

Spectral Analysis of Catalytic Oxidation and Degradation of Bromophenol Blue at Low pH With Potassium Dichromate

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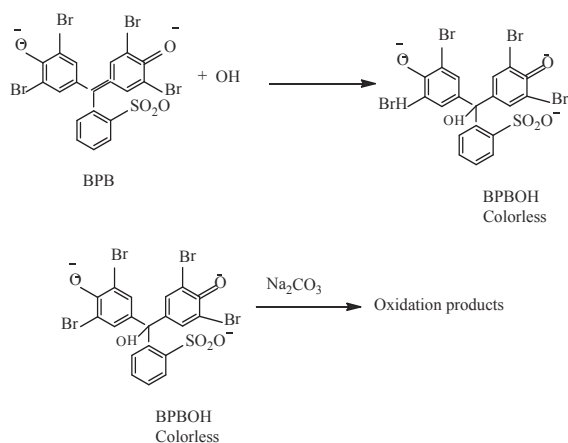
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Graphical Abstract



Abstract

This research investigated the efficacy of potassium dichromate (K₂Cr₂O₇), ultraviolet (UV), solar irradiation and UV in combination with two diprotic acids i.e sulphuric and oxalic acid and UV chromate/oxalate system, for decolorizing bromophenol blue (BPB). The results suggested that alone UV and solar exposure was the poor decolorizer of the dye waste water. Up to 10% color removal with alone UV and solar treatment were achieved which indicated that, only solar and UV were not effective for dye removal even though UV was slightly more effective as compared to solar one. The decline reaction rate was observed as a result of increased concentration of dye. Increase in concentration

of dichromate showed two peaks at 592 and 515 which showed that bromophenol degraded into two smaller components through complex formation. Addition of sodium carbonate as a catalyst in dye chromate-oxalate system found to be effective in degradation of BPB with reduced time period. The reaction was rapid and almost maximum of the dye converted into CO₂. Research outcome suggests that chromate-oxalate system is very effective techniques for reducing color of dye waste water for safety of aquatic environment. Reaction pathway of oxidation of BPB is discussed in the relevant section of the paper.

Key words: Potassium dichromate (K₂Cr₂O₇); UV and Solar irradiation; Oxalic acid; Sodium carbonate; Bromophenol

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INTRODUCTION

Bromophenol blue is a prominent acid dye, accomplished of making direct links with basic groups in tissue-constituents, used as a color mark to monitor the process of agarose gel electrophoresis and polyacrylamide gel electrophoresis, colouring proteins in paper electrophoresis. Bromophenol blue is also a pH indicator, at neutral pH, solution of the dye is blue because the dye absorbs red light most strongly and transmits blue light. At lower pH, solution appears yellow since it absorbs ultraviolet and blue light most strongly. At pH 3.6 characteristic green red color dichromatic shade phenomenon is obtained by dissolution in water without any pH adjustment, with highest known value of Kreft's dichromaticity index (Olumuyiwa, Isaac,

Adegunmi, & Ololade, 2012), indicating it has the largest change in color hue related with concentration of observed sample increases or decreases. Dimers to pentamers by oxidation of bromophenol with cellulose-binding domain (CBD) and horseradish peroxidase (HRP) separated by high power liquid chromatography (HPLC) and confirmed by mass spectrometry. It was also observed that findings may have potential impact in terms of enzyme supply in high-rate treatment of wastewater contaminated with toxic phenols, since the susceptibility of peroxidases to both H_2O_2 and product-dependent inactivation demands continuous supply of fresh enzyme (Kreft & Kreft, 2007). The oxidative color removal and degradation of bromophenol blue with H_2O_2 in Copper-supported alumina and zirconia catalysts was observed (Levy, Ward, Hadar, Shoseyov, & Dosoretz, 2003). The rate of reaction with alumina was greater than that with zirconia, which ascribed to the increased amount of copper loaded on the catalyst as well as to the increased surface area. A brown intermediate (peroxo-compound), formed at the early stages of the reaction, and inhibited the reaction rate. The rate of reaction increased with increase in pH of the medium as well as with added chloride ions. Both catalysts are very stable and can be used for several times without notable loss in their catalytic activities.

