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Research Article

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Extraction of chitosan from prawn shell waste and its application in dye decolorization

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ABSTRACT

This paper presents an approach to remove the dye using chitosan coated glass beads at various pH, temperature and contact time. Dye decolorization using biopolymers are recent method of interest to remove the dyes from the waste water. In this initial attempt, the chitosan was extracted from prawn shell wastes and applied in bio sorption of azo dyes. This polymer was encapsulated over glass beads. The encapsulated glass beads were packed in a glass column and azo dye decolorization was carried out and determined calorimetrically using UV-Visible spectrophotometer and different isotherms were calculated. The isotherms such as Langmuir, Freundlich and Temkin were examined and the appropriate model was identified. The interaction of the dye with chitosan was studied using SEM and FTIR.

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

INTRODUCTION

Azo dyes are used varying quantities all around the world in textile, paper and Tannery industries. Such widely used chemicals are of great concern with regard to their potential toxicity and carcinogenic properties [1-2]. Different decolorization methods were developed by physical, biological and chemical techniques in last few decades e.g. tricking filter, activated sludge, coagulation-flocculation, chemical precipitation, carbon absorption, aerobic and anaerobic treatment and phytoremediation processes. However, most of the methods bear very elevated operation expenditure and some of them even need complicated operation practices [3-4].

EXPERIMENTAL SECTION

Preparation of Chitosan

Chitosan was the compound of interest for this study. The shell waste of prawn have been gathered from Royapuram fishing harbour (13.1256° N, 80.2976° E) and washed using distilled water and dehydrated under sunlight. This process was repeated thrice for a complete removal of impurities. In 4% NaOH, the samples was boiled and allowed to cool for 30 minutes at 28°C [5-6]. For demineralization 1% HCl was used four times its quantity and the samples were allowed to immerse for 24 h to remove the unwanted calcium carbonate [7-8]. The demineralised shrimp shell samples were then treated for one hour with 50 ml of a 2% NaOH solution to decompose. The remaining chitin is washed with deionised water, which is then drained off. The chitin was further converted into chitosan by the process of deacetylation [10]. 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 drenched in Potassium di chromate solution and washed with water was dipped in a bio-polymer for encapsulation and the encapsulate glass beads are taken in a Petri plate for drying purpose and this encapsulate glass beads is dried in a room temperature [11].

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.

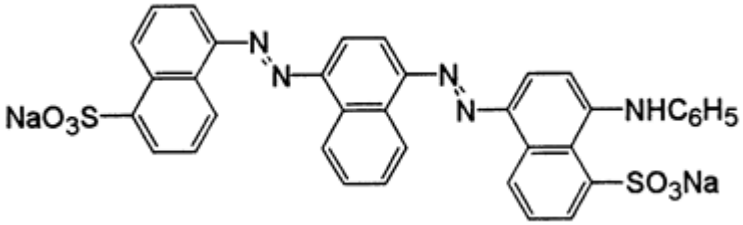


Figure -1: Structure of Acid black 24

Dye decolorization

For dye decolorization, 1st burette, the encapsulated chitosan glass beads which was filled to 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 analysed the change in the colour by using Varian Cary UV-Vis Spectrophotometer [12-14].

Mathematical modelling study

Adsorption Isotherm design

Equilibrium sorption isotherms illustrate the ability of an adsorbent, distinguished by certain constants these values defines the surface properties and affinity of the adsorbent [15-18].

Langmuir Isotherm

The Langmuir sorption isotherm has been the most extensively used isotherm and has been efficaciously applied to many dye adsorption processes. Langmuir basic hypothesis was to adsorb a specific homogeneous site within the adsorbent. The saturated monolayer adsorption isotherm can be represented as.

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, indicating the highest adsorption ability 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

Freundlich isotherm is an empirical isotherm that is used for non-ideal adsorption and is symbolized by the equation. It 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,

$$\textbf{Log } q_e = \log K_f + (1/n) \log Ce$$

Where K_f & n are the Freundlich constants, the features 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 engaged to generate the intercept value of K_f and the slope of n.

