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# COORDINATIVE INTERACTION OF CHITOSAN-AZO DYES TOWARDS SELECTED FIRST ROW TRANSITION METALS

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## ABSTRACT

Chitosan is an abundant bio-polymer obtained by alkaline deacetylation of chitin in the exoskeleton of crustaceans. Chitosan was found to be an attractive alternative to other bio materials due to its significant physicochemical behavior and ability to selectively bind to transition and post transition metals. In order to improve the performance of this bio-polymer, chemical modification of chitosan composite and its derivatives have gained much attention. In this study, a new biopolymeric ligand was synthesized by functionalizing chitosan with eriochrome black T (EBT) and sudan III (S3) dyes. The functionalized compounds were interacted with Co(II), Ni(II), Cu(II) and Zn(II) metal ions at varied concentrations leading to complex formation. Both the new ligand and the complexes obtained at high yields were characterized using Fourier Transform Infrared (FT-IR) and Uv-Vis Spectroscopy. The FT-IR spectra revealed a possible hydrogen bonding between chitosan and the azo dye. It also suggests an interaction between the N=N of the ligand with the metal ions. In addition, the Uv-Visible spectra studies showed that on reacting various concentrations of metal ions with ligand the absorbance increases with decreasing concentration of the metal ions and was able to interact with as low as 0.001 M of the studied metal salts.

**Key words:** Chitosan, Biopolymeric ligand, Eriochrome black T, Sudan III, Transition metals

## INTRODUCTION

The increasing demand for a more environmentally friendly ecosystem has triggered research in novel processes for waste water treatment (Guibal *et al.*, 2005). Transition metals are naturally found in the earth's crust. They are introduced into the environment as a result of human activities and rapid industrialization. Despite the fact that trace amounts of these metals are essential to the human body, higher concentrations can be dangerous to human health due to their non-biodegradability and bioaccumulation in living tissues (Rasha and Amany,

2013). Chitosan is a good cationic biopolymer with free amines and hydroxyl group in some of its repeat units, which gets protonated in dilute acidic media (Adewuyi *et al.*, 2008). These protonated functional groups form the multiple bonding sites that are useful in chelating and stabilizing heavy metals like Cu<sup>2+</sup>, Ni<sup>2+</sup> and Zn<sup>2+</sup> ions (Guibal, 2004; Lui *et al.*, 2006; Adel *et al.*, 2011; Fajardo *et al.*, 2012).

Chitosan has widely been reported for chelating metal ion because it possesses metal binding functional groups (Guibal, 2004;

Meng *et al.*, 2012; Crini *et al.*, 2014; Kyzas and Bikiaris, 2015), high thermal stability, non-toxic, biodegradable (Ma and Sahai, 2013) and ease for chemical and physical modifications etc. (Pillai *et al.*, 2009). Functionalizing occurs when a reagent introduces intermolecular bridges between the polymer macromolecules (Crini and Badot, 2008; Krishnapriya and Kandaswamy, 2010). Therefore, functionalizing chitosan reduces segment mobility in the polymer and a number of chains are interconnected by the formation of new inter-chain linkages on the chitosan backbone (Adel *et al.*, 2011; Shewta and Sonia, 2013). The insertion of functional groups into the chitosan polymer matrix may improve its capacity of interaction with metallic ion by complexation. We therefore report a new chelating ligand based on chitosan functionalized azo dye for complexation with selected first row transition metal ions.

## MATERIALS AND METHODS

Chitosan powder was purchased from Sigma Aldrich (USA). Other analytical grade reagents were used as received and distilled water was used for the preparation of aqueous solutions. A T92+ PG UV-Visible spectrophotometer available at Chemistry Laboratory, Federal University of Agriculture, Abeokuta was used for spectral studies while the presence of reacting functional groups were determined on Shimadzu FT-IR Spectrophotometer available at the Central Research Laboratory, LAUTECH, Ogbomoso.

### **Preparation of Chitosan Functionalized Azo Dye**

Chitosan solution was prepared by dissolving 1.0 g of chitosan in 100 mL of 1% aq. glacial acetic acid with constant stirring for about 1 h at 60 °C until a clear homogene-

ous solution was formed. The azo dye (EBT and S3) solutions were prepared by dissolving 1.0 g of the dye in 100 mL of ethanol with stirring for 45 mins at room temperature. The resulting solution was filtered to remove the undissolved particles. Thereafter, the dye was mixed with chitosan solution in molar ratio 1:1 under magnetic stirring condition for about 1 hour at room temperature to form chitosan functionalized compound (Adewuyi *et al.*, 2012). The product was decanted and air dried at room temperature for 72 hours in a Petri dish to give a yield of 85 %.

