International Journal of Basic and Applied Chemical Sciences ISSN: 2277-2073 (Online)
An Open Access, Online International Journal Available at http://www.cibtech.org/jcs.htm
2014 Vol. 4 (2) April-June, pp.1-9/Haleim and Abbo
Research Article

FORMATION AND STABILITY OF NICKEL (II), IRON (II) AND COPPER (II) CHELATES OF INDIGOID

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ABSTRACT
The interactions of Fe(II), Ni(II) and Cu(II) with indigo carmine (IC) were studied by UV–Vis. absorption spectrophotometer. The effect of time on the stoichiometry and stability of the metal chelate formed , revealed a ratio of (1:2) for all chelates, except for Cu(II) which form two chelates with a ratio of (1:1) and (1:2) depending on the concentration of the metal ion and the ligand. The mean values of log k_2 for the chelates of Fe and Ni were found to be 7.2 and 8.05 respectively. For Cu chelate(1:1) the mean value of log k was found to be 5.98. The value of log k_2 of Cu chelate (1:2) for the first day was found to be 9.2.The stability of these complexes was found to be in the order: Cu(1:2) > Ni > Fe > Cu(1:1).
The effect of time on the stability of these complexes showed that, Cu(1:1) and Fe chelates were not affected by time, while there was a decrease in the absorbance of Ni and Cu(1:2) chelates. pH of these complexes were measured without adjustable and plotted against the absorbance. All the complexes were found to be stable in neutral and alkaline media. The study of the effect of direct sun light ensured that the complexes in acidic media were more stable toward sun light, except for Ni which was more stable at the neutral to alkaline media.

***Keywords**: Metal Chelates, Dye, Stability*

INTRODUCTION
Natural dyes extracted from natural living sources such as plants and animals. These dyes, which include mainly carotenoids, hydroxyketones, anthraquinones, naphthoquinones, flavones, flavonols, flavonones, indigoids and related compounds, are obtained either as coloured compounds or as colorless extracts turn into colored compounds by certain reactions such as hydrolysis, oxidation, condensation, and complexation with transition metal ions (Bener *et al.*, 2010).
Many metal chelates of indigo have been prepared (Larkworthy and Nyholm, 1959; Larkworthy, 1961; Ovarlez *et al.*, 2011; Angewandte, 1989; Nawn *et al.*, 2011; Oakley *et al.*, 2010; Domenech *et al.*, 2009; Raya *et al.*, 2010), one of these chelates is the iron bis-indigo whose magnetic measurements suggests a tetrahedral configuration for the apparently 4-coordinate metal atom, but octahedral coordination to neighboring molecule is also possible. The study of catalytic activity of Rhodium-indigo complexes showed that they are effective catalysts for isotope exchange reaction between hydrogen and water (Sakharovskii *et al.*, 1978). Indigo is considered as a new source of valuable antioxidants (Kim *et al.*, 2012), its contents of bioactive compounds such as antioxidants and antiproliferative and their activities compare to that of another medicinal plant Prolipid has been studied (Xia *et al.*, 2011). Most studies on indigo have focused on their properties as dyes (Littmann, 1982; Domenech and Domenech, 2009; Papanastasiou *et al.*, 2012; Giustetto *et al.*, 2011; Balfour, 1998). Indigo carmine have been used in the test for nitrate found as impurity in Bismuth salts (Ashutosh, 2005). Indigo carmine is not found to have any toxicity to human luteal cells (Mahadevan *et al.*, 1993) when used as an alternative contrast-enhancing agent to methylene blue in carcinoma of the esophagus (Lamsabhi *et al.*, 2005).
The disposal of industrial waste containing dyes is considered as one of serious pollutants to aquatic environment. Several methods are adopted for removing dyes from waste water (Olak *et al.*, 2009;

Bayramoglu *et al.*, 2009; Merzouk *et al.*, 2009; Eyvaz *et al.*, 2009; Ahmad and Puasa, 2007), among which the photodecomposition method is the most popular and widely studied (Saien *et al.*, 2009; Mao and Weng, 2009). Several approaches are employed for the degradation of indigo carmine (Lichtfouse and Schwarzbauer, 2005; Guaraldo *et al.*, 2011; Gemeay *et al.*, 2003; Barka *et al.*, 2008).