Temkin isotherm

Tempkin isotherm assumes that the fall in the heat of sorption is a linear rather than the logarithmic, as implied in the Freundlich equation. The equation is given by

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

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

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

$$\mathbf{q_e = B \log A + B \log C_e}$$

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 examine the adsorption kinetics on Chitosan, the pseudo-first-order and pseudo-second-order models were used to measure the experimental results [19-22].

Pseudo first order equation

The **first order equation** of Lagergren is generally expressed as follows. Lagergren's kinetics equation has been most widely used for the adsorption of an adsorbate from an aqueous solution.

$$\mathbf{dq/dt = k_1 (q_e - q_t)}$$

where q_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:

$$\mathbf{\log (q_e - q_t) = \log q_e - k_1 t}$$

Pseudo-second-order

If the rate of sorption is a second order mechanism, the pseudo-second order chemisorption kinetic rate equation is expressed as follows

$$\mathbf{dq_t/dt = k_2 (q_e - q_t)^2}$$

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→qe) the following expression is obtained:

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

Where q_e, q_t 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 (C)

Scanning Electron Microscope (SEM) [23-24]

The scanning electron microscope (SEM) 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 SEM module, Hitachi 5415 A, and micrographs were taken at different magnification.

FTIR analysis

The absorbance FT-IR spectra of the samples were documented using an FT-IR Perkin–Elmer spectrometer. The spectra were collected within a scanning range of 400-4000 cm^{-1}.

RESULTS 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 U-V spectroscopy.

The Graph is drawn between pH and % removal of Chitosan.

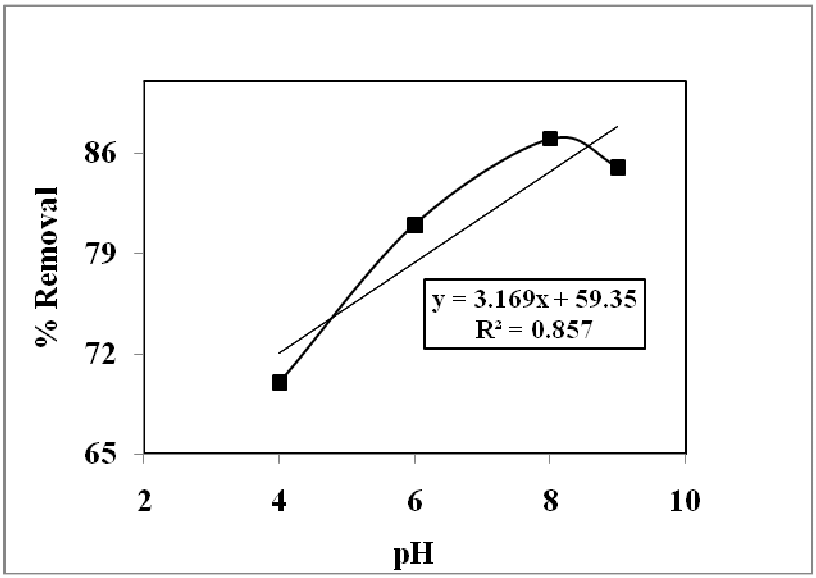


Fig 1: Variation of % Removal at different pH at 100ppm

Effect of Contact Time

The effect of contact time for dye adsorption on chitosan glass beads is shown in fig.4.2 and it was observed that in the 1st hour the %removal was very high. After 4th hour equilibrium attains so there is negligible % Removal.