### **Preparation of Chitosan Functionalized Azo Dye Metal Complex**

Molar concentrations (0.1, 0.05, 0.01, 0.005 and 0.001 M) of the metal salt solution ( $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  and  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) were prepared by dissolving accurately weighed amount of the metal salt in 100 mL distilled water. The functionalized chitosan solution was added to the metal salt solution in molar ratio 1:1 under magnetic stirring at 60 °C for about 1 hour to allow for the formation of the chitosan- azo dye-metal complex. Furthermore, the liquid supernatant was decanted while the complex residue was emptied into a petri dish and air-dried at room temperature for about 72 hours (Adewuyi *et al.*, 2012).

## RESULTS AND DISCUSSION

### **FTIR Spectroscopy Analysis**

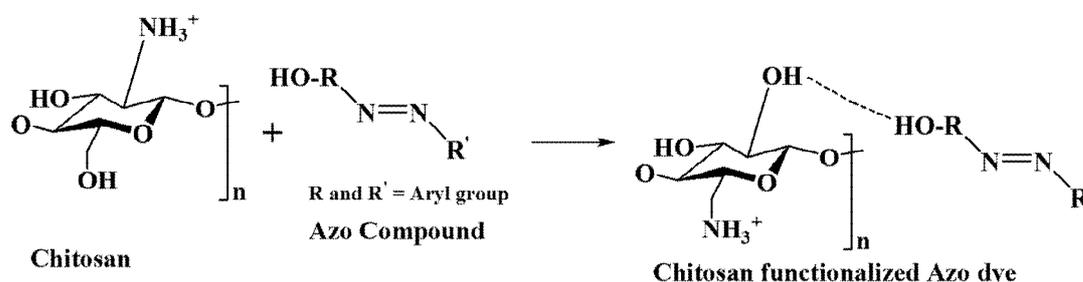
The FTIR spectrum of EBT and S3 (Table 1) shows a weak and broad band at 3329 and 3298  $\text{cm}^{-1}$  respectively, tentatively assigned to O-H functional group inherent in the dyes. Upon functionalization with chitosan, there was a slight shift to 3296  $\text{cm}^{-1}$ , which is broader and intense, suggesting interaction between the dye and chitosan via hydrogen

bonding. Furthermore, the sharp and intensified peak at  $1045\text{ cm}^{-1}$  in EBT characteristic of azo bond, was slightly weakened at  $1043\text{ cm}^{-1}$  in the spectrum of chitosan functionalized eriochrome black T (CFEFT). A sharp peak due to azo bond in S3 was prominent at  $1043\text{ cm}^{-1}$  and was weakened upon functionalization. In addition, when

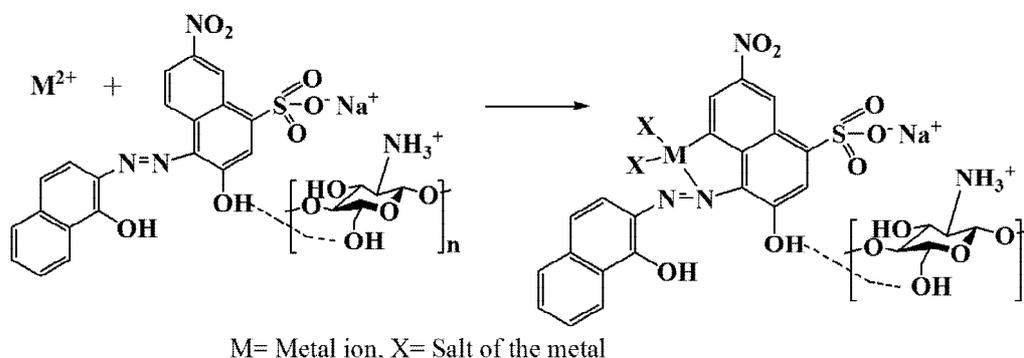
the metals were introduced to form the complexes, the peaks due to the azo bond were greatly weakened, suggesting an interaction between the metal and the  $\text{N}=\text{N}$  of the functionalized compound which could be attributed to the formation of cyclo-metalated – functionalized azo compound (Shun-Hua *et al.*, 2004).