A sensitive catalytic method was developed for the spectrophotometric determination of oxalic acid based on the oxidation of bromophenol blue by dichromate in dilute sulfuric acid medium through spectrophotometrically at 600 nm. This method can also be used as a determination of oxalic acid in water extracts from vegetables such as spinach, mushrooms and fresh kidney beans (Salem, 2000).

The decomposition of 2-Bromophenol was observed in aqueous sodium hydroxide at 200–250 °C (Xu & Zhang, 2000). The decomposition rate was remarkably faster at 250 °C than at 225 or 200 °C, and the percentage debromination reached almost 100% in 1 M NaOH at 250 °C for 4 h. The percentage increased with NaOH concentration over the range 0.1–1 M. Aliphatic compounds, such as 2, 2-dimethoxypropane and 4-hydroxy-4-methyl-2-pentanone, and aromatic compounds, such as phenol and cresol, were formed as decomposition products. The formation of carboxylic acids, such as formic, acetic, and propionic acids, in the presence of oxygen was also confirmed. Under a nitrogen atmosphere, the oxidation caused by oxygen in solution was suppressed and hydrolysis became the dominant reaction in the decomposition of 2-bromophenol. The thermal oxidation of bromophenol (88ppm) was studied in flow reactor containing fused silica yield various oxidative products which was attributed to hydroxyl radical (Uchida, Furusawa, & Akitsugu, 2003; Catherine & Dellinger, 2005; Asim, Chaudhuri, Bhattacharjee, & Dutta, 1999; Gogate & Pandit, 2004; David, Marotta, Andreozzi, Napolitano, & Ischia, 2004).

In this paper, the oxidative color removal and degradation of bromophenol blue dye (3', 3'', 5', 5''-tetrabromophenolsulfonephthalein, sodium salt) has been investigated using dichromate supported sodium carbonate and oxalic acid. This dye, which is a triphenylmethane derivative, and its structurally related compounds, e.g. fluoresceins and xanthenes are widely used as industrial dyes for foods, drugs, cosmetics, textiles, printing inks or laboratory indicators. The degradation was observed in presence of Solar and UV radiation.

1. METHODOLOGY

All chemicals were of analytical grade from Merck and stock solutions were prepared in deionized water and dilutions were made at the time of each run. Reaction mixture of various compositions were prepared and kept in UV light and solar radiation for half an hr. and after that the UV–VIS spectrophotometric measurements were performed with a Shimadzu 180A UV–VIS spectrometer (Gemeay, Ikhlas, Rehab, El-Sharkawy, & Ahmed, 2003; Mario, et al., 2000; Sanabria, Molina & Moreno, 2012; Bali, 2003).

1.1 Kinetic Measurements

In a typical kinetic experiment, 30 ml of a known concentration of bromophenol blue dye solution were mixed with a known concentration of oxalic acid and $K_2Cr_2O_7$ and sodium carbonate. The mixture was then thermostated at 30°C and the reaction was investigated. At different time intervals, aliquots of the aqueous phase were withdrawn and the absorbance was recorded at 590 nm. The initial absorbance change dA was plotted against t and order of reaction was determined through the intercept (Azmat Saleem, 2011). The % decolorization was determined by using the following formula:

$$\% \text{ Decolorization} = \frac{\text{Initial absorbance value} - \text{final absorbance value}}{\text{Initial absorbance value}} \times 100$$

1.2 Reaction Products

Bromophenol blue (10^{-3} mol) was mixed with oxalic acid and $K_2Cr_2O_7$ and sodium carbonate. Carbon dioxide gas evolved during the reaction was tested by lime water. It was observed that reaction mixture was of green color in the last which clearly indicate that Cr^{+6} change to Cr^{+3} (Azmat, Qadri, & Uddin, 2011).

