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## PREPARATION, CHARACTERIZATION AND PERFORMANCE EVALUATION OF CHITOSAN AS AN ADSORBENT FOR REMAZOL RED

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**ABSTRACT:** In this present study, waste prawn shell was used as raw material for chitosan preparation. Various analytical tools e.g. Fourier-transform infrared spectroscopy (FT-IR), x-ray diffraction (XRD) and scanning electron microscopy (SEM) were employed for the characterization of prepared chitosan. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were used for the determination of thermal stability of chitosan. For the determination of elemental composition, CHNS elemental analyzer was used. The chitosan was applied as an adsorbent for a reactive textile dye, Remazol Red. Batch studies were performed to investigate the effects of pH, contact time and initial dye concentration. Chitosan showed an adsorption capacity of 313.4 mg/g at pH 3.0 and a desorption ratio of 0.967. Experimental adsorption data showed good agreement with Langmuir adsorption isotherm and pseudo-second order kinetics. Therefore, it can be said that chitosan can be used economically as a potential adsorbent for Remazol Red.

**Keywords:** Chitosan, Remazol Red, Adsorption, Desorption.

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### 1. INTRODUCTION

The dyestuffs from textile industries are present in moderate concentration range of 10-200 ppm in waste water which find their ultimate way in the water bodies[1]. These colored compounds are not aesthetically appealing and adversely affect the aquatic ecosystem by inhibiting sunlight into the stream and by reducing the photosynthetic reactions[2]. Various physical, chemical and biological methods have been widely used for the removal of dyes from industrial effluents. These methods include adsorption, coagulation, flocculation, membrane filtration, ozonation, advanced oxidation, liquid-liquid extraction, biosorption etc[3-6]. Among them adsorption is considered to be the effective and superior technique for wastewater treatment in terms of initial cost, simplicity of design, ease of operation and insensitive nature to toxic substances[7-10]. Although activated carbon is an efficient adsorbent for organic contaminants for its higher adsorption capacity, the higher cost of treatment and difficulties of regeneration led to the search for cheap and alternative adsorbent materials[11, 12]. Various adsorbents e.g. naturally occurring materials, biomaterials, industrial waste, agro-waste materials, polymers etc. have been employed for the removal of dyes[13]. Chitosan contains amino ( $-NH_2$ ) and hydroxyl ( $-OH$ ) functional groups which can serve as the coordination and reaction sites and as a result it has been used widely as an adsorbent[14-19]. The biodegradable and non-toxic nature of chitosan has made it a highly efficient adsorbent in the removal of anionic dyes[20]. Chitosan can reduce dye concentration to ppb levels and is often much more selective than conventional ion-exchange resins and commercial activated carbon[21]. In this present study, chitosan was prepared from waste prawn shells and was employed as an adsorbent for Remazol Red.

### 2. MATERIALS AND METHODS

Waste prawn shells were collected from a local prawn hatchery of Bangladesh. Purified sodium hydroxide pellets and 35% hydrochloric acid were supplied by Active Fine Chemicals Limited, Dhaka, Bangladesh. Anhydrous glacial acetic acid was obtained from Merck KGaA, 64271 Darmstadt, Germany. All of these chemicals were used without further purification. Remazol Red (RR) dye was collected from a local textile industry of Bangladesh.

#### 2.1. Preparation of Chitosan

The raw prawn shells were washed with distilled water in a 2L beaker for 1.5 hours at 80°C with occasional stirring. The shells were then dried in a digital drying oven (DO-150, Han Yang Scientific Equipment Co. Ltd., Seoul, Korea) at 60°C for 10 hours. The deproteination was carried out by treating the washed and dried prawn shells with 3% (w/w) sodium hydroxide at a ratio of 1:18(w/w) for 3 hours at 80°C. The proteins were removed by decantation. The shells after deproteination were dried in the oven at 60°C for 10 hours. Demineralization was carried out by treating the deproteinated shells with 3M hydrochloric acid at a ratio of 1:18 (w/w) for

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3hours at 25°C. Demineralization process progressed with the evolution of CO<sub>2</sub>. After this step chitin was obtained which was washed several times to remove residual acid. Chitin was separated by decantation and was dried in the oven at 60°C for 10hours. The final step for the preparation of chitosan was the deacetylation of chitin. Deacetylation was carried out by treating chitin with 50% (w/w) sodium hydroxide at a ratio of 1:18 (w/w) for 3hours at 80°C. The product chitosan was obtained by filtration. The chitosan was washed several times to remove alkali which was confirmed by pH meter. The product chitosan was confirmed by the solubility in 1% (v/v) acetic acid solution[22].