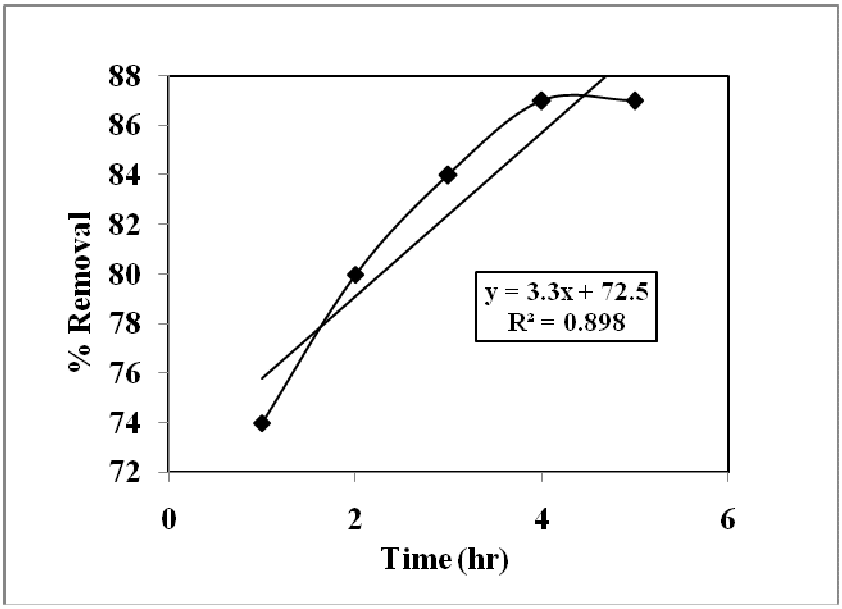


Fig 2: % Removal of dye at different time interval

From the above figure -2 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.

Langmuir isotherm

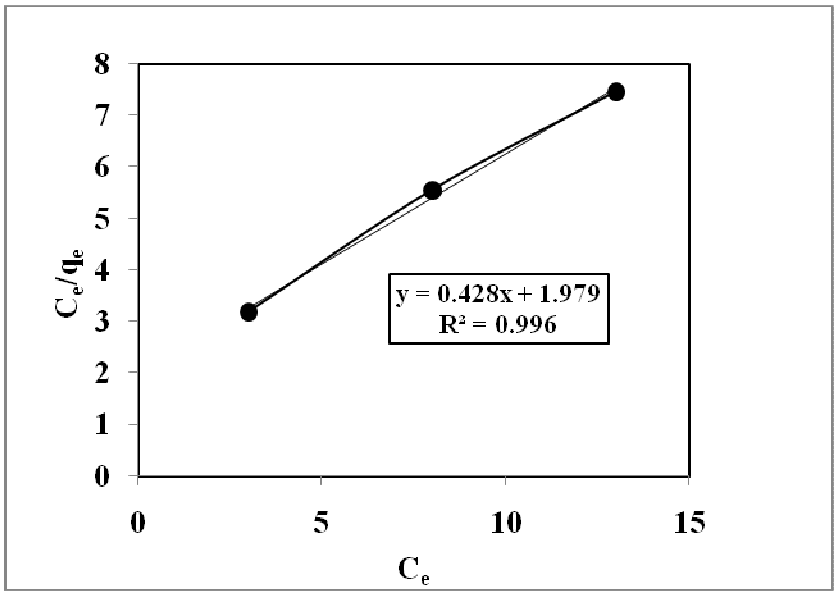


Fig3: Langmuir equilibrium isotherm model for the absorption of the dye on chitosan (C) glass beads at pH 8

The Langmuir isotherm model was selected for the evaluation of highest adsorption ability corresponding to complete monolayer coverage on the glass beads surface

