CHAPTER VIII

DYE ADSORPTION BEHAVIOUR

8.1 Introduction

In the chapter 6, it was concluded that Z15N45 nanostructures prepared by simple and eco-friendly way showed better optical band gap with good crystallinity. In this chapter, the effect of sodium hydroxide concentration (30% and 45%) on the dye adsorption property of on the as-prepared chitosan-ZnO composite samples Z15N30 and Z15N45 were explained. For comparison purpose, commercial chitosan (CCS) and prepared chitosan (PCS) was also used for dye adsorption property. The preparation procedure for the above samples was given in the section 4.4.4, 4.4.1, 4.2.2 and 4.2.4 respectively. The results and discussion were made in the subsequent sections.

8.2 Batch adsorption

Adsorption experiments were carried out at room temperature (27°C). Exactly 100 ml of chromium complex dye solution with initial concentrations (25-100 mg/l) were shaken at constant agitation speed (200 rpm) with required amount of adsorbents (250-1000 mg/l) for a specified period of contact time (15 min) in a mechanical shaker. After the completion of experiment, equilibrium concentration is noted and the quantity of dye adsorbed, $q_e$ (mg/g) was calculated using the following equation (1):

$$q_e = \frac{(C_o - C_e) \times V}{W}$$

(1)
Where, $C_0$ is the initial concentration of dye, $C_e$ is the equilibrium concentration of dye; $V$ is the volume of the solution and $W$ is the weight of the adsorbent (chitosan-ZnO composites). The same experiment was repeated for PCS (prepared chitosan) and CCS samples.

8.3 Characterization of chitosan-ZnO composite

8.3.1 FTIR spectroscopy

Figure 8.1 (a-c) illustrates the infrared spectra of PCS and chitosan-ZnO composite. The FT-IR spectrum of PCS shows the characteristic peaks of chitosan at 1600 and 1352 cm\(^{-1}\) which are attributed to primary amines and C-H bonds of the CH\(_3\) group respectively.

The bands at 1021-1068 cm\(^{-1}\) corresponds to the stretching vibration of C-O bonds in primary alcohol [228-230]. The vibrational peaks at 880 and 774 cm\(^{-1}\) were assigned to glucopyranose ring of chitosan. A wide peak is appeared at 3423 cm\(^{-1}\), corresponding to the stretching vibration of hydroxyl, amino and amide groups (Figure 8.1a). On substitution of ZnO, this peak moved to lower wave numbers (3418, 3414 cm\(^{-1}\)) and became stronger, which indicated the strong interaction between these groups and ZnO [12]. Appearance of new peaks at 451 (Figure 8.1b) and 436 cm\(^{-1}\) (Figure 8.1c) in the chitosan–ZnO composite, is an indicative of ZnO immobilization onto the Chitosan [31, 11 & 231].
Figure 8.1: FTIR spectra of chitosan-ZnO composites (a) PCS (b) Z15N30 and (c) Z15N45.
8.3.2 SEM analysis

SEM image of PCS and chitosan-ZnO composite were shown in Figure 8.2 (a-c). The surface morphology of prepared chitosan (PCS) sample was observed with deformed particles, which is due to the presence of denser semicrystalline chitosan polymer. When the mixture of zinc chloride and sodium hydroxide solution were added to the extracted chitin the crystals are agglomerated in the form of flakes like structure. With increase of sodium hydroxide concentration in the mixture, more number of sheets and rods were observed on the surface. The presence of sheet and rod like structure confirm the formation of chitosan-ZnO composite.

ZnO composition for the Z15N45 sample determined by energy dispersive X-ray analysis (EDAX) showed as 74:26 (Figure 8.2 d), which indicate that the surface of the samples is rich in zinc metal and deviation of atomic ratio Zn: O to the expected 1:1. To concluded that the increase in sodium hydroxide concentration reduces the Zn ion content. Based on the stoichiometric composition of the samples, the nanostructures obtained are of good quality. The existence of Ca and Cl impurities was believed to have originated from the reactants of chitin and ZnCl₂ absorbed on the nanostructures.
Figure 8.2: SEM image of chitosan-ZnO composites (a) PCS (b) Z15N30 (c) Z15N45 and (d) EDAX analysis of Z15N45.
8.4. Dye adsorption

8.4.1. Calibration of dye

Calibration study was carried out with known concentrations of dye solution such as 25, 50, 75 and 100 mg/l. The absorbance intensity of prepared solution was measured in the UV-Visible spectrophotometer. The structure of chromium complex (Lanasyn) dye used for adsorption study is shown in Figure 8.3.

