

# Isotherm and Thermodynamic Studies on the Bio Adsorption of Textile Industrial Effluents onto Chitosan Nanoparticle from Macolor Niger (White Snapper)

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## Abstract

Fish scale wastes are generally discarded in the environment through fish processing industries and local market vendors. It is one of the excellent and efficient renewable bioproducts. Consequently, a number of bioactive compounds have been identified including bioactive peptides, collagen, chitosan, and gelatin which are commercially marketed. The current study involves the extraction and generation of chitosan nanoparticles from fish scales. The synthesized chitosan nanosubstances were categorized by Field Emission Scanning Electron Microscopy (FESEM). The viability of utilizing fish scales as an economical bio-adsorbent for elimination of textile dye was studied on industrial effluent. Fourier transform infrared spectroscopy (FTIR) was used to study the dye adsorption of chitosan nanoparticles before and after the dye treatment. With chitosan nanoparticle treatment of the textile effluents, removal of COD was improved to 80% and the turbidity removal efficiency was improved up to 90%. Thus, the present study provides an excellent bio-adsorbent chitosan nanoparticle generated from fish scales which have potential application as an adsorbent in bioremediation like wastewater treatment.

## Keywords

Chitosan Nanoparticle, Fish Scale, Bio Adsorption, Textile Effluents

## 1. Introduction

Functional bioactive ingredients are known to attract the scientific community, consumers and food manufacturers and there is a steady growth in the scientific evidence supporting the concept of health-promoting ingredients [1] [2].

Chitosan, natural polysaccharide is a partially deacetylated polymer of N-acetyl glucosamine obtained through alkaline deacetylation of chitin [3] [4] [5] [6]. Chitin is found in the exoskeleton of crustaceans and also in fungi and yeast [7] [8].

Apart from this, chitosan is known to have medical, therapeutic, pharmaceutical and biomedical properties and also used in agricultural sector as well [9]-[15]. The attribution of chitosan to the textiles industry is considered multi-functional, both chemically and microbiologically [16]-[22].

The white snapper otherwise called as Macolor Niger is common tropical saltwater fish. Large amounts of scale wastes were discarded post consumption of these species and harmed the environment. Hence, chitin and chitosan can be extracted from the discarded fish scales and thus protect the environment.

This study deals with the preparation of chitosan nanostructures from fish scale wastes and their application as a bio-adsorbent in wastewater treatment from textile industrial effluents.

## 2. Material & Methods

### 2.1. Collection of Fish Scales

The scales of white snapper were collected from Chennai fish market in. The scales were dried at 50°C in an oven for 24 hours. The scales were then crushed and preserved in air tight containers (Figure 1).

### 2.2. Deproteination

It was refined by adding 2 N NaOH solution and then stirred and heated at a temperature of 90°C for 1 hour. Once separated from the solution, fish scales are washed with distilled water and then dried at 80°C for 8 hours.



**Figure 1.** Scales of white snapper.

### 2.3. Demineralization

Dry solids deproteinase subsequently demineralized by using a solution of HCl 1 N and stirred at room temperature for 1 hour. Once filtered, the solids are washed with distilled water and then dried at 80°C for 8 hours.

### 2.4. Deacetylation

After boiling chitin in 50% NaOH solution at 120°C for 3 hours, the solid is then washed with distilled water and are dried at 80°C for 8 hours. This resultant is called chitosan.

### 2.5. Chitosan Nanoparticles

Chitosan 1 g, 15 mL of 1% acetic acid and NH<sub>3</sub>(c) were mixed and the resulting gel formed is washed with distilled water and is dried at a temperature of 80°C for 24 hours.

### 2.6. Silver-Loaded Chitosan Nanocomposite

Silver nanoparticles were obtained by dissolving AgNO<sub>3</sub> for about 20 min post which sodium citrate and sodium borohydride solutions were added and mixed. The settled particles were collected by filtration. For the synthesis of C-Ag nanocomposite, 0.5 g of chitosan, 2% acetic acid, 1% PVA solution, 20% Na<sub>2</sub>SO<sub>4</sub> solution and 0.1 g of synthesized silver were added and mixed.