### 2.2. Characterization of Chitosan

FT-IR spectrum of chitosan was recorded on a FT-IR 8400S spectrophotometer (Shimadzu Corporation, Japan) in the wavenumber range of 4000-400 cm<sup>-1</sup>. XRD pattern of chitosan was recorded by an x-ray diffractometer (Ultima IV, Rigaku Corporation, Japan) at room temperature. Cu K $\alpha$  radiation ( $\lambda=0.154$  nm), from a broad focus Cu tube operated at 40 kV and 40 mA, was applied to the sample for measurement. The morphology of the sample was analyzed by an analytical scanning electron microscope (JEOL JSM-6490LA, Tokyo, Japan) operated at an accelerating voltage of 20 kV in the back-scattered electron mode. Thermogravimetric analysis of chitosan was performed by a thermogravimetric analyzer (TGA-50, Shimadzu Corporation, Japan) with alumina cell under nitrogen atmosphere at the flow rate of 10 mL/min and at the heating rate of 10°C/min. Thermal stability of chitosan was also examined by using a differential scanning calorimeter (DSC-60, Shimadzu Corporation, Japan) with aluminum seal under nitrogen atmosphere at the flow rate of 20 mL/min and at the heating rate of 10°C/min. The elemental analysis was carried out with CHNS elemental analyzer (varioMicro V 1.6.1, GmbH, Germany) in a tin boat sample pan at a combustion temperature of 1150°C and at a reduction temperature of 850°C. Gas flow rate was 200 mL/min and 14 mL/min for helium and oxygen respectively.

### 2.3. Adsorption Study

Batch experiments were performed for the determination of the adsorption capacity of chitosan. 5mg of chitosan was taken in a 100mL Erlenmeyer flask with an air tight stopper. 20 mL of dye solution having various concentrations was added to the flasks. The pH of the solutions was adjusted by using 0.1M NaOH and 0.1M HCl. Different initial concentrations of dye solutions were used to measure the uptake of dye by chitosan. The flasks were shaken at room temperature of 25°C by a shaker at 150rpm until the equilibrium point reached. The concentration of RR in the solution was determined by taking absorbance at 518nm by a UV-Vis spectrophotometer (UV-2100PC, HumanLab Instrument Co., Korea).

The adsorption capacity ( $q_e$ ) was calculated using the following formula:

$$q_e = \frac{(C_0 - C_e)V}{m}$$

where,  $C_0$  is the initial concentration of RR (mg/L),  $C_e$  is the equilibrium concentration of RR(mg/L),  $m$  is the weight of chitosan used for the adsorption studies (g) and  $V$  is the volume of RR solution (L).

### 2.4. Desorption study

After adsorption, the dye-loaded adsorbents were separated from the suspension by filtration and the cake was washed three times with deionized water to remove any unadsorbed dye. The cake was then air dried. The desorption study was performed by mixing 5 mg of dye-loaded adsorbent with 20 mL of alkaline media of pH 8.0, 9.0 and 10.0 respectively. The desorption ratio was calculated as follows:

$$\text{Desorption ratio} = \frac{\text{Amount of dye desorbed}}{\text{Amount of dye adsorbed}}$$

## 3. RESULTS AND DISCUSSION

### 3.1. Characterization

FT-IR spectrum of chitosan showed various characteristic peaks as shown in Fig. 1. In this spectrum, the absorption band at 3444.87cm<sup>-1</sup> is assigned for O-H stretching overlapped with N-H stretching, 2920.23cm<sup>-1</sup> for aliphatic C-H stretching, 1398.39cm<sup>-1</sup> for C-O stretching vibration of primary alcoholic groups and 1085.92cm<sup>-1</sup> for stretching vibration of hydroxyl group of C<sub>3</sub>-OH[21, 23].