Table 1 Linear Langmuir isotherm parameters

Bio Polymer	q_m	K_L	R^2
C	2.336	0.216	0.9965

Freundlich Isotherm

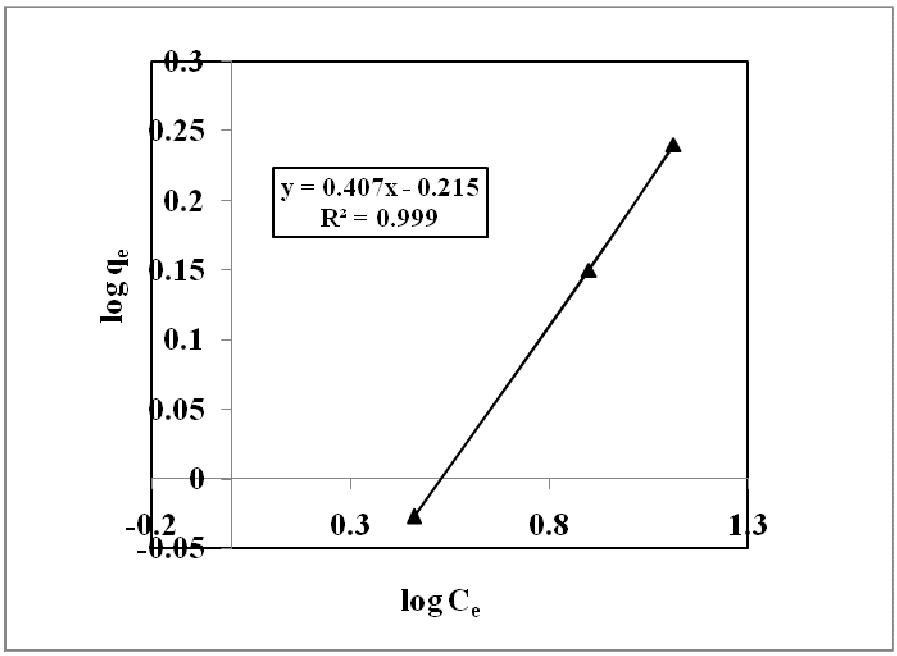


Fig 4 Freundlich equilibrium isotherm model for the adsorption of the dyes on Chitosan (C) beads at pH 8

Table 2 Freundlich equilibrium isotherm model for the adsorption of the dyes on chitosan (C) glass beads at pH 8

Concentration (ppm)	% Removal	C_e	q_e	$\log c_e$	$\log q_e$
100	87	13	1.74	1.113	0.24
80	90	8	1.44	0.90	0.15
50	94	3	0.94	0.46	-0.027

The Freundlich model was chosen to estimate the adsorption intensity of the adsorbate on the adsorbent surface. The experimental data from the batch adsorption indicates that the dye removal is plotted logarithmically using the linear Freundlich isotherm equation.

Table 3: Freundlich isotherm parameters

Bio polymer	1/n	K_f	R^2
C	0.4079	0.6092	0.999

Temkin isotherm

Table 4: Temkin equilibrium isotherm model for the adsorption of the dyes on chitosan (C) glass beads

Concentration (ppm)	% Removal	C_e	q_e	log C_e
100	87	13	1.74	1.113
80	90	8	1.44	0.90
50	94	3	0.94	0.46