### 2.7. Scanning Electronic Microscopy (SEM)

The features of the nanoparticles were examined by Scanning electron microscope (Model 2360, Leo Oxford, England).

### 2.8. Particle Size

The particle size was observed by Shimadzu SALD-2300.

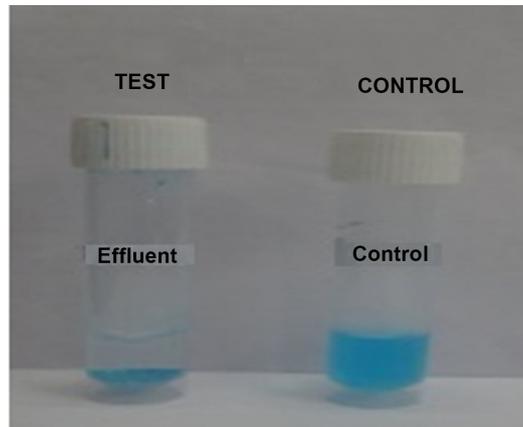
### 2.9. Photo Catalytic Degradation of Dye

The stock solution was prepared by adding 1000 mL of double distilled water to 10mg of Torque blue and Orange dye. A control was also preserved without the addition of silver nanoparticles. The suspension was stirred for half an hour and was kept under sunlight. Aliquots of 2 - 3 ml suspension were sieved and utilized to estimate the photo catalytic degradation of dye (**Figure 2**). The absorbance spectrum of the supernatant was calculated using UV-Vis spectrophotometer at different wavelength.

### 2.10. Percentage of Dye Degradation

$$\% \text{Decolourization} = 100 \times \left[ \frac{(I - F)}{I} \right]$$

where *I* is the initial concentration of dye solution and *F* is the final concentration of dye solution after photocatalytic degradation.



**Figure 2.** Textile effluents treated with Chitosan Nanoparticle.

### 2.11. Fourier Transform Infrared Spectra (FTIR)

The chitosan were then categorized in potassium bromide pellets by infrared spectrophotometer.

### 2.12. Estimation of Thermodynamic Parameters

- a) Langmuir Isotherm
- b) Freundlich Isotherm

$$\text{Langmuir Isotherm } qe = ((C0 - Ce) * V) / m$$

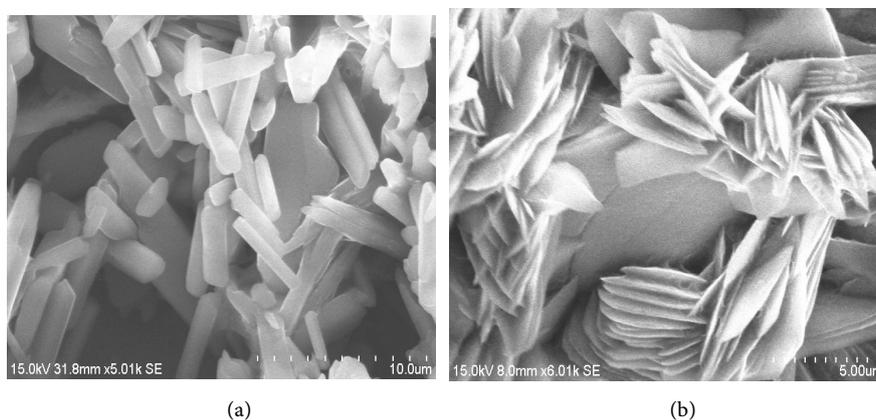
$$\text{Freundlich Isotherm } KF = qm / (C0)^{1/n}$$

where  $qe$ , amount of solute adsorbed per unit weight of solid at equilibrium (mg/g);  $Ce$ , equilibrium concentration of solute remaining in solution (mg/L);  $qm$ , maximum adsorption capacity for single layer formation;  $KF$ , Freundlich constant. From among above isotherms an isotherm that is close to the dye removal process must be selected so that further analysis of the adsorption system could be carried out.