2. RESULTS AND DISCUSSION

The dye bromophenol blue (BPB) is an acid-base indicator. The oxidation of BPB with potassium dichromate ($K_2Cr_2O_7$) in an acidic medium was monitored into the series of experiments in presence of solar and UV radiation using Shimadzu 180 A spectrophotometer. The outdoor experiment was performed in the duration of 10 am to 12 pm when radiation of Sun at its maximum level. Spectral change of bromophenol was observed in

two separate sets of experiment in aqueous medium with UV and solar radiation. This showed that alone UV and solar radiations were not effective in photo oxidation or decoloration of bromophenol but however UV radiation was more effective as compared to solar ones as shown in Figures 1-3. These figures reflect no remarkable change in dye decoloration in both type of radiation. Investigation results are quite comparable with the earlier reports in which it was mentioned that the degradation rates of phenol and chlorophenols were insignificantly small with either UV radiation or hydrogen peroxide, but the synergistic effect of H_2O_2 /UV results in a marked enhancement of the rates of degradation (Catherine & Dellinger, 2005; Asim, Chaudhuri, Bhattacharjee, & Dutta, 1999; Gogate, & Pandit, 2004; David, Marotta, Andreozzi, Napolitano, & Ischia, 2004; Azmat, Qadri & Uddin, 2011). The UV-Vis. photons produce oxidizing free radicals from H_2O_2 and H_2O , and excited state species or from the organic compound. In these studies, either a complete or partial degradation of the organic pollutants occurred.

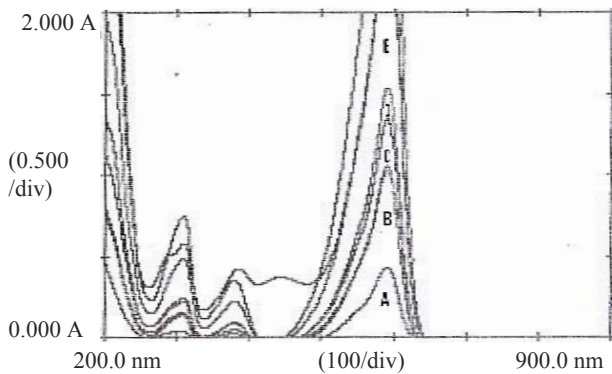


Figure 1
Spectral Changes of Dye Bromophenol at Variable Concentration (5-40ppm) Before Irradiation in UV & Solar Radiation (Peaks of the dyes at variable concentration are a = 5ppm, b = 10ppm, c = 15ppm, d = 20ppm, e = 25, f = 30ppm, g = 35, h = 40ppm)

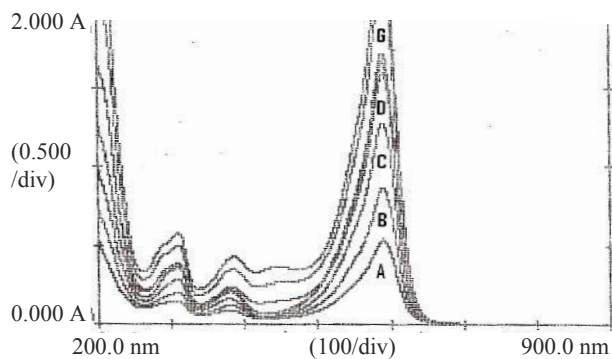


Figure 2
Spectral Changes of Dye Bromophenol at Variable Concentration (5-40ppm) After Irradiation in UV Radiation (Peaks of the dyes at variable concentration are a = 5ppm, b = 10ppm, c = 15ppm, d = 20ppm, e = 25, f = 30ppm, g = 35, h = 40ppm)