MATERIALS AND METHODS

AmmoniumFerrous Sulfate (Hopkins and Williams grade), Copper Chloride, Nickel Chloride and Indigo Carmine, (BDH grade) were weighted and dissolved in a double disstilled water.

Apparatus:-

Measurements of absorption spectra were carried out using UV/Vis. Spectrophotometer (PerkinElmer , model Lambda 2, Germany), the solvent was used as a reference solution, Colorimeter Lab system (5826).pH measurements were carried out using WPA pH Meter Bench CD510C.which calibrated against standard buffer solutions.

Procedure:-

Solutions were made by dissolving an appropriate amount of the compounds in in a double disstilled water.The stoichiometry of the prepaired complexes was determined by Continuous Variation Method (Werner, 1971). The Mole ratio method (Meyer, 1957) was used to confirm the empirical formula of 1:2 Copper complex.

RESULTS AND DISCUSSION

Absorption Spectra:- Figure 2. shows typical absorption curves for equi- molar solutions of $Cu^{(II)}$, $Ni^{(II)}$, and $Fe^{(II)}$ with Indigo Carmine. The molarities of all solutions were kept at 0.001M , and 0.0002 M for 1:2 Copper complex.

The peaks at ratios of 0.34 and 0.45 for copper (II) complex indicate that, under these conditions, two complexes containing $Cu^{(II)}$ and indigo carmine(Figure.1) in the ratios of 1:2 and 1:1(respectively) are formed, which means that $Cu^{(II)}$ at low concentration combines with indigo carmine at the ratio of 1:2, while at higher concentration the complex formed was in the ratio of 1:1. Molar ratio method was employed to confirm these stoichiometries (Figure 3.)

The resulting curves for $Ni^{(II)}$ and $Fe^{(II)}$ (Figure 2.), showed sharp absortion maxima at 0.39 and 0.36 respectively. This indicate that the only $Ni^{(II)}$ and $Fe^{(II)}$ complexes formed with Indigo carmine in these solutions are in the ratio of 1:2.

All these solutions which were prepared according to continuous variations were kept for six days and the stability constants were then determined. It was very interesting to show that the stability constant of Cu(1:2) Chelate is greater than those of the corresponding $Fe^{(II)}$ (1:2) ,$Ni^{(II)}$ (1:2) and Cu (1:1) chelates. The mean value of logk for $Fe^{(II)}$ (1:2) , $Ni^{(II)}$ (1:2) and $Cu^{(II)}$ (1:1) was 7.9 ,8.05 and 5.98 respectively ,while log k for $Cu^{(II)}$ (1:2) for the first day was 9.7. (Figure4.) showed the plot of stability constant (log k) of $Fe^{(II)}$,$Ni^{(II)}$ and $Cu^{(II)}$ (1:1) versus time (in days).