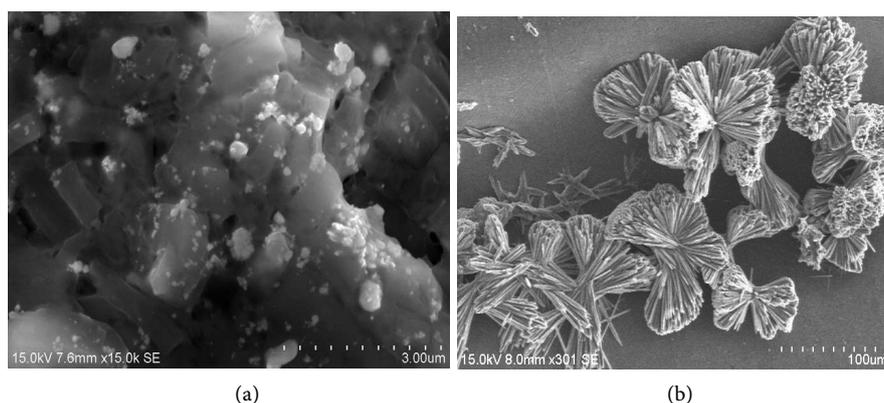
## 3. Results and Discussion

Chitosan was extracted from the fish scales from fish stalls of Kanathur by using chemical treatments (**Figure 1**). The prepared chitosan nanoparticle exhibited, rough, thick and rod shaped surface morphology under electron microscopic examination at 50X magnification (**Figure 3(a)** & **Figure 3(b)**). The silver-loaded chitosan nanocomposite exhibited silver particle embedded, rod shaped morphology under electron microscopic examination at 50X magnification. (**Figure 4(a)** & **Figure 4(b)**).

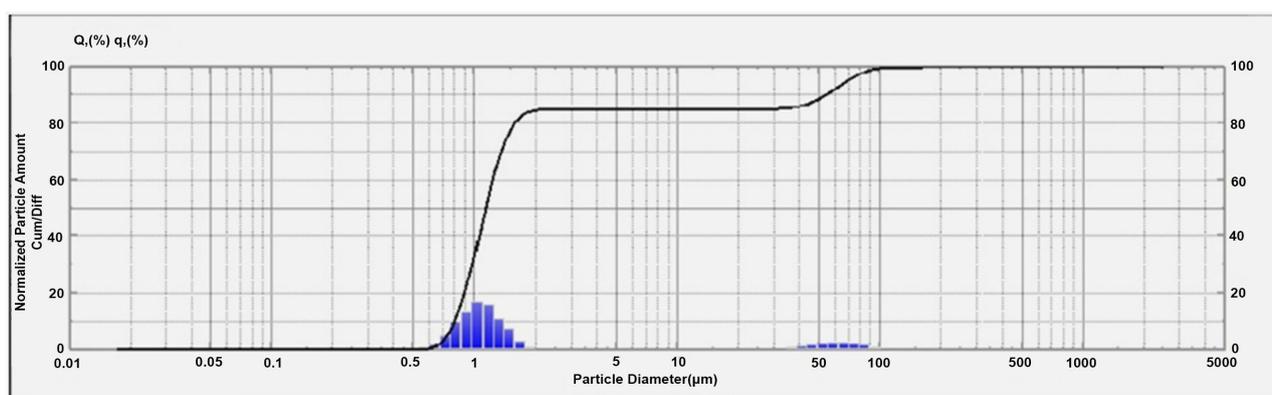
The particle size of chitosan nanoparticle was around 1.123 nm (**Figure 5**). The absorbance spectrum of chitosan nanoparticle was calculated by means of UV-Visible spectrophotometer at the different wavelength (**Figure 6(a)-(c)**). The time duration for the adsorption of the dye is 2 hours (**Figure 7**). Langmuir