**Table 1: IR stretching frequencies of major functional groups**

Materials	$\nu\text{O-H}/\nu\text{N-H}$ ( $\text{cm}^{-1}$ )	$\nu\text{N}=\text{N}$ ( $\text{cm}^{-1}$ )
Chitosan	3460/3266 (broad and weak)	-
EBT	3329 (broad and weak)	1045 (sharp and intense)
CFEFT	3296 (broad and intense)	1043 (sharp and weak)
CFEFT-Cu(II) Complex	3313 (broad and intense)	1045 (very weak)
CFEFT-Zn(II) Complex	3305 (broad and intense)	-
S3	3298 (broad and intense)	1045 (sharp and weak)
CFS3	3298 (broad and intense)	1043 (sharp and intense)
CFS3-Co(II) Complex	3309 (broad and intense)	-
CFS3-Ni(II) Complex	3284 (broad and intense)	-



**Scheme 1: Proposed hydrogen bonding between chitosan and Azo dye**



**Scheme 2: Proposed reaction scheme for metal complex formation**

### Uv-Visible Spectroscopy Analysis

S3 and EBT dyes are highly conjugated chromophore bearing compounds; hence, they are expected to absorb light in the visible region of the spectrum (Pandey *et al.*, 2007). In this study, S3 and EBT dyes (Figures 1 and 2) absorbed at wavelength around 500 and 520 nm with intensities of 0.66 and 0.91 respectively. On further func-

tionalization, hypochromic shift was observed at 0.11 and 0.29 respectively. This large reduction in the absorbance could be due to the hydrogen bonding between the chitosan and dyes (Scheme 1). The negative inductive effect due to the OH group could be responsible for reduced chromophoric property of functionalized compounds.