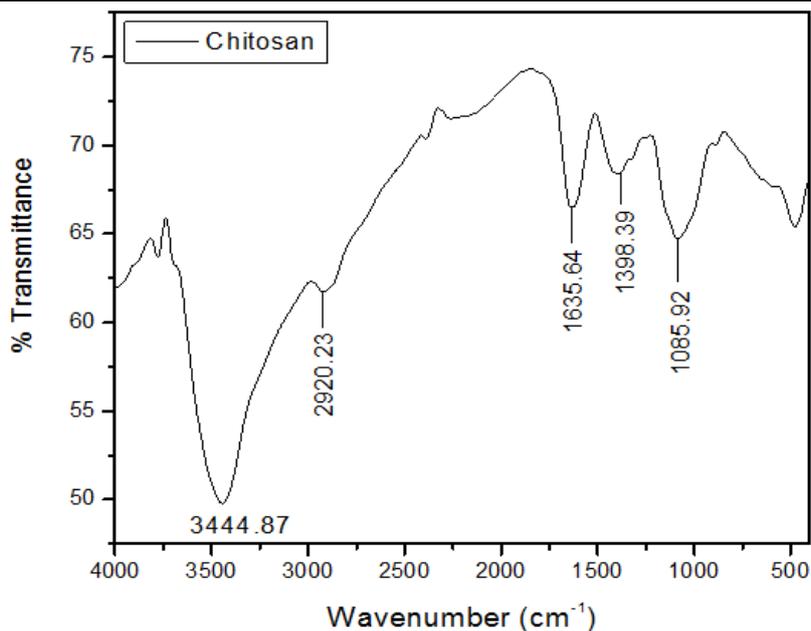


Figure 1: FT-IR spectrum of chitosan

The intense peak at  $1635.64\text{cm}^{-1}$  is assigned to the in-plane N-H bending vibration which is a characteristic peak of chitosan polysaccharide[24].

The XRD pattern of chitosan prepared from waste prawn shells exhibited two characteristic broad diffraction peaks at  $2\theta$  around 9.63 and 20.53 that are typical fingerprints of semi-crystalline chitosan as indicated in Fig. 2[25].

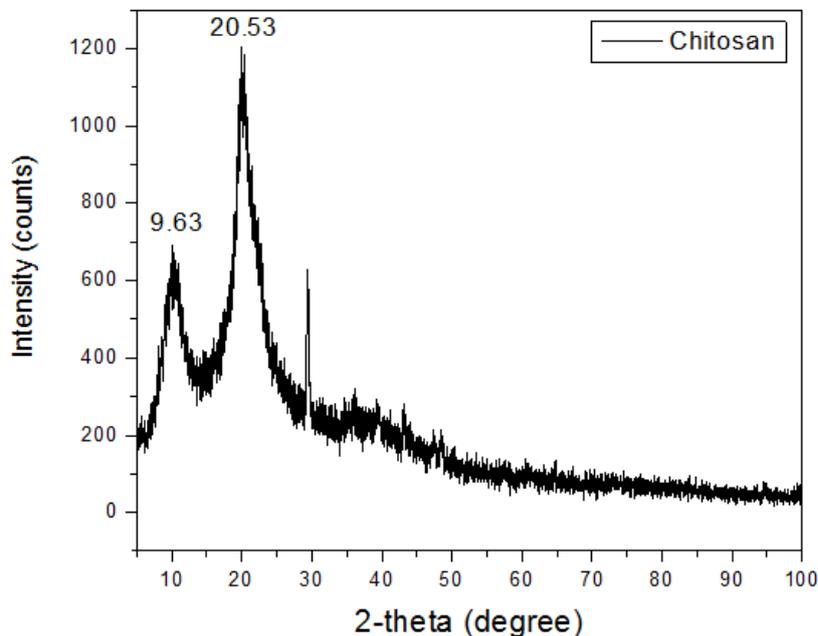


Figure 2: XRD pattern of chitosan

The peaks around 9.63 and 20.53 are related to crystal-I and crystal-II in chitosan structure and both of these peaks attribute a high degree of crystallinity to the prepared chitosan[26, 27].

The SEM micrographs illustrated the morphological features of chitosan prepared from waste prawn shells as depicted in Fig. 3.

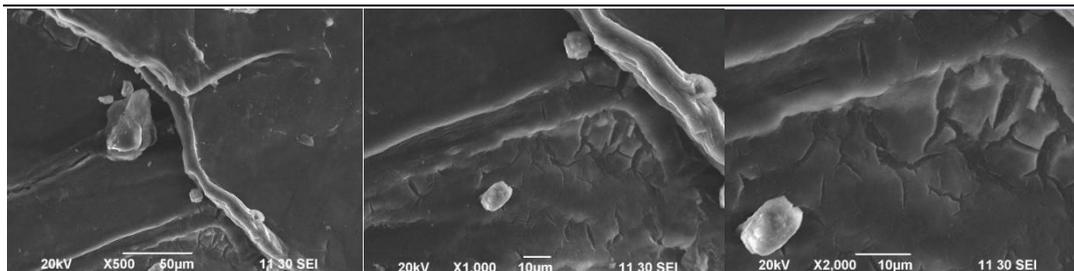


Figure 3: SEM images of chitosan at various magnifications

The micrographs showed non-homogeneous and non-smooth surface with straps and shrinkage[28].