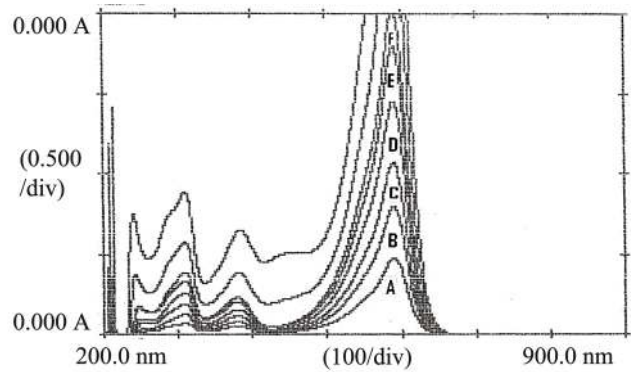


Figure 3
Spectral Changes of Dye Bromophenol at Variable Concentration (5-40ppm) After Irradiation in Solar Radiation (Peaks of the dyes at variable concentration are a = 5ppm, b = 10ppm, c = 15ppm, d = 20ppm, e = 25, f = 30ppm, g = 35, h = 40ppm)

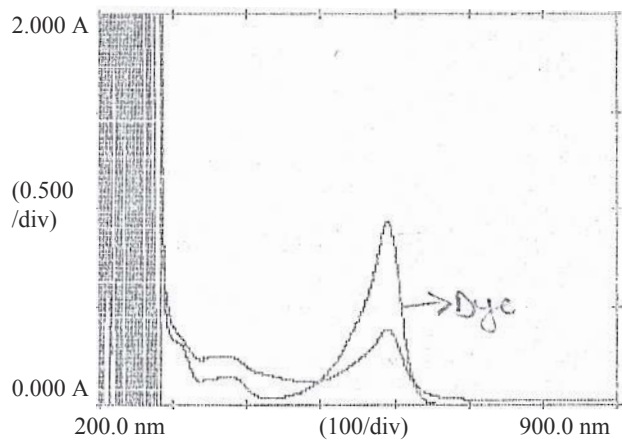


Figure 4
Spectral Changes of Dye Bromophenol at Variable Concentration (10 ppm) with $K_2Cr_2O_7$ (5ppm) with Oxalic Acid (0.1M), (Dye = 10ppm, oxidant = 5ppm, oxalic acid = -1N, Na_2CO_3)

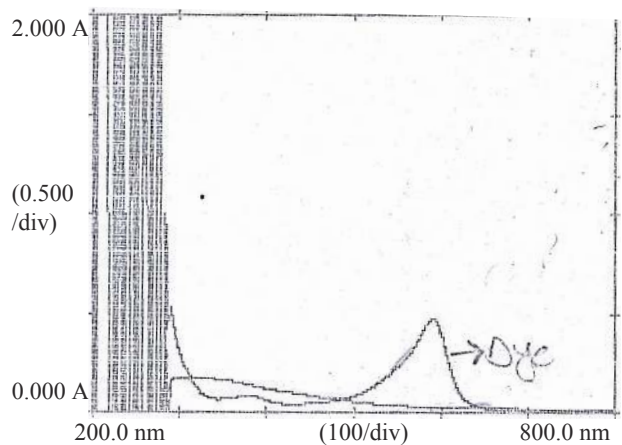


Figure 5
Spectral Changes of Catalyzed (Na_2CO_3) Dye Bromophenol at a Concentration (10 ppm) With $K_2Cr_2O_7$ With Oxalic Acid (Dye = 10ppm, oxidant = 35ppm, oxalic acid = -1 N, Na_2CO_3)