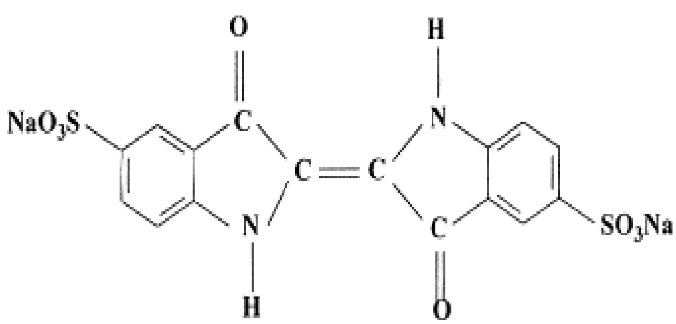

Figure 1: Indigo Carmine

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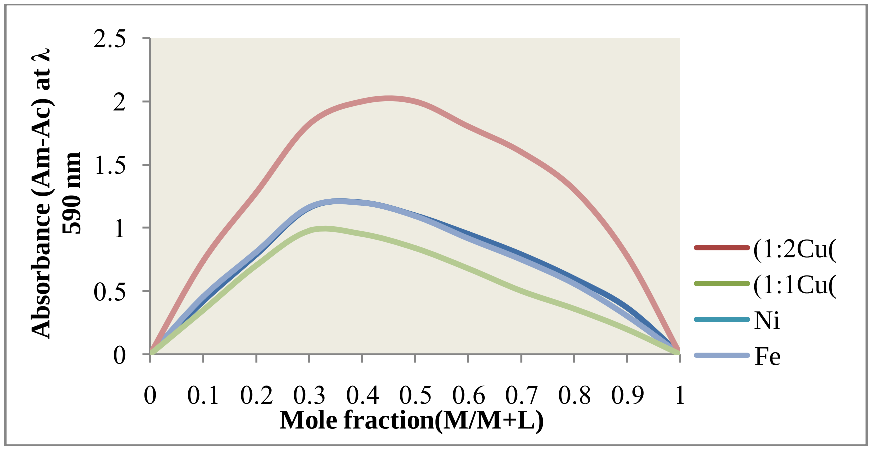

Figure 2: Continuous variation method. Volume of solutions,20 cc; curve 1, $CuCl_2H_2O$(0.0002M), curve 2, $NiCL_2.6H_2O$, curve 3, $FeSO_4(NH_4)_2SO_4.6H_2O$, curve 4, $CuCL_2.2H_2O$

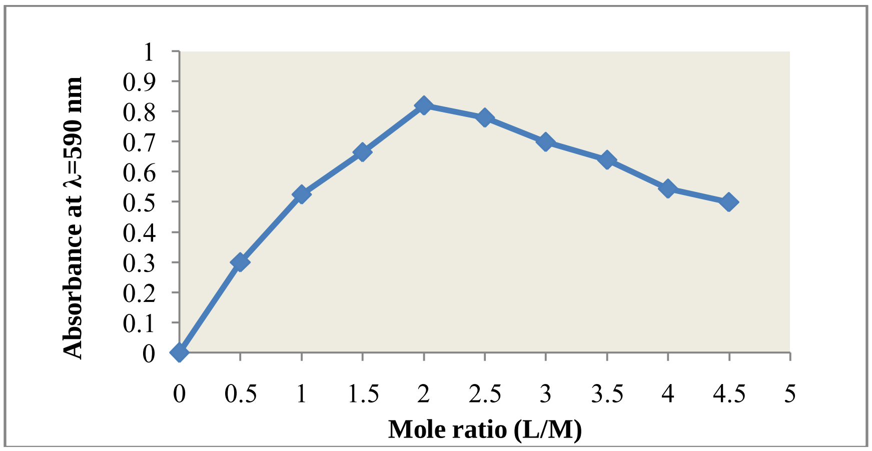

Figure 3: Molar ratio method of Cu-Indigo carmine(1:2); Cu and indigo =0.002 M

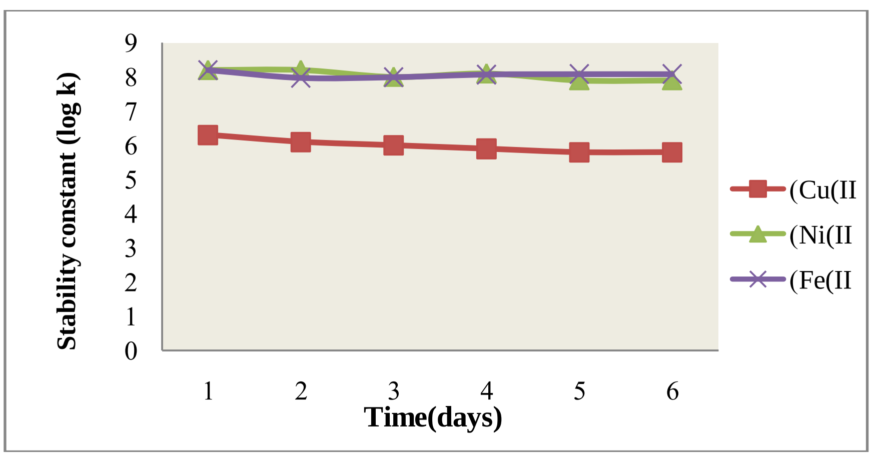

Figure 4: Stability constant (log k) of solutions containing 0.001M metal ions (Fe, Ni and Cu) with 0.001M indigo carmine

All the stability constants were calculated using the following equation :

$$K_n = [(A/A_{ex}).C_M]/[C_M(1-\{A/A_{ex}\})(A/A_{ex}.1/n)^n C_L^n]$$

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Where :
n = number of moles of ligand per mole of metal.
A=maximum absorbance on the curve.
A_{ex} = extrapolated absorbance
C_M = Total concentration of metal.
C_L = Total concentration of ligand.