![Chemical structure of chromium complex dye](image)

**Figure 8.3: The chemical structure of chromium complex dye**

For each dye solution five tests were carried out and the average of maximum absorption intensity value (absorbance at $\lambda_{\text{max}}$ 579 nm) were recorded. A plot of maximum absorption intensity against the known dye concentration gives a straight line (subset of Figure 8.4).
Figure 8.4: Absorption spectra of (a) chromium complex Lanasyx Navy M-DNL with subset (b) dye calibration of linear regression.
8.4.2 Adsorption of dye

In this present study we evaluated the effect of chitosan-ZnO composite on dye removal without addition of any other chemicals for maintain the pH. Initially, when the dye dissolved in the distilled water the pH was 7.2. After addition of absorbent it raised to the pH of 10.8. The Chitosan contains amino group, –NH₂, which is easily protonated to form –NH₃⁺, in acidic solutions. At lower pH more protons will be available to protonate amino groups of chitosan molecules to form groups NH₃⁺, thereby increasing electrostatic attractions between negatively charged dye anions and positively charged adsorption sites and causing an increase in dye adsorption [231, 232].

As the pH of the system increases, the number of negatively charged sites is increased. A negatively charged site on the adsorbent does not favour the adsorption of anionic dyes due to the electrostatic repulsion [233]. Recently, lower adsorption of AB26 and DB78 dyes at alkaline pH was reported due to the presence of excess OH⁻ ions destabilizing anionic dyes and competing with the dye anions for the adsorption sites [12].

8.4.3 Langmuir adsorption isotherm

Langmuir theory was based on the assumption that the adsorption was a type of chemical combination or process and the adsorbed layer was unimolecular. The theory can be represented by the following linear form equation (2):

\[
\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \quad (2)
\]
Where $C_e$ is the equilibrium concentration of dye (mg/l), $q_e$ is the amount of dye adsorbed at equilibrium (mg g$^{-1}$), $Q_0$ (mg g$^{-1}$) and $b$ (mg/l) are Langmuir constants related to adsorption capacity and energy of adsorption respectively. The $C_e/q_e$ versus $C_e$ is obeying Langmuir isotherm model and its linear plot with various dye concentrations were shown in Figure 8.5.

Figure 8.5: Langmuir adsorption isotherm of different concentration of PCS adsorbent samples (a) 25 mg/l (b) 50mg/l (c) 75 mg/l and (d) 100 mg/l of chromium complex Lanasyr.
The initial concentration of dye was chosen from 25, 50, 75 and 100 mg/l. The each dye certain amount of adsorption, 25, 50, 75 and 100 mg/l dyes were observed the value of 0.0033, 0.0015, 0.0017 and 0.0019 mg/g, respectively.

To conclude that the 25 mg/l dye sample was observed better adsorption than 50, 75 and 100 mg/l. The following dye adsorption studies 25 mg/l dye substance selected for the all components. The results concluded that the dye solution of 25 mg/l was observed to have higher adsorption capacity than the dye solutions of 50, 75 and 100 mg/l concentrations. The values of $Q_0$ and $b$ were determined from intercept and slope of the linear plot were represented in Table 8.1.

Table 8.1: Langmuir and Freundlich adsorption isotherm of different concentration of PCS adsorbent samples with 25 mg/l, 50mg/l, 75 mg/l, and 100 mg/l of chromium complex Lanasyn dye.

<table>
<thead>
<tr>
<th>Dye(mg/l)</th>
<th>$Q_0$ (mg/g)</th>
<th>$b$ (mg/l)</th>
<th>$R^2$</th>
<th>$K_F$ (mg/g)</th>
<th>$1/n$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>0.0033</td>
<td>0.42</td>
<td>0.92</td>
<td>0.52</td>
<td>0.8215</td>
<td>0.93</td>
</tr>
<tr>
<td>50</td>
<td>0.0015</td>
<td>0.38</td>
<td>0.78</td>
<td>0.44</td>
<td>0.6364</td>
<td>0.71</td>
</tr>
<tr>
<td>75</td>
<td>0.0017</td>
<td>0.44</td>
<td>0.91</td>
<td>0.50</td>
<td>0.7778</td>
<td>0.88</td>
</tr>
<tr>
<td>100</td>
<td>0.0019</td>
<td>0.49</td>
<td>0.97</td>
<td>0.36</td>
<td>0.6001</td>
<td>0.95</td>
</tr>
</tbody>
</table>
Figure 8.6: Langmuir adsorption isotherm of different adsorbents with 25 mg/l of chromium complex Lanasy (a) CCS (b) PCS (c) Z15N30 and (d) Z15N45.
Figure 8.6 shows the adsorption isotherm for dye solution with initial concentration of 25 mg/l was by taking different adsorbents such as CCS, PCS, Z15N30 and Z15N45.

The values of $Q_0$ and $b$ were determined from intercept and slope of the linear plot of $C_e/q_e$ versus $C_e$ obtained by varying adsorbent and represents in Table 8.2. The good fit of the experimental data and the correlation coefficients ($R^2$) higher than 0.95 indicated the applicability of the Langmuir isotherm model.