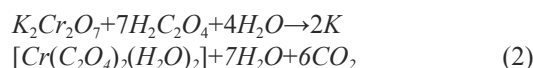
It was observed that when a solution of bromophenol blue was mixed with potassium dichromate in neutral medium, almost no reaction was observed. Then redox reaction was monitored in presence of organic and inorganic diprotic acids i.e sulphuric and oxalic acid. Oxalic acid found to be more effective as compared to sulphuric acid which showed that the dye decoloration was depended upon the nature of the acid. The changes of the color from blue to yellow indicate that dye decolorized in an acidic medium or proton abstracted by the dye molecule form leuco dye without shift in λ_{max} Figure 4. This indicated that the $K_2Cr_2O_7$ /oxalic acid reaction system was effective for the decoloration of BPB. It was established from the Figure 4 that initially de-coloration followed by abstraction of H^+ ion due to which hypochromic shift obtained without change in λ_{max} then de-coloration was the results of chromate oxalate complex system. This complex generates OH^* radical which is strong oxidizing agent that reacts with the dye and causes dye decoloration. This proved that an acidic medium plays a considerable role in dye decoloration with potassium dichromate. The involvement of free radicals in the reaction mechanism was proposed which was release after the dissociation of the intermediate complex. Potassium dichromate being a strong electrolyte completely dissociated into CrO_4^{2-} , $HCrO_4^-$, $Cr_2O_7^{2-}$ ions and possibly $HCr_2O_7^-$ ions in a solution, depending upon the pH of the solution, therefore it may be suggested that variation in the rate of oxidation reaction will track the variation in the concentration of photochemical species.

The effects of change in pH on the reaction rate were studied using acid and alkali. The reaction was observed at a constant concentration of other reactants and the sodium carbonate catalyst. The degradation of the dye was more efficiently take place in acidic media instead of an alkali and it was established that addition of alkali cause the quenching the reaction which results in increase in absorbance. The quenching of the oxidation of BPB at higher pH may be related with the reaction of OH and H. This reaction provides the neutral medium to the reaction that result in the extinguishing of the reaction. It was observed during reaction that in an acidic medium, de coloration from blue to yellow was take place slowly. It may be due that $K_2Cr_2O_7$ in acidic medium is a moderately strong oxidizing agent and three electrons are added in the Cr ion; according to the following equation (1),



while decreasing rapidly as solution becomes more neutral. It was found that as the concentration of oxalic acid increases the decoloration efficiency of oxidizing agent but however no particles of the degraded dye product was observed in a reaction mixture. It can easily be infer from the absorption spectrum of dye that dye bleached without shift in wavelength (Figure 4) and absorbance were

decreases sharply. In addition, this decrease in absorbance became greater with increasing oxalic acid concentrations. This enhanced efficiency of de-coloration may be related to the formation of dioxalato-diaquachromate complex (Azmat, Qadri, & Uddin, 2011; Azmat, Qamar, & Naz, 2011) during $K_2Cr_2O_7$ and oxalic acid reaction according to following reaction



The complex also known as trans isomer of potassium dioxalato-diaquachromate as reported earlier (Garth & Randall, 1963). This transition metal complex dissociated to yield OH_2 radical which in turns dissociate into OH radical and H^+ that act as a strong oxidizing agent and provide acidic medium too due to which dye degradation occur. Literature search reported that the transition metal complexes, metal oxides and mixed (Al-Cu) supported clays were used as potentially active catalysts for decomposing H_2O_2 with the oxidation and degradation of several organic contaminants (Giles, 1972). This radical is capable for reacting with a variety of organic compounds leading to either partial or complete degradation. However, when the oxalic acid with sodium carbonate as a catalyst was added, a reaction occur leading to complete degradation of the dye and no small peak of the dye was observed (Figure 5). The electronic absorption spectra recorded for this reaction (Figure 5) clearly shows that, the absorption band at 590 nm disappear with the progress of the reaction. Experiments carried out at varied concentration of $K_2Cr_2O_7$, keeping all other parameters constant, revealed that the rate of reaction decreased with increase in potassium dichromate, reaching a maximum and thereafter decreased (Figure 6). The decrease in oxidation with the increase in the concentration of dichromate may be related to the increase in Cr contents that may involve in complex formation or some other side reactions or quenching of OH radical. On the other hand, upon varying the concentration of bromophenol blue up to 10ppm keeping concentration of the other reactants constant, the rate of reaction increased with a first-order dependence on $[BPB]_0$. While, with an increase in concentration, the order of reaction decreases and almost a limiting rate was attained at higher concentrations (Figure 7). It was reported that the Ruthenium (II) complexes were used for the oxidative degradation of chlorinated phenols and chlorinated ethylene (Gemeay, Ikhlas, Rehab, El-Sharkawy, & Ahmed, 2003). Extensive de chlorination was found with all compounds whereas about 50% of carbon was transformed into CO_2 with chlorinated phenols and trichloroethylene and 100% with tetrachloroethylene. The same phenomena were observed in the current investigation, CO_2 evolved and tested by lime water. Besides, oxidation of phenol with hydrogen peroxide catalyzed by pillared clays was intensely predisposed by the copper content and the system of catalyst preparation