The results, in general, showed that there is a convergence in the stability constant throughout the week. It is noted that the stability constant of indigo carmine with the metal ions $Fe^{(II)}$, $Ni^{(II)}$ and $Cu^{(II)}$ increases steadily to reach maximum with copper 1:2. The copper 1:1 Chelate is less stable than all complexes in this study.

The relative stabilities of these chelates are in general, agreement with Irving – Williams, order (Catherine *et al.*, 2008). The stability order increases in the order shown below.

$$Cu(1:1) \prec Cu(1:2) \succ Ni \succ Fe\ .$$

Effect of experimental variables on the extent of formation and stability of transition metal ions chelates.

Effect of time:

The effect of time on the absorption of chelates was measured at interval of 24 hours for 6 days. The result showed that no change in the absorption of $Fe^{(II)}$ and $Cu^{(II)}$ (1:1), while the absorbance was remain constant for the first three days for $Ni^{(II)}$ Chelate ,then decreased, steadily, for the rest of the days.For $Cu^{(II)}$ (1:2) chelate the absorbance was decreased steadily (Figure.5).

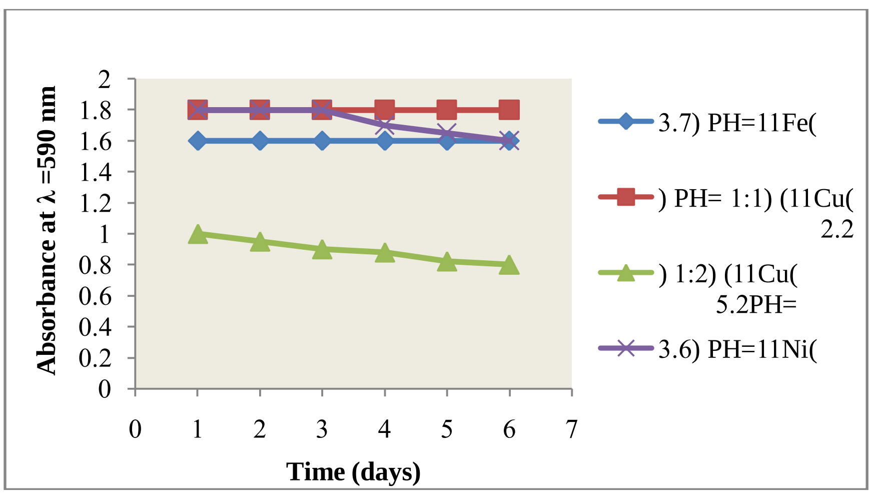

Figure 5: Effect of time on the absorbance ; Temp.=37˚c

Effect of pH

The effect of pH on the extent of formation and stability has been investigated. An appropriate amount of metal ion and ligand in the ratio required for complex formation were introduced into each of seven sample tubes. The pH of solutions was varied using 0.1 M Sodium hydroxide solution in the range of 3.5 – 10.2. The initial concentration of both metal ion and ligand was kept equal. The result showed that the absorbance of $Fe^{(II)}$ and $Cu^{(II)}$ (1:1) complexes decreases above pH 9.4, while for $Cu^{(II)}$ (1:2) chelate the maximum absorbance occurred at pH 5.2. As the pH increases, the absorbance decreases steadily. The absorbance of $Ni^{(II)}$ chelate slightly increases up to the maximum at pH 7.2,then starts to decrease at constant rate at pH range of 7.9 – 9.3. above this value the absorbance decreases again. For $Cu^{(II)}$ (1:1) chelate the extent of complex formation increases with increasing in the pH up to 9.4 above which the absorbance starts to decrease. The absorbance reaches its maximum at pH between 6.8 and 8.8. For $Cu^{(II)}$

(1:2) chelate the maximum absorbance obtained at pH 5.2. It was shown that as the pH increases , the absorbance decreases steadily. The result shown in Figure 6.