### 3.2. Thermal Stability

The TGA thermogram of chitosan showed the weight loss profile at various temperatures as shown in Fig.4.

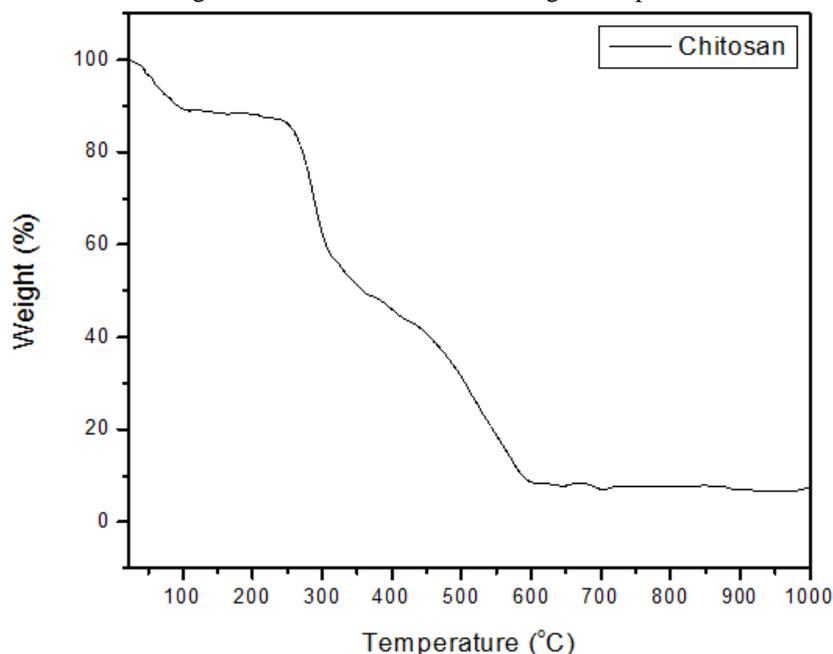


Figure 4: TGA thermogram of chitosan

The first weight loss step was seen in the temperature range of 22-100°C corresponding to the loss of moisture (around 10%). Under nitrogen flow a non-oxidative thermal degradation occurs in chitosan which was observed in the temperature range of 248-600°C, indicating the deacetylation of chitosan, vaporization and elimination of volatile products[29]. The degradation of chitosan starts with amino groups forming unsaturated structures[30]. During the pyrolysis of polysaccharides a random split of the glycosidic bonds occur, which are further followed by decomposition forming acetic and butyric acids and a series of lower fatty acids, where C2, C3 and C6 predominate[31].

The DSC thermogram of chitosan showed an endothermic peak between 77.78 – 80.44°C and an exothermic peak between 303.77 – 304.28°C as indicated in Fig. 5. The endothermic peak, also called dehydration temperature ( $T_D$ ), is assigned to the loss of water associated with the hydrophilic groups of chitosan[32, 33].