**Figure 3.** (a) FESEM photographs of prepared Chitosan nanoparticle; (b) FESEM photograph of Chitosan nanoparticle.

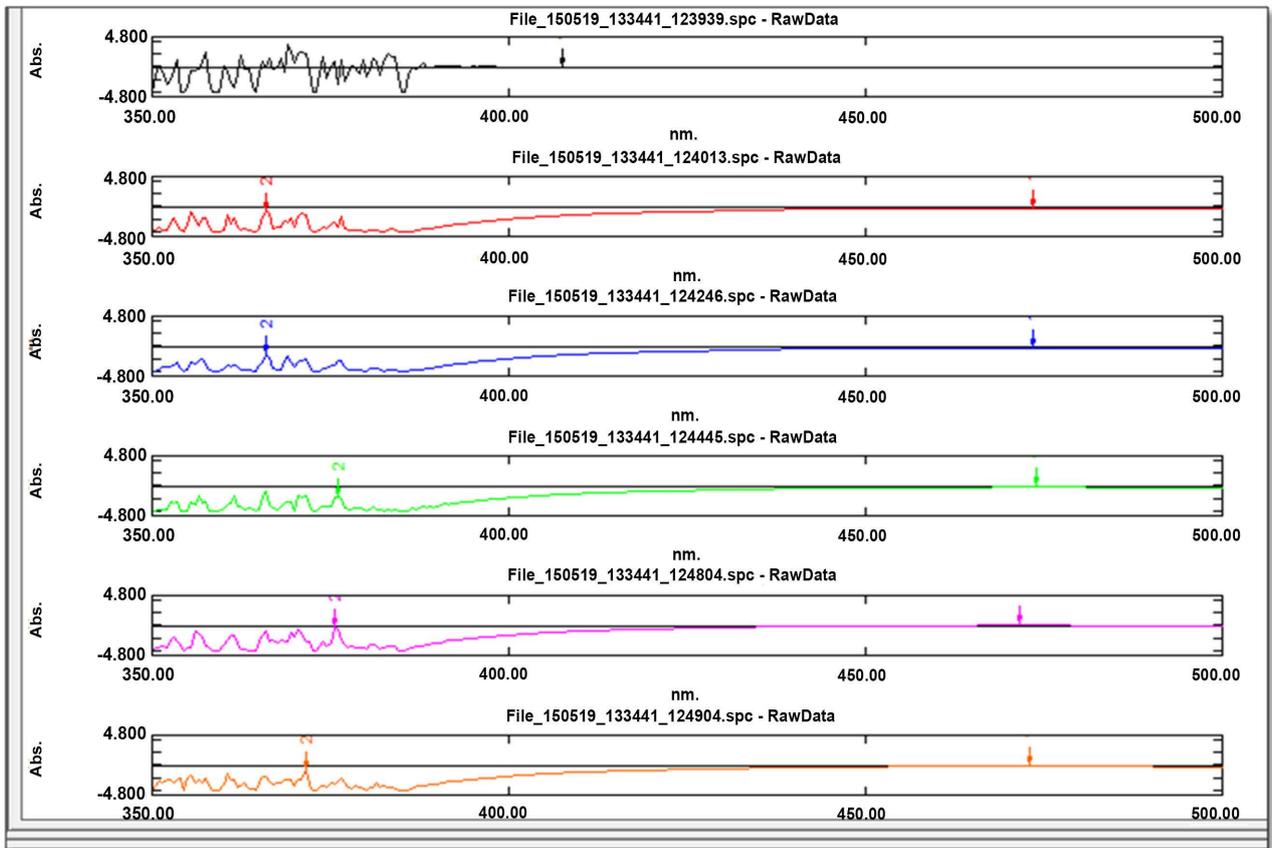


**Figure 4.** (a) FESEM photograph of Silver-loaded Chitosan nanocomposite; (b) FESEM photograph of Silver-loaded Chitosan nanocomposite (Rod shaped).