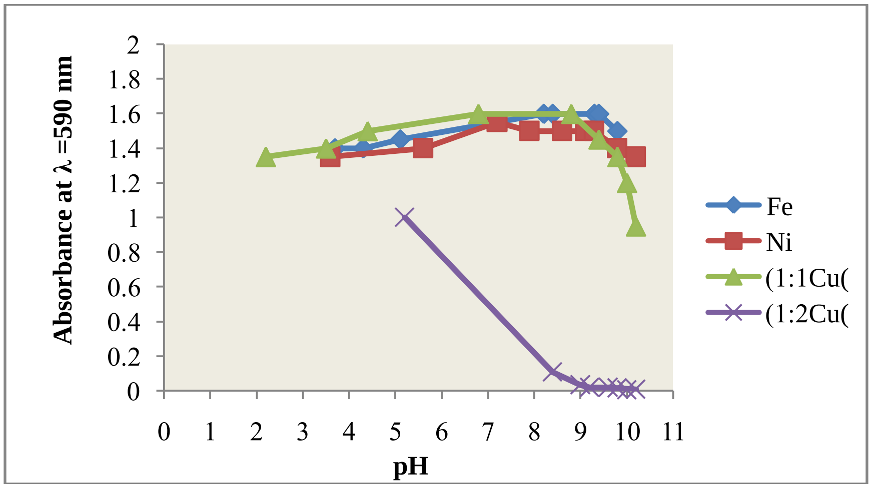

Figure 6: The plot of absorbance versus pH for four metal chelates ; Temp. =35 ± 2˚C

Effect of direct sun light:-

The solutions of metal chelates at different pH were exposed to direct sun light for five hours a day and the absorbance was measured at interval of one hour. For $Fe^{(II)}$ complex ,the result revealed that, at pH 3.7,5.8,and 8.2 the absorbance were remained constant, which means that the chelate is stable in both acidic and basic media within the given pH range and time. Strong alkaline solution caused decrease in the absorbance after exposure for three hours. For $Ni^{(II)}$ complex, the absorbance at pH 3.6 was slightly decreased to a constant value at the end of the first hour exposure. At pH 7.2 the absorbance remains constant, and at pH 7.9 the absorbance decreases at the end of the fourth hour exposure. At pH 10.2 the absorbance decreases steadily and the color of the complex was changed from blue to green after the fifth hour. This result concluded that Nickel chelate was stable towards sun light at pH 7.2. For $Cu^{(II)}$ (1:1) the absorbance at pH 3.5 and 4.4 were not changed. At pH 8.8 the absorbance decreases after one hour and the color was changed from blue to green after four hours exposure. The absorbance at different pH were plotted against the time of exposure (Figure 7, 8, 9).

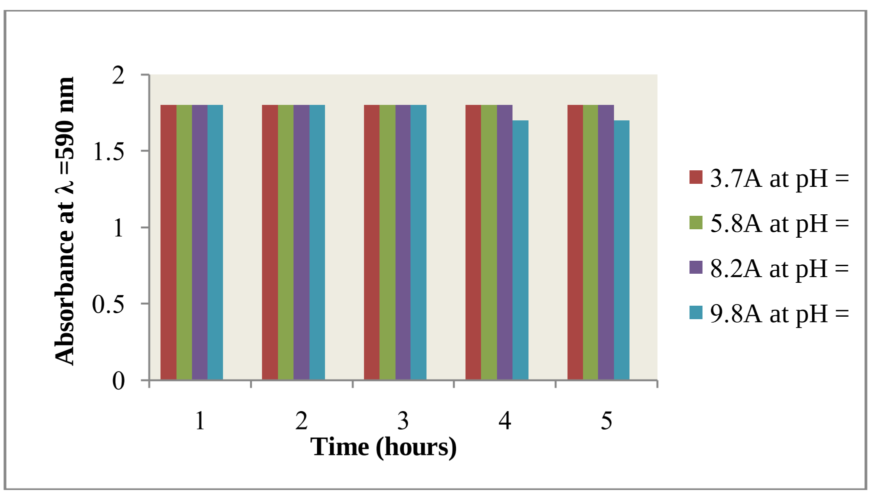

Figure 7: The plot of the absorbance versus exposure's time (hours) of Fe(II)-indigo carmine chelate; Temp 35˚±2˚C.