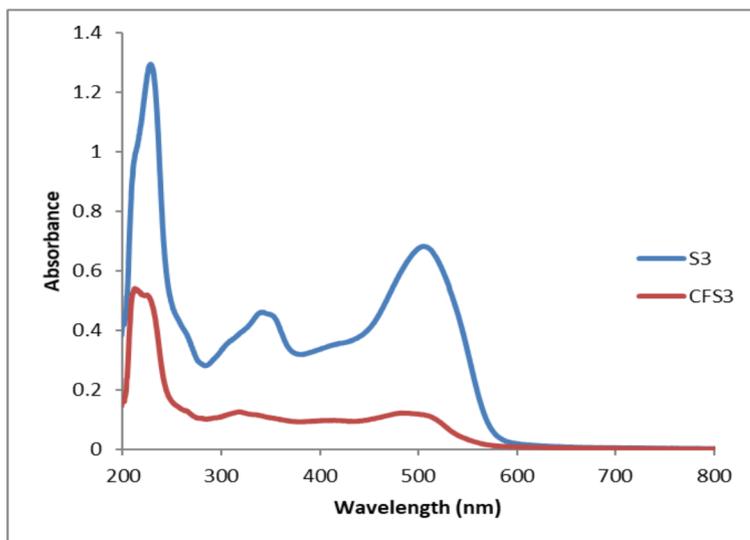


Figure 1: Uv-Vis Spectra of S3 and CFS3

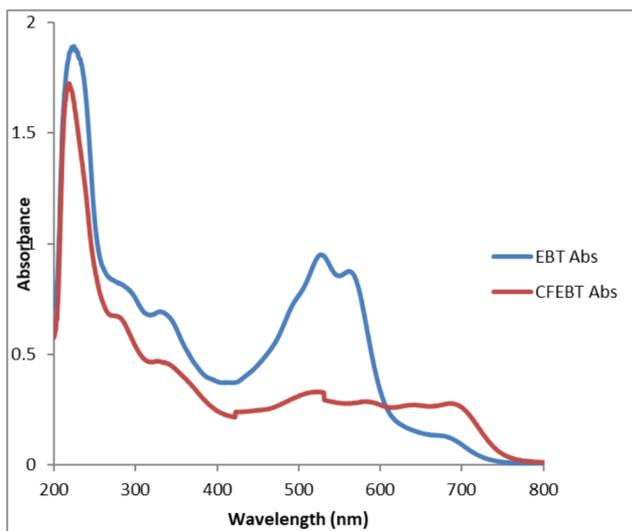


Figure 2: Uv-Vis Spectra of EBT and CFEBT

On complexation, (Scheme 2), three bands were observed in the UV-Visible spectra of CFEBT-Zn(II) complex (Figure 3) at 273, 335 and 510 nm. Zn(II) being a  $d^{10}$  compound, no  $d-d$  transition are expected (Loft *et al.*, 2008), thus, the bands are tentatively assigned to  $\pi-\pi^*$  (due to the benzene ring),  $\pi-\pi^*$  (due to azomethine chromophore) and charge transfer bands respectively (Boghaei and Gharagozlou, 2007). Furthermore, two peaks were observed for CFS3-

Ni(II) complex (Figure 4) at 298 and 510 nm which are tentatively assigned to  $d-d$  electronic transition and MLCT band respectively. The charge transfer band arises from molecular orbital with metal-like character to those with ligand-like character and is commonly observed in complexes with ligands having low lying  $\pi^*$  orbitals, especially aromatic ligands.

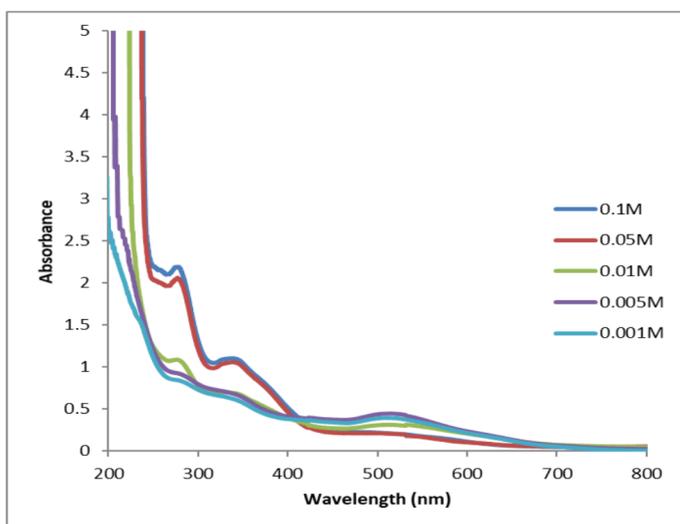


Figure 3: Interaction of CFEBT with different concentrations of Zn(II)

