Molecular Structural Difference of the Irradiated and Control Samples of Indigo Dye Solution

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ABSTRACT

Irradiated/ decolourized and control samples of natural indigo dye solution are subjected to ion mass spectrometric analysis to get the mass spectra of the respective dye samples. The main ion (M+H) at 263 which symbolizes the molar mass of indigo dye (262.7g/mol) appeared predominantly on the mass spectrum of the control as well as that of the irradiated dye samples indicating that there is no mass difference between the dye molecules of the two samples. However, the mass spectra of the two dye samples agree in 11 fragments including the one at 263 (45%) and disagree in 13 fragments (55%). This disagreement translates into decolourization of the dye due to irradiation leading to the destruction of hydrogen bond and two other colour-bearing chromophores in the dye molecules. Indigo dye degradation mechanism had also been suggested in this work.

Key Words: Irradiation, Chromophores, Functional group, Radicals

INTRODUCTION

Previous work on natural indigo dye revealed that when the dye is exposed to optical radiation sources such as mercury light and sunlight, absorbance of the dye solution consistently increase with increase in exposure time (Bichi, 2007). On the other hand, the exposure of dye to ionizing radiation such as gamma (γ)- and neutron radiations, consistently results in the decrease of absorbance as the radiation dose/exposure time increases (Bichi et al., 2010). In fact the spectral peak of the dye completely disappeared when the dye sample was irradiated with γ-radiation dose of 0.6kGy at the radiation dose setting of 0.45kGy/hr. The same result was obtained when the dye was exposed to neutron radiation for only 160 seconds with neutron flux of 2.17x10\(^{10}\)n/cm\(^2\)-s.

Further investigation showed that unlike the control dye solution, the irradiated dye solution did not impart the blue colour to a piece of white cloth during the dyeing process and this motivated the start of the work. The unanswered questions on this previous work include:

i) Is there any mass difference between the irradiated and the control dye samples arising from the degradation process on the dye?

ii) Is there any structural difference between the molecules of the irradiated and control samples of the dye?

Activities conducted in this research are geared to propose answers to the above questions.

Effect of ionizing radiation on water molecule

When water is subjected to ionizing radiation free reactive radicals of hydrogen and hydroxyl are produced. These radicals may recombine to form gaseous H\(_2\), O\(_2\), H\(_2\)O\(_2\), hydroxyl radicals and peroxide radicals (Chmielswki, 2004). The processes leading to the production of such oxidants due to irradiation of the dye with γ-radiation are called advanced oxidation processes (Pera-Titus et al., 2003). The processes are complex and take several stages. The stages may last for between a fraction of a second to few seconds as detailed below:
Initial Physical Stage

This stage lasts for about $10^{-18}$ second in which energy is deposited to a water molecule which forms the dye solution. This causes ionization as:

$$H_2O \xrightarrow{\text{radiation}} H_2O^+ + e^- \quad (1.1)$$

The positive and negative ions produced in this initial stage undergo further reaction in the next stage:

Physico-Chemical Stage

This stage lasts for about $10^{-6}$ second and the positive ion previously produced in the initial stage undergoes dissociation as:

$$H_2O^+ \rightarrow H^+ + OH \quad (1.2)$$

The electron from equation (1.1) attaches itself to a neutral water molecule to form a complex:

$$H_2O + e^- \rightarrow H_2O^- \quad (1.3)$$

which then dissociates as:

$$H_2O^- \rightarrow H + OH^- \quad (1.4)$$

The time dependence of dye disappearance can be described by the differential rate equation

$$-\frac{d([\text{Dye}])}{dt} = k[I][([\text{Dye}])] \quad (1.5)$$

where $[\text{Dye}]$ represents the dye concentration, $[I]$ is the intermediate radical concentration and $k$ is the second order rate coefficient [Takacs et al, 2007]. This is in line with Beer-Lambert’s law which states that:

$$\frac{I}{I_0} = 10^{-kc} = T \quad (1.6)$$

where $I_0$ is the intensity of light passing through a blank, $I$ is the intensity of light passing through the sample, $k$ is a constant and $T$ is the transmittance of the sample (Banat et al, 1996).

MATERIALS AND METHOD

The sample (indigo dye solution) was collected from one of the dye pits at Kofar Mata dyeing center in Kano City. About 75ml of the dye solution was added into each of two amber (to protect sample from light) plastic bottles. One bottle was labeled control while the other was irradiated for 1.33 hours at the radiation dose setting of 0.45kGy/hr (equivalent to radiation dose of 0.6kGy), using Cobalt-60 Gamma Irradiation Facility (GIF). The purpose was to decolourize/degrade the dye solution.

Both the control and degraded dye solutions were run in the LXQ ion trap mass spectrometer using 80% methanol as the mobile phase, to produce the mass spectra of the two samples. The purpose was to study change(s) (if any) in molecular mass or structure of the degraded and the control dye molecules.

RESULTS AND DISCUSSIONS

Figure 1.1 and Figure 1.2 give the mass spectra for the control and degraded indigo dye samples respectively. It is clear from the Figures that the main ion at (M+H)$^+$263 is present in both mass spectra. This ion symbolizes the molecular mass of indigo dye which is 262.7g/mol. The presence of this ion on the two mass spectra suggests that there is no molecular mass difference between the control and the degraded indigo dye molecules. This implies that decolourization of indigo dye may not lead to molar mass difference between the unirradiated dye solution and the one in which the colour-bearing chromophores of the dye are destroyed. However, the mass spectrum of the control contains 24 fragments while that of the irradiated dye sample contains 25 fragments. These fragments (in addition to
the major ion) appearing at their respective positions (104-589) are due to other ingredients such as potash, ash and locust bean powder that form the dye solution. Additionally, the spectra of the two samples coincide at 11 points and differ at 13 points leading to 55% disagreement in the fragments of the two dye samples. Thus the dye molecules in the two samples are likely to exhibit structural difference.

It was also observed that whereas the control sample imparted blue colour to white fabric the degraded dye solution did not impart any colour to the fabric during the dyeing process.
Figure 1.3 (a) shows the structure of indigo dye molecule which consists of two benzene rings, two carbonyl functional groups and two amine groups (Chrisstine et al, 2004). The hydrogen atom from the amine functional group forms a bond with the oxygen atom from the carbonyl group of the dye molecule. These two functional groups (C=O and NH) are the colour-bearing chromophores responsible for imparting blue colour on cloth fabric during the dyeing process (Tyagi, 2001). In Figure 1.3 (b) however, the reactive hydroxyl radical (OH⁻) produced due to irradiation attacks the unsaturation in the carbonyl functional group thus destroying the unsaturation, the hydrogen bond and the two colour-bearing chromophores. The absence of the hydrogen bond and the chromophores (C=O and NH) in the structure of the degraded dye molecule leads to the decolorization of the dye and subsequent structural difference between the control and the irradiated dye samples as proposed in the Figure 1.3 (b).

CONCLUSION

The following conclusions are drawn based on the results obtained:

a) The persistent presence of the molecular ion at (M+H) 263 positions on both the mass spectra confirms that there is no molecular mass difference between the degraded solution and the control.

b) The destruction of colour-bearing chromophores (C=O and NH) and the hydrogen bond in the dye molecule leading to decolourization of the dye translates into the structural difference of the dye molecule as proposed in Figure 1.3 (b).

c) The decolourization/degradation process of the dye molecule is not destructive.

REFERENCES


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