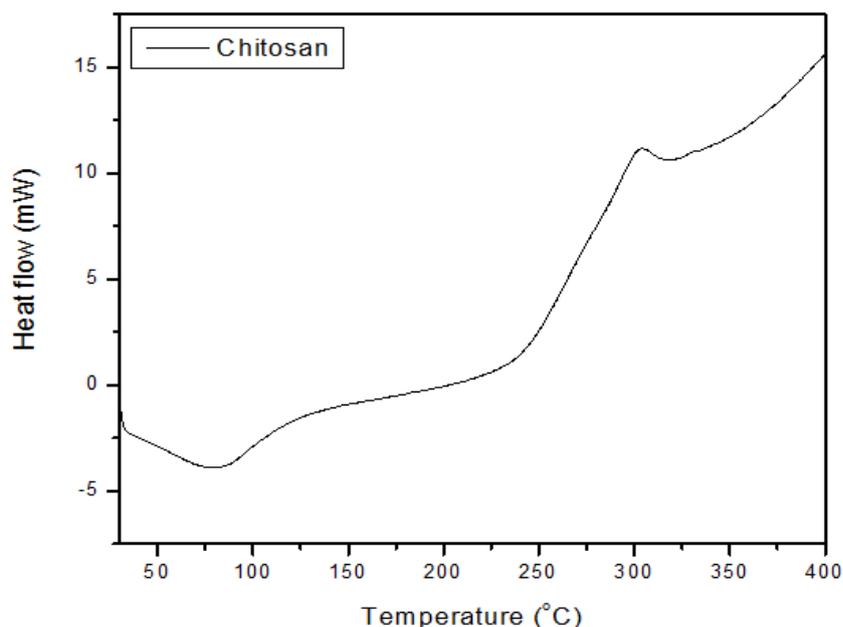


Figure 5: DSC thermogram of chitosan

In solid state, chitosan polysaccharide has disordered structure and has strong affinity for water and as a result it can be easily hydrated[34]. This peak suggested that chitosan was not completely dried and still there was some bound water which was not removed during drying. The exothermic peak is assigned to the thermal degradation of chitosan (monomer dehydration, glycoside bond cleavage and decomposition of the acetyl and deacetylated units)[35, 36].

### 3.3. Elemental Composition

The elemental analysis showed the presence of C, H, N and S in the chitosan polymer as depicted in Fig. 6.

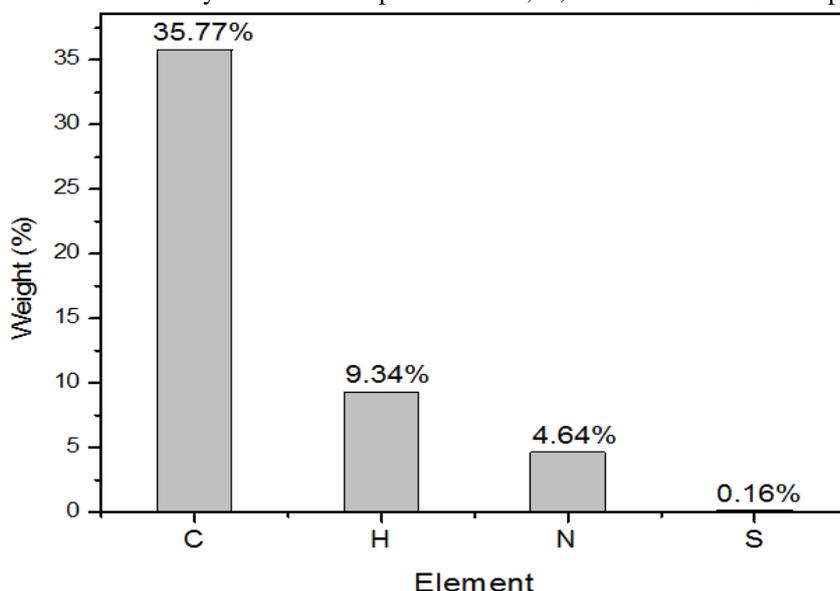


Figure 6: Elemental composition of chitosan obtained from CHNS analyzer

### 3.4. Adsorption Study

The pH of solution has strong influence on the surface charge of an adsorbent, dissociation of functional groups on its active sites, the degree of ionization and structural changes of dye molecules[37]. In this present study, pH of the solution played a vital role in the adsorption of RR onto chitosanas indicated in Fig. 7.

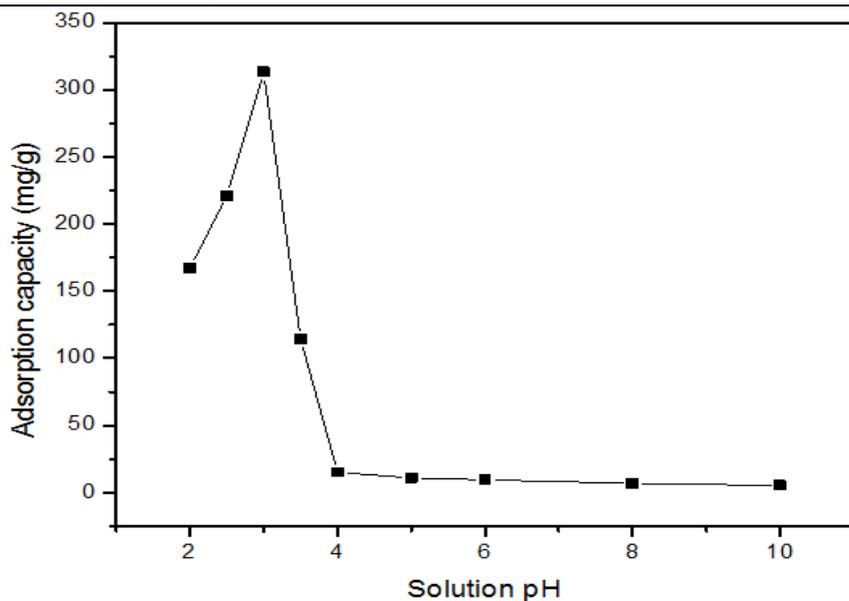


Figure 7: Effect of solution pH on the adsorption capacity of chitosan for RR (RR concentration: 100 mg/L, contact time: 30 minutes, temperature: 25°C, shaking speed: 150 rpm, amount of chitosan: 5 mg and volume of RR solution: 20 mL)