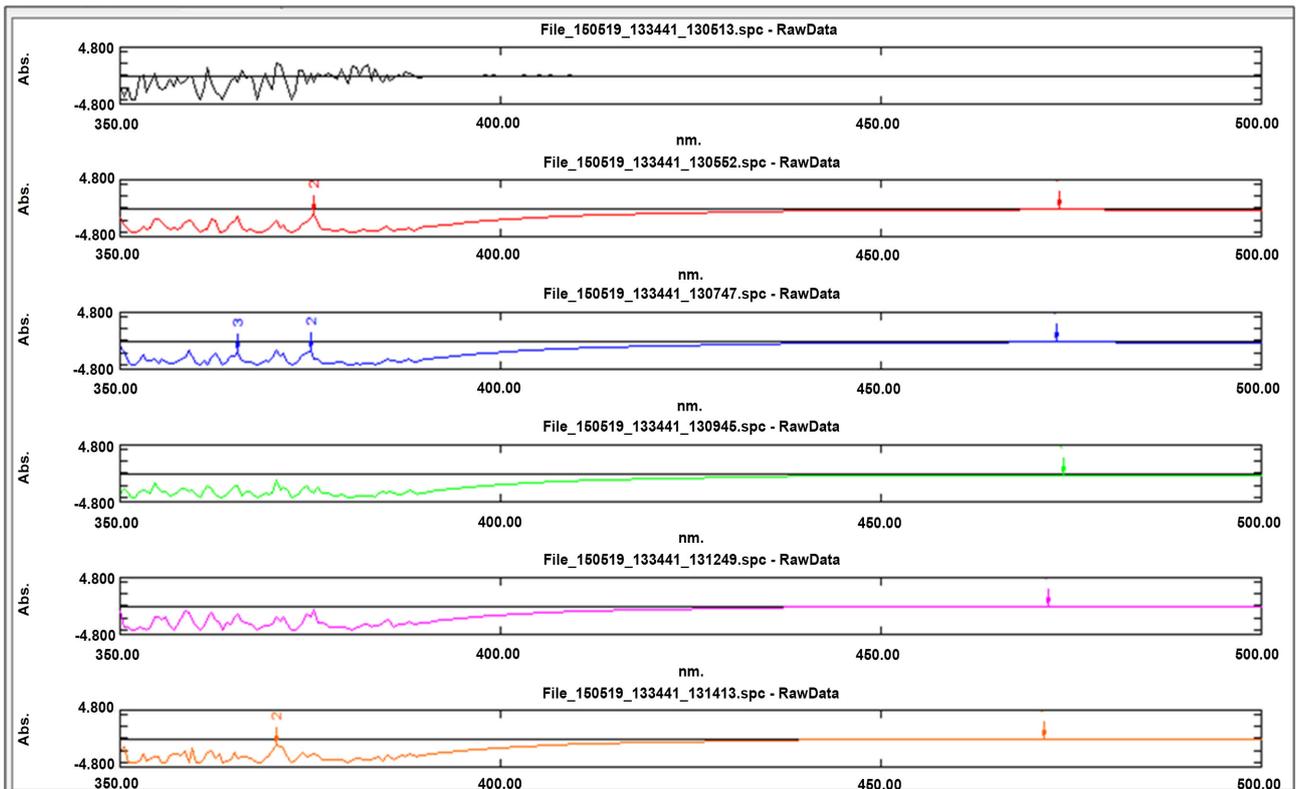


**Figure 5.** Particle size of Chitosan nanoparticle.

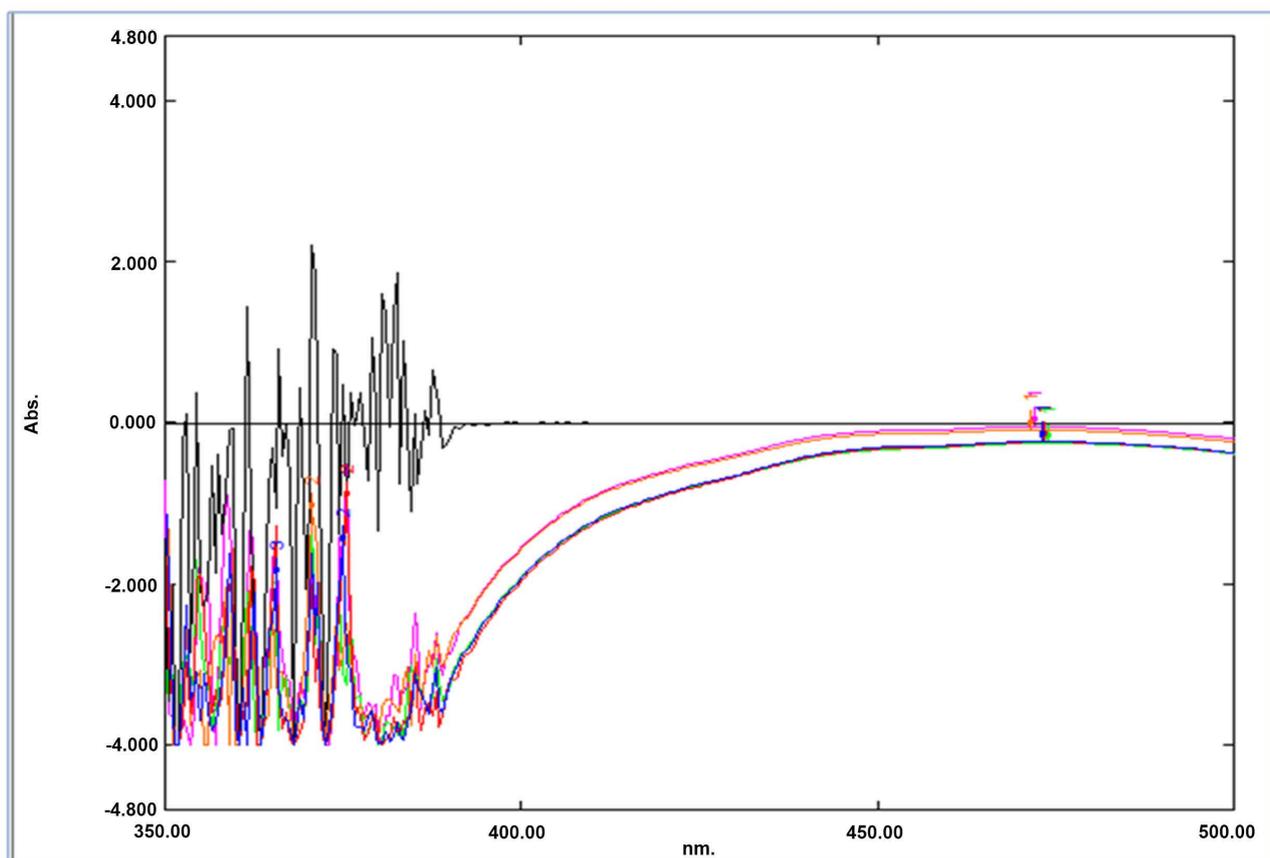
model is considered to be the best the dye removal isotherm model showing a monolayer adsorption, with a correlation coefficient value ( $R^2$ ) of 0.4912 (**Figure 8**). According to the Langmuir model maximum adsorption capacity for forming single layer. So this study shows that chitosan has a high adsorption capacity that is over 65% of its weight.



(a)

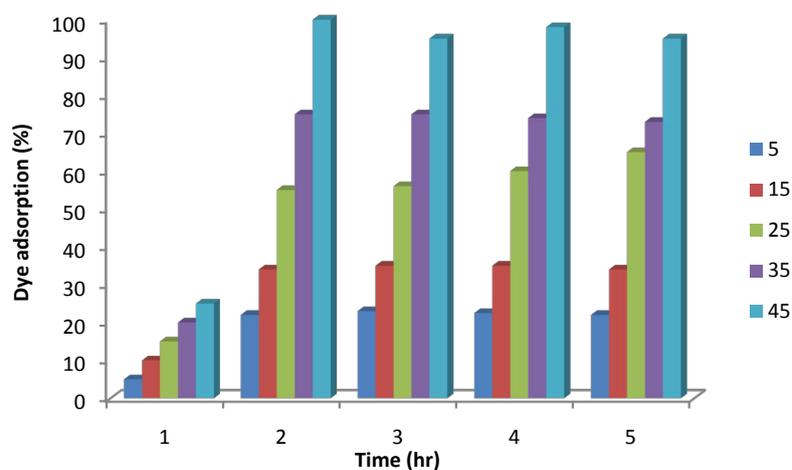


(b)