(Mario, et al., 2000; Sanabria, Molina, & Moreno, 2012). The identical spectacles was observed in this investigation that an increase in concentration of dichromate retard the rate of degradation which was attributed with trans isomer of potassium dioxalatoaquachromate (III). Figures 1-3 show the absorption spectra of BPB before the catalytic oxidation. Addition of sodium carbonate into the reaction mixture at 35ppm of dye and 40ppm of oxidant gives complete degradation of the dye with the reduction of Cr^{6+} into the Cr^{3+} which appeared as a green color in a reaction mixture. It indicated that addition of sodium carbonate as a catalyst caused the complete degradation of the dye and all the dye converted into CO_2 . It is clearly observed from Figure 5 that there is no absorption peak of the dye reflecting that dye is completely degraded with the release of Cr^{3+} which is essential macronutrient of the living organism. This is suggested that this reaction may be beneficial for the elimination of the colored material with the release of Cr^{3+} from Cr^{6+}

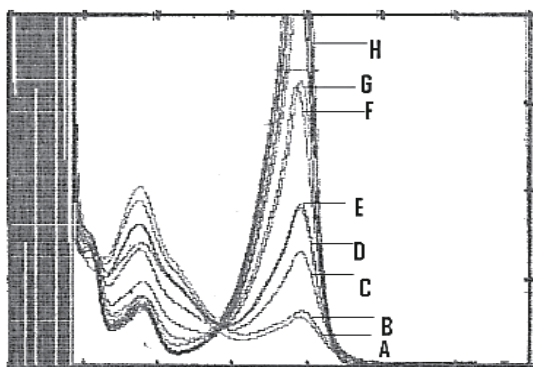


Figure 6
Spectral Changes of Catalyzed (Na_2CO_3) Dye Bromophenol (10 ppm) at a Variable Concentration of $\text{K}_2\text{Cr}_2\text{O}_7$ (5ppm-40ppm) with Oxalic Acid (Peaks of the dyes complex at variable concentration of oxidant are a = 5 ppm, b = 10 ppm, c = 15 ppm, d = 20 ppm, e = 25, f = 30 ppm, g = 35, h = 40 pp)

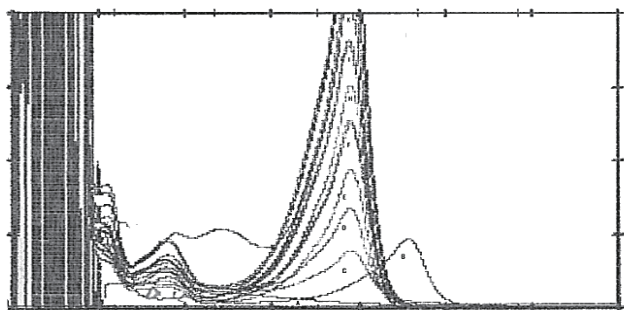
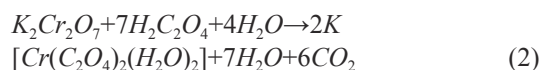


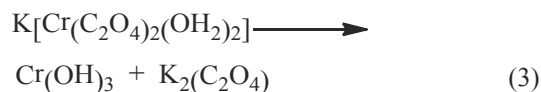
Figure 7
Spectral Changes of Catalyzed (Na_2CO_3) Dye Bromophenol at a Variable Concentration of Dye (10 ppm-40 ppm) with $\text{K}_2\text{Cr}_2\text{O}_7$ (5ppm) and Oxalic Acid (Peaks of the dyes complex at variable concentration of PBP are a = 5 ppm, b = 10 ppm, c = 15 ppm, d = 20 ppm, e = 25, f = 30 ppm, g = 35, h = 40 pp)