The maximum adsorption capacity of 313.4 mg/g was observed at pH 3.0. In acidic media the, amino functional groups of chitosan become protonated and a strong electrostatic attraction occurs between the protonated amino groups of chitosan and the anionic dye, RR. From the figure it can be said that the maximum protonation occurred at pH 3.0 resulting in highest adsorption capacity. When the pH was decreased below 3, adsorption capacity decreased due to higher solubility of chitosan at pH below 3.0. An increase in pH above 3.0 also resulted in the decrease in adsorption capacity due to lower degree of protonation of amino functional groups up to pH 4.0. At alkaline pH, very low adsorption capacity was observed because the amino functional groups of chitosan were no longer in protonated form and also there was a competition between the hydroxyl ions and anionic dyes in basic media for the adsorbent[6, 38]. For optimization of time and initial concentration, pH 3.0 was selected.

The fundamental basis of adsorption kinetics is the effect of contact time on the adsorption capacity[39]. From the Fig. 8, it was evident that the adsorption capacity increased rapidly during first 20 minutes and then increased slowly and after 30 minutes reached equilibrium.

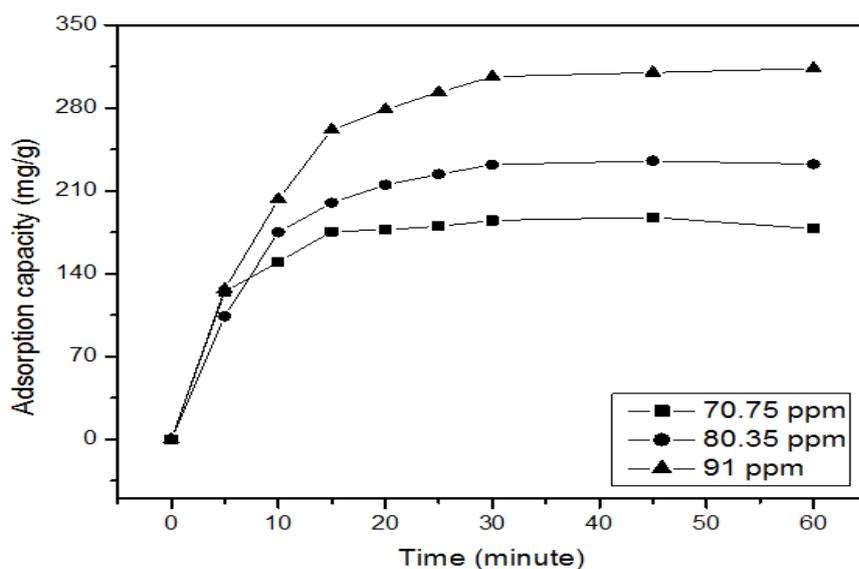


Figure 8: Effect of contact time on the adsorption capacity of chitosan for RR (pH: 3.0, temperature: 25°C, shaking speed: 150 rpm, amount of chitosan: 5 mg and volume of RR solution: 20 mL)

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Initially there was higher number of vacant active sites on the surface of the adsorbent which was the reason for higher initial rate of adsorption. Gradually the active sites were occupied by the dye molecules and near the equilibrium the remaining active sites were difficult to be covered probably due to the slow pore diffusion of the dye molecules[40].

Initial RR concentration influenced the adsorption capacity of chitosan as shown in Fig. 9. The adsorption capacity increased almost linearly with increasing initial concentration of RR.