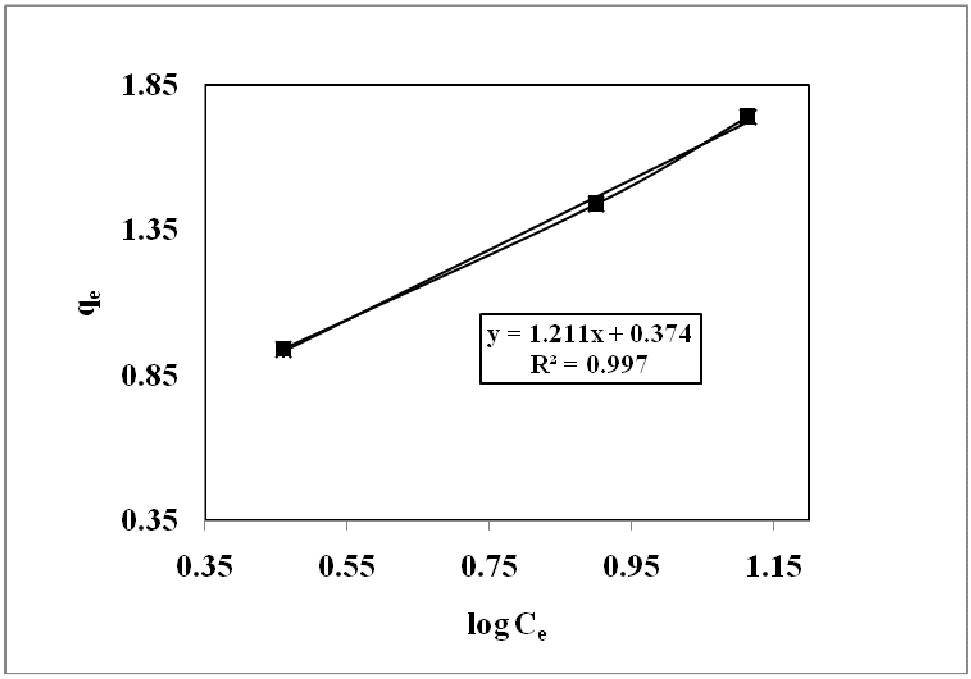


Fig 5: Temkin equilibrium isotherm model for the adsorption of the dyes on Chitoson (C) glass beads at pH 8

Table 5: Temkin isotherm parameters

Biopolymer	K_T	B_T	R^2
(C)	2.03	1.2118	0.997

Adsorption kinetics

Table 6: Kinetic models for the adsorption of dye on Chitosan (C) glass beads

Time (hr)	q_t	q_e-q_t	$\log(q_e$-$q_t)$
1	1.48	0..26	-0.585
2	1.6	0.14	-0.853
3	1.68	0.06	-1.22