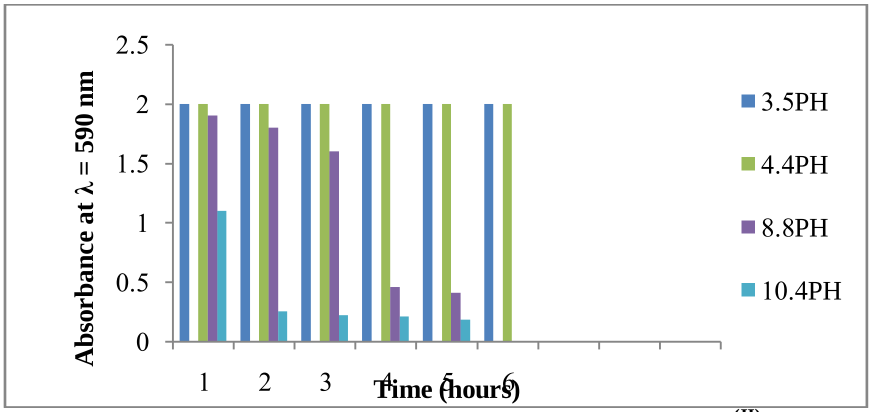

Figure 8: The plot of absorbance versus exposure's time(hours) of $Cu^{(II)}$ -indigo carmine (1:1); Temp. 35˚ ± 2

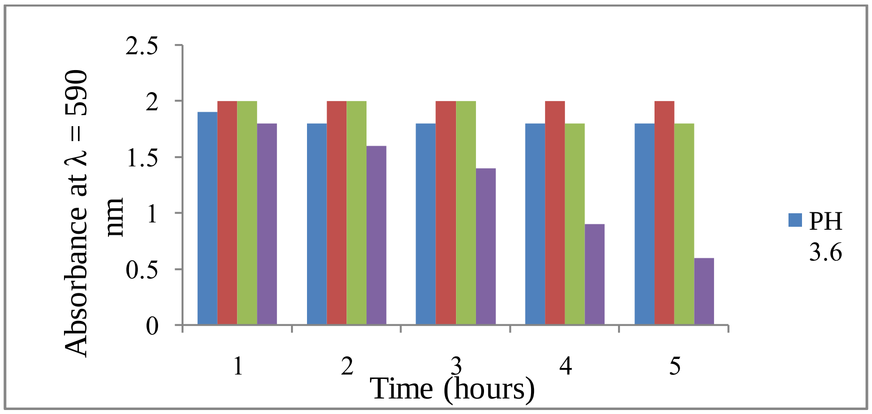

Figure 9: The plot of absorbance versus exposure's time (hours) of Ni -indigo carmine;Temp. =35 ± 2℃

Other solutions of $Fe^{(II)}$, $Ni^{(II)}$and Cu(1:1) chelates with indigo carmine at different pH were exposed to direct sun light for five hours a day for 6 days. The absorbance was measured at the end of every five hours exposure. The result showed that the stability of $Fe^{(II)}$ complex at pH 3.7 remain constant for the six days. For $Cu^{(II)}$ (1:1) complex, it is observed that there is a decrease in the stability on going from the first day to sixth day , where the stability at pH 3.5 remains constant throughout the six days.The study of $Ni^{(II)}$ complex (Figures 10,11,12) showed a maximum absorbance at pH 5.6 and 7.2 on the second day of exposure. Above pH 7.2 the absorbance decreases steadily. It is concluded that the metal chelates of indigo carmine, in general, are unstable upon exposure to direct sunlight.