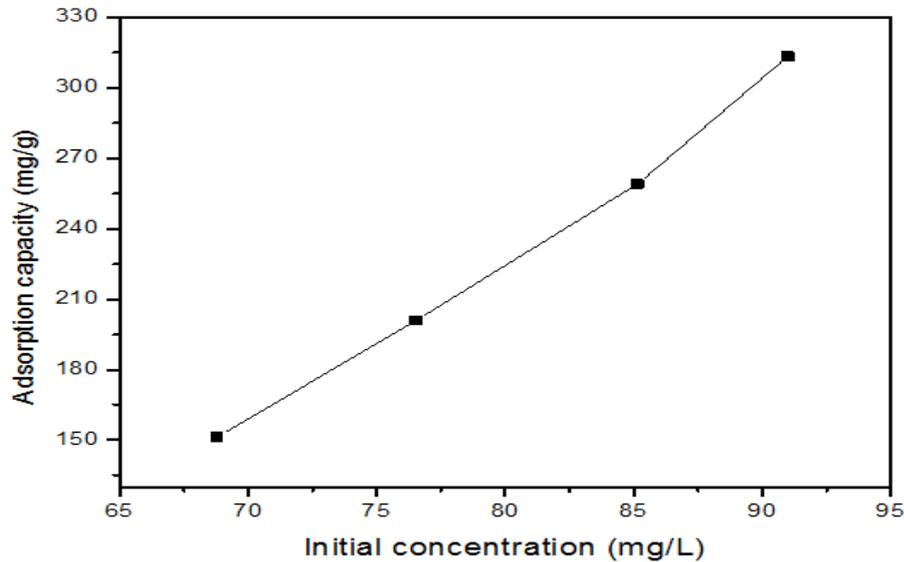


Figure 9: Effect of initial concentration on the adsorption capacity of chitosan for RR (pH: 3.0, contact time: 30 minutes, temperature: 25°C, shaking speed: 150 rpm, amount of chitosan: 5 mg and volume of RR solution: 20mL)

Increase in initial RR concentration resulted in an increase in concentration gradient which is the driving force for adsorption. As a result the diffusion of the dye molecules from the bulk of the solution to the adsorbent surfaces increased[41].

### 3.5. Isotherm Study

The equilibrium adsorption data showed good agreement with Langmuir adsorption isotherm as shown in Fig. 10.

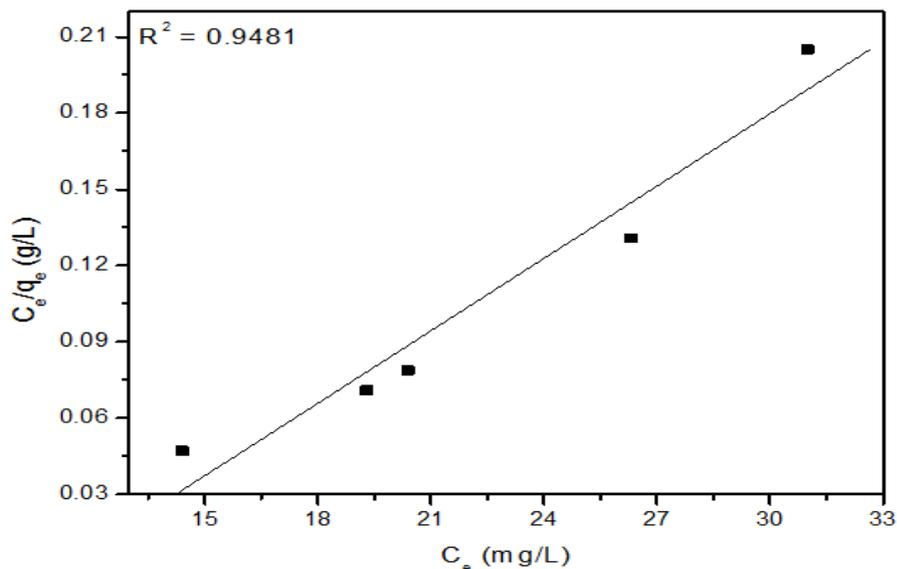


Figure 10: Langmuir isotherm for the adsorption of RR onto chitosan

From this isotherm following conclusions can be drawn i.e. there was a homogeneous adsorption, monolayer coverage of chitosan surface by RR and no interaction between adsorbed RR molecules[41, 42].

### 3.6. Kinetics Study

Experimental adsorption data showed good agreement with pseudo-second order kinetic model as shown in Fig. 11.