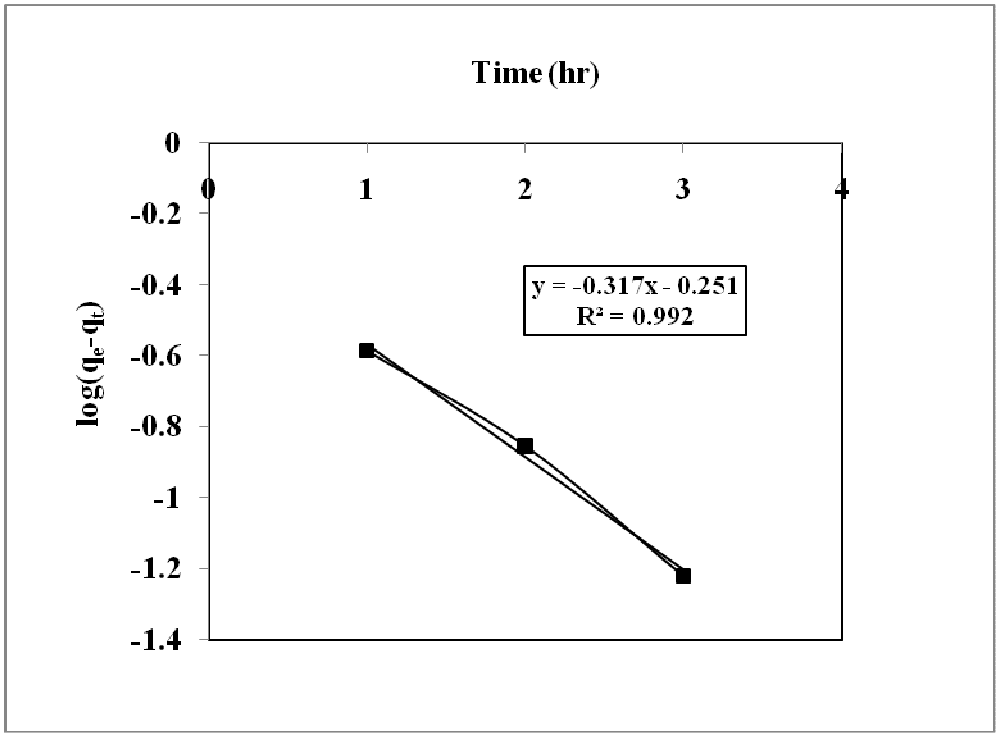


Fig 6 Kinetic models for the adsorption of dye on Chitosan (C) glass beads

Table 7: Kinetic models for the adsorption of dye on Chitosan (C) glass beads

Time (hr)	q_t	t/q_t
1	1.48	0.67
2	1.6	1.25
3	1.68	1.78

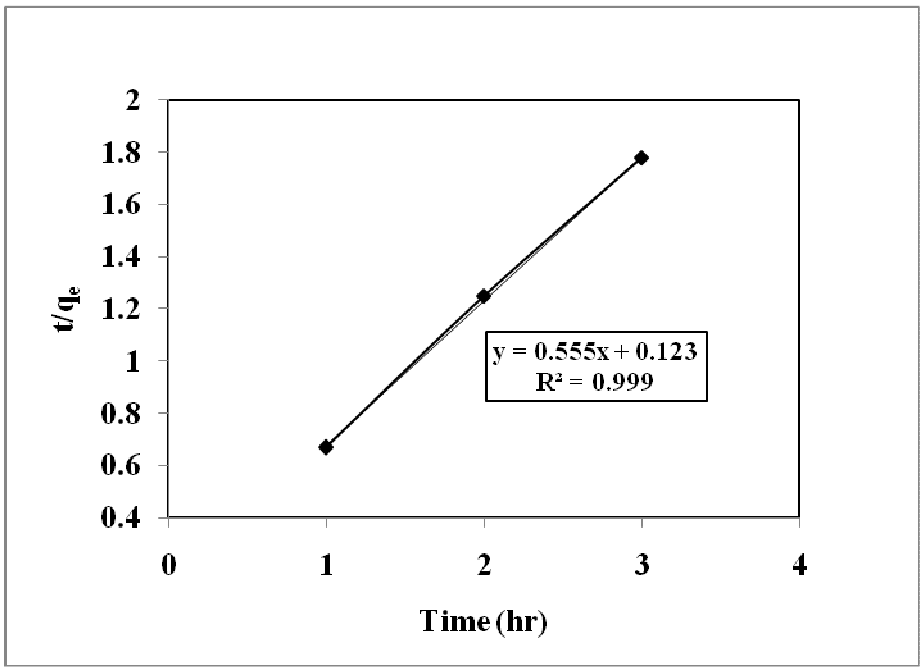


Fig 7: Kinetic models for the adsorption of dye on Chitosan (C) glass beads