3. REACTION PATHWAY

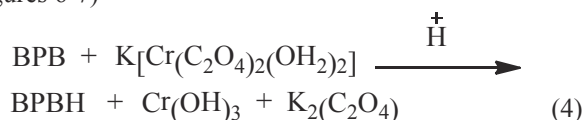
According to the above experimental observations and discussions, the following oxidation reaction mechanism has been proposed for the oxidation of BPB that implies an interaction between complex and the catalyst with the formation of hydroxyl radicals. The latter can attack the substrate forming a highly active intermediate which then decomposes in the rate-determining step giving the final oxidation products as follows:



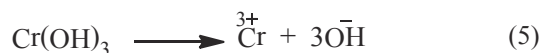
Dissociation of complex during oxidation may be take place according to the equation (3)



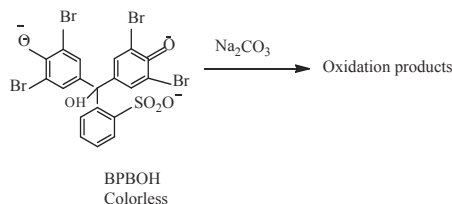
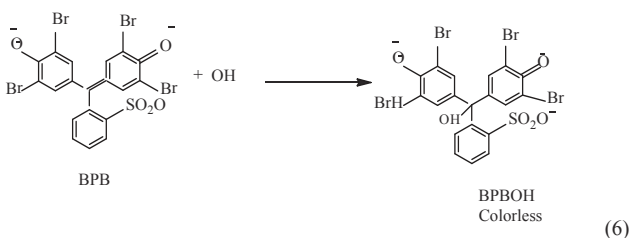
Reaction between Cr complex and Dye in acidic medium leads to the formation of decolorized dye complex (equation 4) without change in the wavelength (Figures 6-7)



$\text{Cr}(\text{OH})_3$ possibly dissociate to releases Cr^{3+} ion which gives green color at the end of the oxidation reaction according to equation (5)

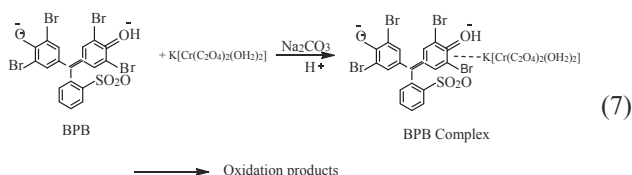


It was proposed the OH^- ion will attack the dye molecule and decoloration of BPB will occur due to the formation of BPBOH molecule without shift in wavelength (Figure 4) which in presence of catalyst completely degraded with the release of CO_2 and other oxidation products that settles in the reaction mixture



Or it may be proposed that dye degradation take place via complex formation (Figure 6) according to the

equation (7) at lower concentration of $K_2Cr_2O_7$

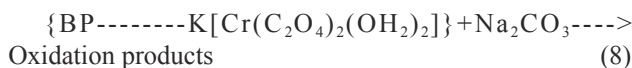


The overall rate law that describes this reaction can be written as follows:

$$\text{Rate} = k [\text{BPB}]^m [\text{H}^+]^n$$

CONCLUSION

Above investigation revealed that when bromophenol blue dye and Potassium dichromate come into contact at neutral pH, there was almost no reaction. However, when oxalic acid and sodium carbonate were added, a complete color removal of the dye was observed according to the following equations (8-9):



The rate of oxidation reaction in presence of sodium carbonate was more than that alone in solar radiation or UV radiation. The rate of reaction acquired a first order dependent on [BPB] and $[\text{CrO}_4^-]$ only at lower concentrations. However, at higher concentrations of potassium dichromate, the rate of reaction decreased, while enhanced after the addition of sodium carbonate. This was ascribed to the fast interaction between the highly active hydroxyl radicals and sodium carbonate as a catalyst. The reaction was depended upon the pH of the medium as well as with added sodium carbonate.

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