Table 8.2: Langmuir and Freundlich adsorption isotherm of different adsorbents with 25 mg/l of chromium complex Lanasyn dye with CCS, PCS, Z15N30, and Z15N45.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>$Q_0$ (mg/g)</th>
<th>$b$ (mg/l)</th>
<th>$R^2$</th>
<th>$K_F$ (mg/g)</th>
<th>$1/n$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCS</td>
<td>0.0086</td>
<td>2.6</td>
<td>0.82</td>
<td>0.31</td>
<td>0.42</td>
<td>0.76</td>
</tr>
<tr>
<td>PCS</td>
<td>0.0135</td>
<td>2.7</td>
<td>0.91</td>
<td>0.34</td>
<td>0.64</td>
<td>0.87</td>
</tr>
<tr>
<td>Z15N30</td>
<td>0.0167</td>
<td>5.0</td>
<td>0.95</td>
<td>0.43</td>
<td>0.88</td>
<td>0.97</td>
</tr>
<tr>
<td>Z15N45</td>
<td>0.0214</td>
<td>6.4</td>
<td>0.96</td>
<td>0.54</td>
<td>0.92</td>
<td>0.98</td>
</tr>
</tbody>
</table>
The essential characteristics of Langmuir dimensionless constant separation factor or equilibrium parameter, $R_L$, which is defined by the through equations (3):

$$R_L = \frac{1}{1 + bC_0}$$  \hspace{1cm} (3)

Where $C_0$ is the initial dye concentration, mg/l and the value of separation factor $R_L$ indicates the nature of the adsorption process to be either unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) or irreversible ($R_L = 0$). In the present study, the $R_L$ values are observed to be in the range of 0-1, and this adsorption process is favourable for all types of prepared chitosan-ZnO complex.

### 8.4.4 Freundlich adsorption isotherm

The Freundlich adsorption model stipulates that the ratio of solute adsorbed to the solute concentration is a function of the solution. The empirical model was shown to be consistent with an exponential distribution of active centers, characteristic of heterogeneous surfaces. The amount of solute adsorbed, $q_e$ is related to the equilibrium concentration of solute in solution, $C_e$, following equation (4) and (5):

$$q_e = K_F C_e^{1/n}$$  \hspace{1cm} (4)

This expression can be linearized to give the following equation:

$$\log q_e = \log K_F + 1/n \log C_e$$  \hspace{1cm} (5)
Figure 8.7: Freundlich adsorption isotherm of different concentration of PCS adsorbent samples (a) 25 mg/l (b) 50 mg/l (c) 75 mg/l and (d) 100 mg/l of chromium complex Lanasyn.
where $K_F$ is a constant for the system, related to the binding energy. $K_F$ can be defined as the adsorption or distribution coefficient and respects the quantity of dye adsorbed onto CCS, PCS and chitosan-ZnO composite adsorbents for a unit equilibrium concentration (a measure of adsorption capacity, mg g$^{-1}$).

The slope $1/n$, ranging between 0 and 1, is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero [235]. A value for $1/n$ below one indicates a normal Freundlich isotherm while $1/n$ above one is cooperative adsorption [236]. A plot of log ($q_e$) versus log ($C_e$) obtained by varying initiated dye concentration was shown in Figure 8.7.

The values of $K_F$ and $1/n$ are determined from the intercept and slope of the linear regressions for chitosan adsorbents and represented in Table 8.1. A plot of log ($q_e$) versus log ($C_e$) obtained by varying adsorbents concentration was shown in Figure 8.8. The values of $K_F$ and $1/n$ are determined from the intercept and slope of the linear regressions for all the adsorbents and represents in Table 8.2.
Figure 8.8: Freundlich adsorption isotherm of different adsorbents with 25 mg/l of chromium complex Lanasyn (a) CCS (b) PCS (c) Z15N30 and (d) Z15N45.
8.5 Conclusion

Presence of chitosan and ZnO in the prepared composites was confirmed by Fourier transform infrared spectroscopy and scanning electron microscopy. The adsorptions of chromium complex dye onto CCS, PCS and chitosan-ZnO composite were investigated in the aqueous dye solution. The adsorption data were mathematically analyzed using Freundlich and Langmuir adsorption isotherms. The observed data fits well with Langmuir adsorption isotherm. From the adsorption isotherm it was found that the chitosan-ZnO composite (Z15N45) has better adsorption capacity than the Z15N30, prepared chitosan (PCS) and commercial chitosan (CCS). The experimental isotherm data for composites were fitted well with the Langmuir isotherm model. Thus, the chitosan-ZnO composite can be used as an effective biosorbent for the removal of anionic dye.