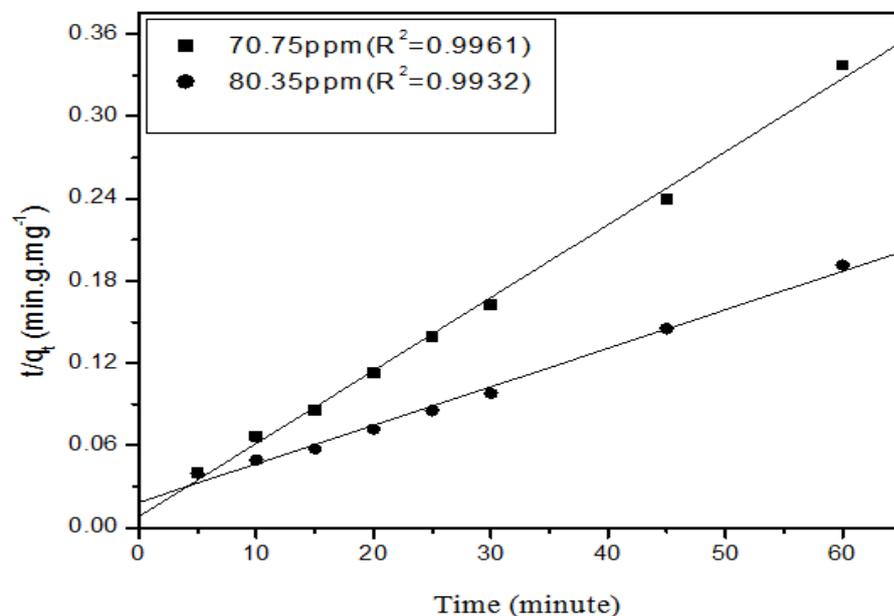


Figure 11: Pseudo-second order kinetic plot for the adsorption of RR onto chitosan

Therefore, it can be said that the rate controlling step of adsorption is chemisorption of RR onto chitosan involving electrostatic forces between RR anions and protonated amino groups of chitosan[43].

### 3.7. Desorption Study

Since chitosan adsorbed dye in acidic media, it was logical to use alkaline media for the desorption study. It was observed that alkaline pH was very effective for the regeneration of the adsorbent because desorption occurred immediately after pH adjustment as indicated in Fig. 12.

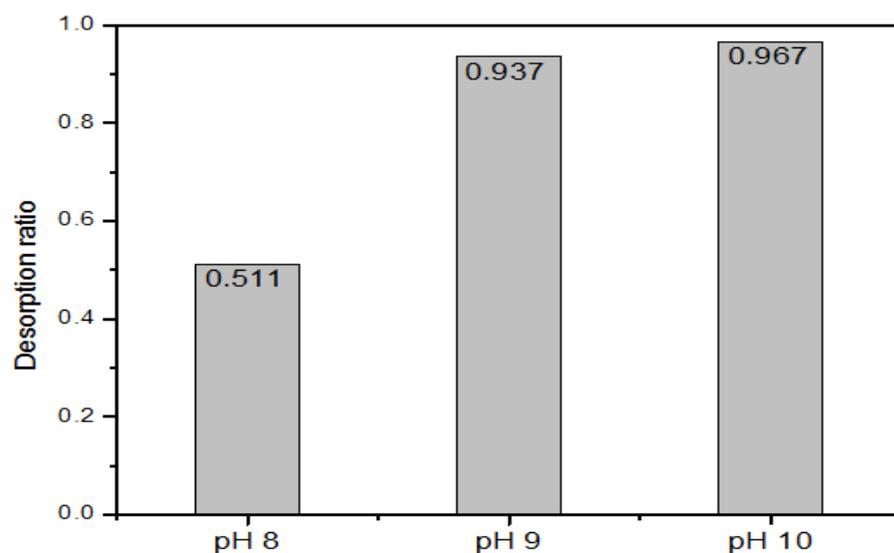


Figure 12: Effect of adjusted solution pH on the desorption ratio

It was also observed that there was a progressive increase in desorption ratio with increasing the pH of the media and highest desorption ratio of 0.967 was found at pH 10.0.

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The adsorption performance of chitosan was compared with commercially used activated charcoal. The activated charcoal showed highest adsorption capacity of 71 mg/g at pH 1.0 which was lower than that of chitosan. Therefore, the comparison told us that for the removal of RR, chitosan should be employed instead of activated charcoal.

### 4. CONCLUSION

In this present study, chitosan prepared from waste prawn shells was applied as an adsorbent for Remazol Red. Adsorption process reached equilibrium at room temperature after 30 minutes of continuous shaking at 150 rpm and at pH 3.0. Equilibrium adsorption data showed good agreement with Langmuir adsorption isotherm and pseudo-second order kinetic model. The adsorption capacity increased with increasing initial dye concentration and after adsorption chitosan was highly regenerable. The availability and cost-effective nature of waste prawn shells, easier preparation method, biodegradability and non-toxicity of chitosan, higher adsorption capacity at room temperature and at lower shaking speed, shorter equilibrium time, higher and quick desorption have made chitosan an effective and economical adsorbent for the removal of Remazol Red. Moreover, commercially used activated charcoal showed lower adsorption capacity than chitosan. Therefore, it can be concluded that chitosan should be prepared commercially from waste prawn shells and applied industrially for the removal of Remazol Red from textile effluents.

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