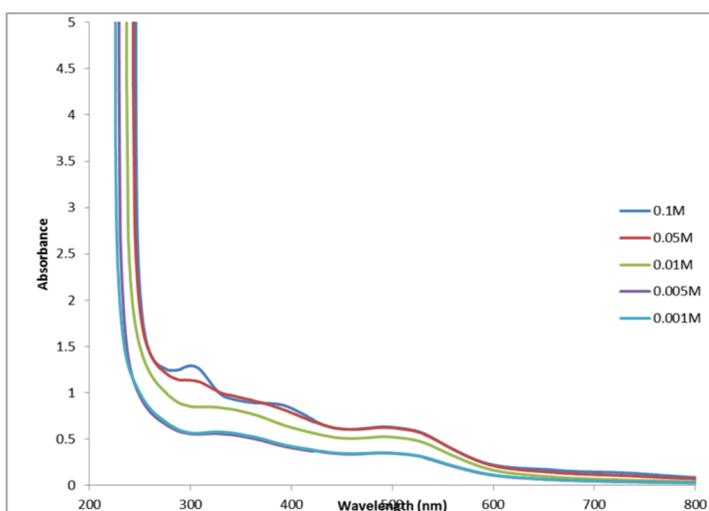
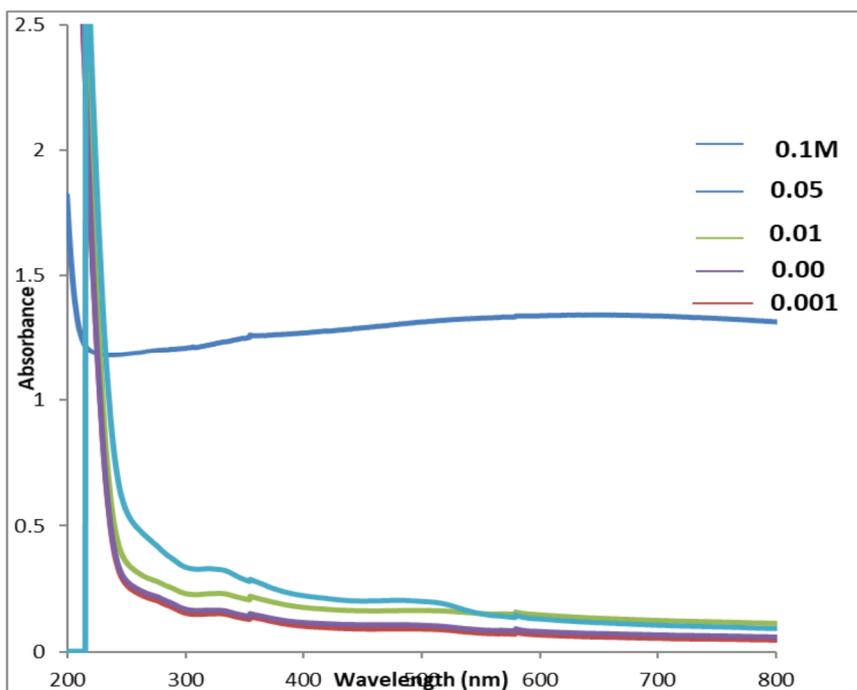
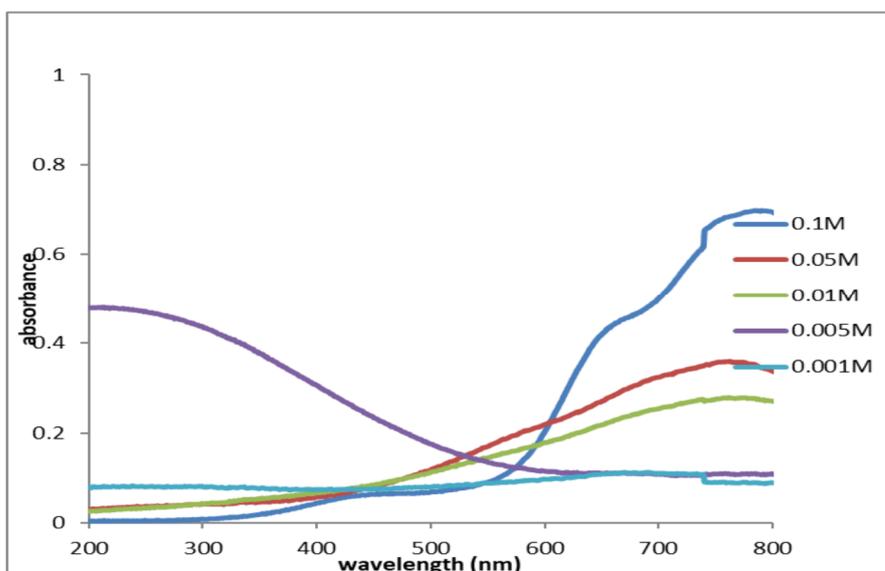


Figure 4: Interaction of CFS3 with different concentrations of Ni(II)

CFS3-Co(II) complex (Figure 5) displayed a weak band due to *d-d* electronic transition at around 303 nm while CFEBT-Cu(II) complex (Figure 6) was highly absorbed in the visible region of the spectrum. Similarly, hyperchromic shift was observed upon interaction of different concentrations (up to 0.001 M) of the metal ions in aqueous solution when compared with the absorbance of the functionalized compounds.



**Figure 5:** Interaction of CFS3 with different concentrations of Co(II)



**Figure 6:** Interaction of CFEBT with different concentrations of Cu(II)

## CONCLUSION

In this study, metal complexes of Co(II), Ni(II), Cu(II) and Zn(II) ions were prepared with chitosan functionalized azo dyes. The complexes were characterized using FT-IR and Uv-Visible spectroscopy. The spectroscopic technique suggests hydrogen bonding interaction between chitosan and the dyes. Interactions observed between the functionalized chitosan-dye and the metal ions could be attributed to charge transfer i.e. movement of electrons from the electron rich metal centre into the empty antibonding  $\pi^*$  orbital of the N=N functional group of the EBT-dye (back donation).

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