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 $q_{e,\ expt}$ so it follows 2nd order kinetics.

Table 8: Parameters of the kinetic models for the adsorption dye onto Chitosan glass beads

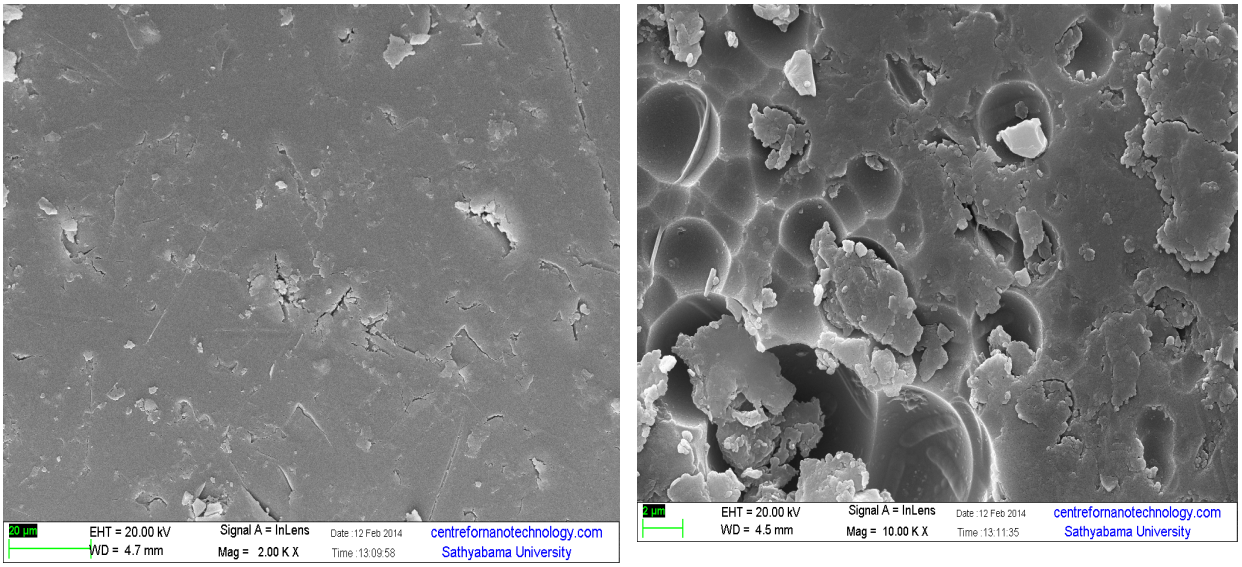
	Pseudo 1st order				Pseudo 2nd order			
Biopolymer	$Q_{e,exp}$	k_1	$Q_{e,cal}$	R^2	k_2	$Q_{e,cal}$	h	R^2
(C)	1.72	0.3175	0.56	0.992	2.49	1.8	8.082	0.9993