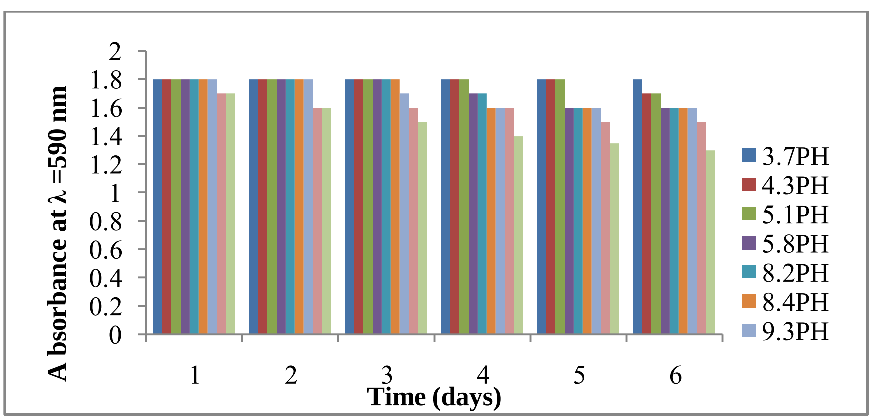

Figure 10: The plot of absorbance versus exposure's time (5 hours a day) for Fe chelates ; Temp. 35˚± 2

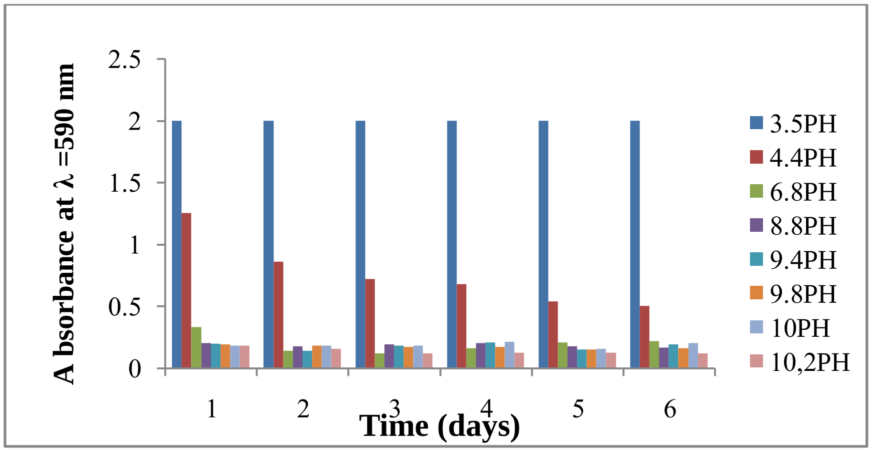

Figure 11: The plot of absorbance versus exposure's time (5 hours a day) for Cu (1:1) chelates ; Temp. 35˚± 2

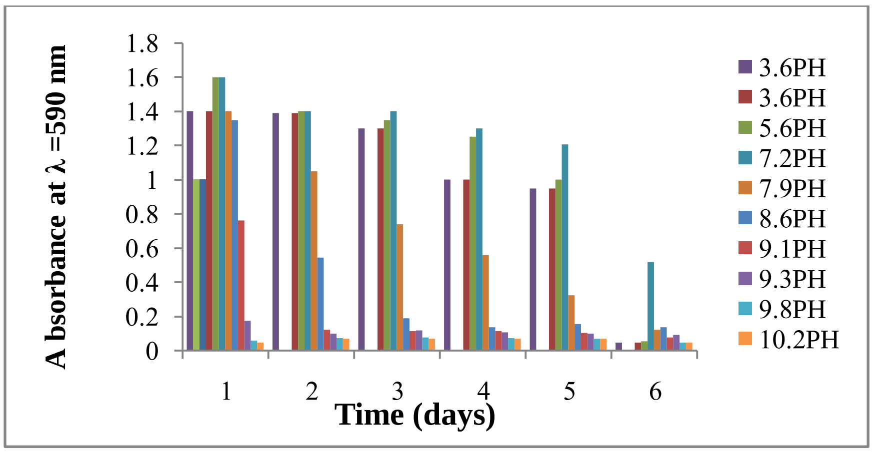

Figure 11: The plot of absorbance versus exposure's time (5 hours a day) for Ni chelates ; Temp. 35˚ ± 2

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