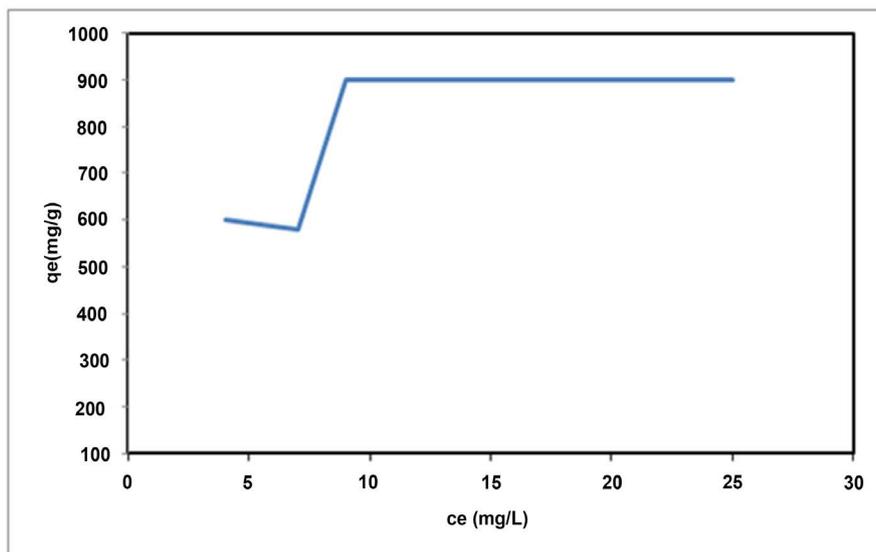
(c)

**Figure 6.** (a) Visible Spectra of Torque blue G treated Chitosan nanoparticle; (b) Visible Spectra of Orange dye treated Chitosan nanoparticle; (c) Combined Visible Spectra of Chitosan nanoparticle treated with Torque blue G and Orange dye.



**Figure 7.** Effect of time duration for the adsorption of the dye.

The absorption bands of FTIR of chitosan were found between 3643 - 3938  $\text{cm}^{-1}$  related to associated in N-H bond primary amines, 700  $\text{cm}^{-1}$  - 3650  $\text{cm}^{-1}$  was associated with C-Cl chloride; C-H aromatics; C-N stretch aliphatic amines; N-O asymmetric stretch nitro compounds; R-C(O)-Cl Acyl Chlorides; O-H



**Figure 8.** Adsorption isotherm of torque blue g and orange dye by Chitosan Nanoparticle.

**Table 1.** (a) FT-IR Analysis of Chitosan Nanoparticle; (b) FT-IR Analysis of Torque Blue G treated Chitosan Nanoparticle; (c) FT-IR Analysis of Orange treated Chitosan Nanoparticle.

(a)		
712.65	C-Cl	Chloride
858.26	C-H	Aromatics
1081.03	C-N stretch	Aliphatic amines
1476.41	N-O asymmetric stretch	Nitro compounds
1788.85	R-C(O)-Cl	Acyl Chlorides
2521.75	O-H stretch	Carboxylic acids
2920.03	C-H stretch	Alkanes
3434.98	O-H stretch	Alcohols
3642.32	O-H stretch	Alcohols
(b)		
711.68	C-Cl	Chloride
873.69	C-H	Aromatic
1047.27	C-N stretch	Aliphatic amines
1470.62	C-H bend	Alkanes
1792.71	R-C(O)-Cl	Acyl Chlorides
2515	O-H stretch	Carboxylic Acids
2921.96	C-H stretch	Alkanes
3404.13	O-H stretch	Alcohols

(c)		
712.65	C-Cl	Chloride
859.23	C-H	Aromatics
1081.99	C-N stretch	Aliphatic amines
1475.44	N-O asymmetric stretch	Nitro compounds
1787.89	C=O stretch (R-C(O)-Cl)	Acyl Chlorides
2521.75	O-H stretch	Carboxylic acids
2852.52	C-H stretch	Alkanes
2920.99	C-H stretch	Alkanes
3642.32	O-H stretch	alcohols

stretch carboxylic acids; C-H stretch alkanes; O-H stretch alcohols; O-H stretch alcohols (**Tables 1(a)-(c)**).

#### 4. Conclusion

In the current study, the chitosan nanoparticles were geared up from white snapper scales and used in wastewater treatment from textile industries as a bio-adsorbent. It is concluded that chitosan nanoparticles can be used as a potential bio adsorptive filter owing to their positive organic possessions.

#### Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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