Characterization of Extracted Chitosan

Characterization is carried out to know quantitatively the elements present in the bio polymer. It is carried out by using Scanning Electron Microscope (SEM), Fourier Transform Infrared Spectroscopy (FTIR).

Scanning Electron Microscope (SEM)

The scanning electron microscope shows a changes in the structure of chitosan coated glass slide that was treated with the dye. The smooth surface of the chitosan was disturbed after attachment of the dye.



(a) **(b)**

Fig 8: SEM images (a) before adsorption of dye with Chitosan (b) after adsorption of dye

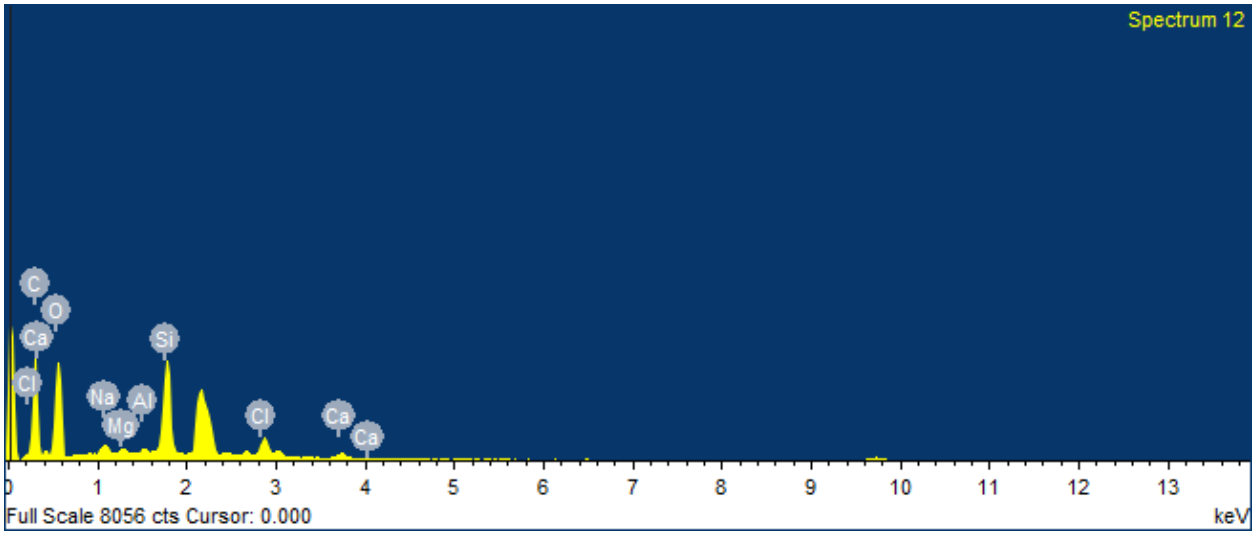


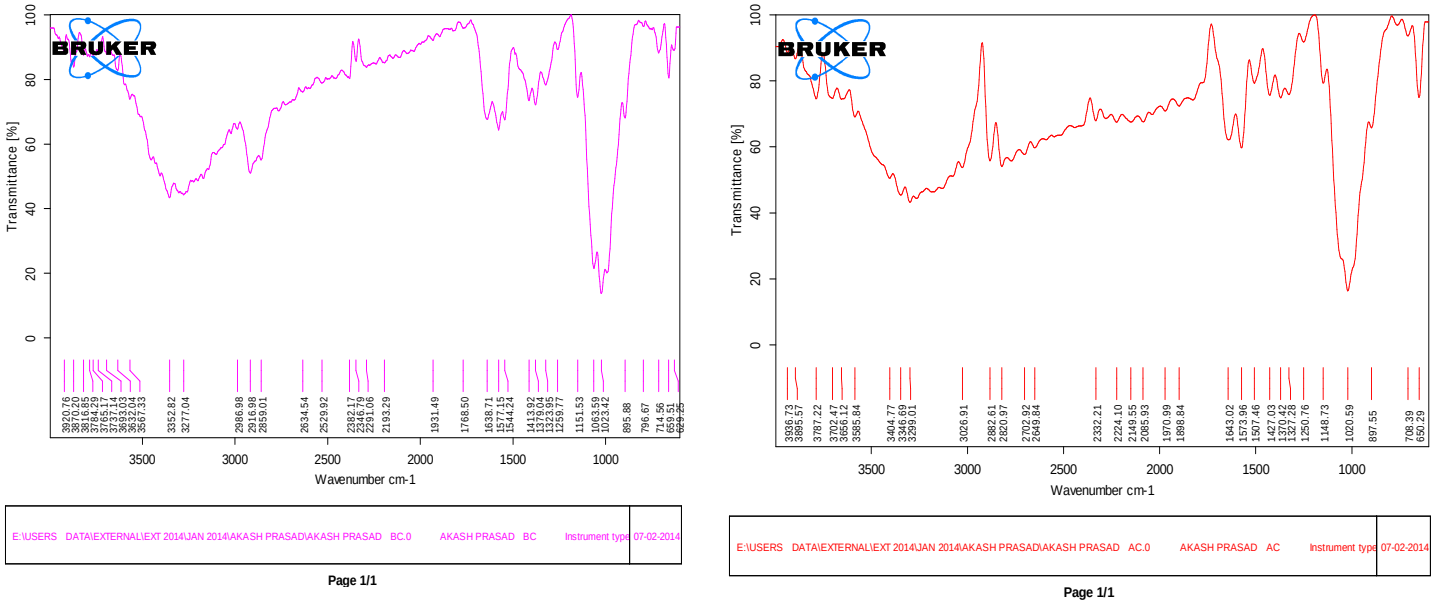
Fig 9: EDAX peaks

The EDAX shows higher concentration of Si, C, O Cl and Ca and traces of Na, Al and Mg.

Fourier Transform Infrared Spectroscopy

The FTIR spectrum of a control dye and chitosan sorbent (24 hours) was compared. The spectrum of the control dye displayed a peaks at 1023.42, 3352.82, 2916, 1544.22 and 1259.77cm^{-1} for cyclohexane vibration, –OH stretch, -CH stretch, –NO stretch respectively. The stretching between1573 to 2600 was commonly seen by the Chitosan sorbent

which represent –C≡O-, C≡N and C≡N. The major stretch were shown in 1020.59, 3299.01 2649 etc that representing the –CC- stretch, C-H stretch were seen.



(a) **(b)**

Fig 9: FTIR images for (a) chitosan before removal of dye (b) after removal of dye

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