	1.21
3	1.72	1.744

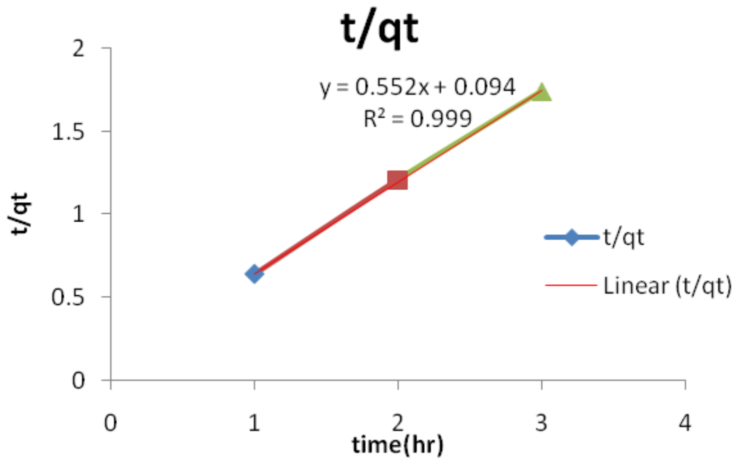


Figure 9: Kinetic models for the adsorption of dye on Chitosan Titanium (CT) glass beads.

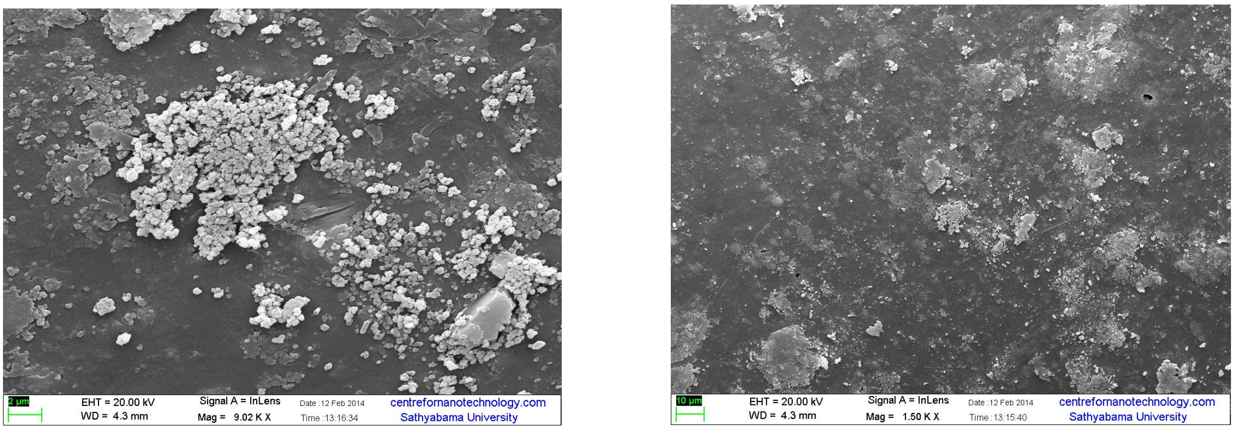
The $q_{e,exp}$ for C is 1.72 and using 1st order kinetics the value of $q_{e,calc}$is 0.56 which is having very large difference with $q_{e,expt}$whereas by using 2nd order kinetics the value of $q_{e,calc}$is 1.8 which is closer to $q_{e,expt}$and same situation is observed for CT that indicates so follows 2nd order kinetics.

Table 5: Parameters of the kinetic models for the adsorption dye onto Chitosan Titanium glass beads

	Pseudo first order				Psedo second order			
Bio polymer	$q_{e,exp}$	k_1	$q_{e,cal}$	r^2	k_2	$q_{e,cal}$	h	r^2
(CT)	1.8	0.2385	0.43	0.9776	3.243	1.82	10.63	0.9996

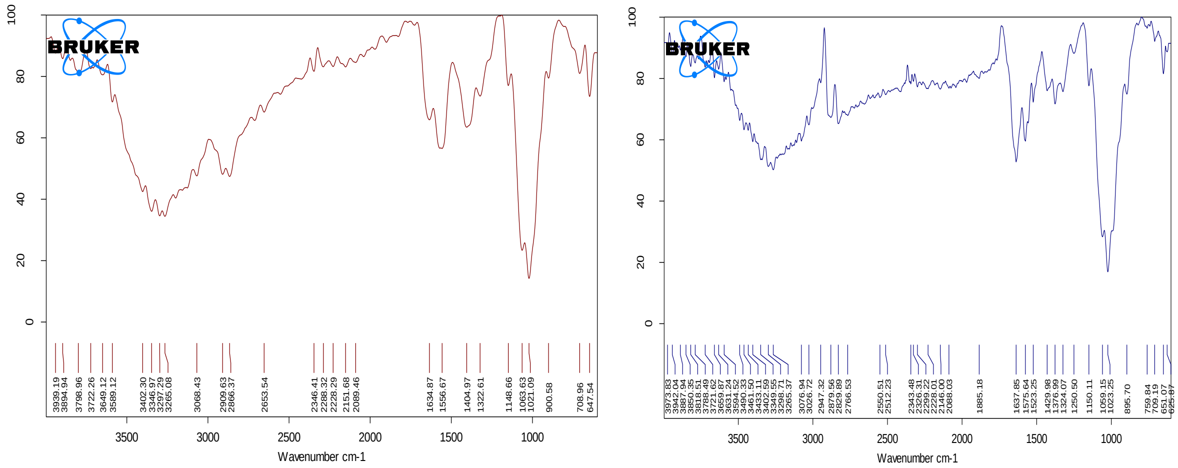
Characterization of Extracted chitosan

Characterization was done to understand the quantitatively the elements present in the bio polymer. It is carried out by Fourier Transform Infrared Spectroscopy (FTIR) which confirms the aliphatic amines and nitro compounds which are usually present in chitosan biopolymer (Fig. 8 a&b). Whereas the images of FESEM reveals the adsorption of azo dyes in a dispersed manner over chitosan and chitosan amended Titanium dioxide glass beads (Fig. 7 a & b).



(a) (b)

Figure 7: SEM images (a) before adsorption of dye with Chitosan with Titanium (b) after adsorption of dye



(a) (b)

Figure 8: FTIR images of Chitosan titanium dioxide after and before removal of dye

The kinetics study and adsorption isotherms vividly explain the mechanism of adsorption of acid black onto chitosan titanium dioxide encapsulated glass beads. The present study also infers that the pH of aqueous solutions significantlyaffect the adsorption capacity of dye. The pseudo second-order kinetic model agrees very wellwith the dynamical behaviour for the adsorption of dye by chitosan titanium dioxide encapsulated glass beads.

Thus the study concludes that chitosan amended with titanium dioxide may be used as alow-cost, energy effective and environmental friendly adsorbent for the removal ofazo dyes from textile wastewater as an alternativeto present adsorbents.

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