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Comparative Study of Salt Effect on Hydroxylation Reaction of Organic Dyes

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ABSTRACT: Crystal violet (CV) and Malachite Green (MG) both are synthetic triphenylmethane dyes and generally basic (cationic) in nature. These are widely used in clothing industry, leather industry and for dyeing many substances. MG & CV can also use as antibacterial, antifungal and anthelmintic agents. Direct contacts of dyes are very much injurious to animal kingdom. Hence, they have become pertinent to find and efficient way to remove it from environment. The kinetics of alkaline hydrolysis of Crystal Violet (CV) and Malachite Gree (MG) in presence of different salt was studied. Reductions were carried out by varying dye concentration, salt concentration and concentration of alkali. In the present study the reduction of dye was carried out in order to reduce the color content. This research work tends to explore salt effect on alkaline hydrolysis of these dyes with focus on kinetics of the reaction. This process can, therefore, be used as technical solutions for the treatment of dye by reducing its colour content for different approaches.

Keywords: Crystal violet (CV), Malachite green (MG), Hydroxylation, Salt effect.

I. INTRODUCTION

Crystal violet is used to dye substrates like cotton, leather, silk, rayon etc. CV like every other triphenylmethane dyes is hazardous to aquatic and terrestrial animals. CV was reported to be able to induce tumour growth in some species of fish. It has been found to cause reduced RNA and protein synthesis and can cause decreased oxygen consumption in rabbit granulation tissues. Due to such dangerous effect of CV it has to be removed from environment.

MG in water originating from contamination as a result of its industrial applications or from its illegal use in aquaculture is efficiently taken up from the water by fish and distributed to all tissues. Due to such detrimental effect, several researches have been reported to remove it. One such method is to fade it by reacting with hydroxyl ion.

The kinetic study of MG will be comparatively slower in rate than that of the CV due to the planar structure of MG^+. In 1932, a Japanese famous scientist Gerald Corsaro describes an experiment in which a photo-colorimetric technique is employed to follow a bimolecular reaction rate [1]. In 1959, two American scientists David T.Y. Chen & Keith J. Laidler explains about the effects of temperature and pressure on the kinetics of alkaline fading of organic dyes *e.g.* CV, MG etc in aqueous solution [2]. In 1992, a chemistry journal "LD Chemistry Leaflets" describe how the rate of chemical reaction depends on the concentrations of the substances involved [3]. In 1997, Vernier Software investigates the kinetics of the reaction between CV and NaOH (Hydroxylation reaction) [4]. In 1998, Beijing University scientists investigate on the basic hydrolysis of CV in mixed reverse micelles formed with AOT and non-ionic surfactants [5]. In 2004, American scientists Rio, Leis, Mejuto, Navarro describes about the basic hydrolysis of CV in mixed systems consisting of β-cyclodextrin and a micelle forming surfactants [6]. In 2007, Romanian scientists are explained about the influence of the surfactants on the fading of MG [7]. In 2009, Iran chemists Babak Samiey & Ali Raoof Toosi explain about the kinetic study of MG fading [8]. In 2011, Dhaka university journal invented about the kinetic study of alkaline hydrolysis of CV in micelles, reverse micelles and microemulsions of cetyltrimethylammonium bromide [9]. In 2011, scientists from Lebanon university describes the kinetic study of the discoloration of triphenylmethane dyes in function of pH, salt effect etc [10]. In 2012, Nigerian scientists A. Tanimu, S.O. Idris, J.F. Iyun explain about the kinetics of redox reaction between MG and hydroxyl ions [11]. In 2017, famous Nigerian scientist Latona Dayo Felix first observes & explains the kinetics of the reaction between MG and OH^- ions in presence of reducing sugars *e.g.* glucose, fructose etc

[12]. In 2018, Latona Dayo Felix explains more accurately and modified kinetic study of discoloration of CV in NaOH medium [13]. Hydroxylation reaction and salt effect of organic dyes are the basic principle for the removal of such dyes [14].

Experimental:

Raw Materials: 0.001% CV & MG dye solution [Sisco research laboratories, Pvt. Ltd], NaOH [SRL, Pvt. Ltd], KNO_3 & $NaNO_3$ [Merck Specialities Private Limited], Methanol (CH_3OH) [Ranbaxy Fine Chemicals Ltd], Ethanol (C_2H_5OH) [Honyon International, Inc.], Oxalic acid [SRL, Pvt. Ltd].

Method: In this experiment, the reaction between crystal violet and malachite green are as follows,

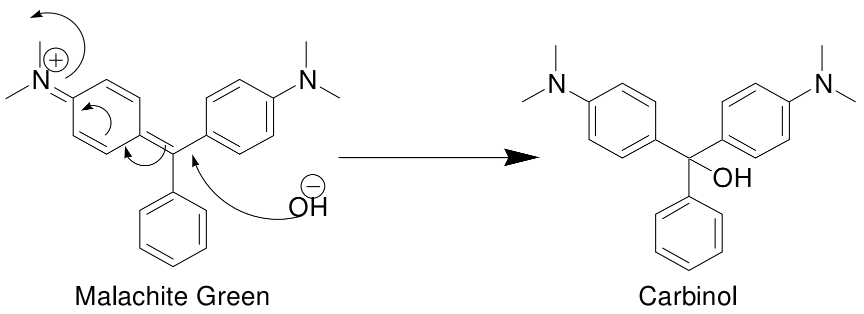

Fig. 1. Reaction of MG with hydroxyl ion.

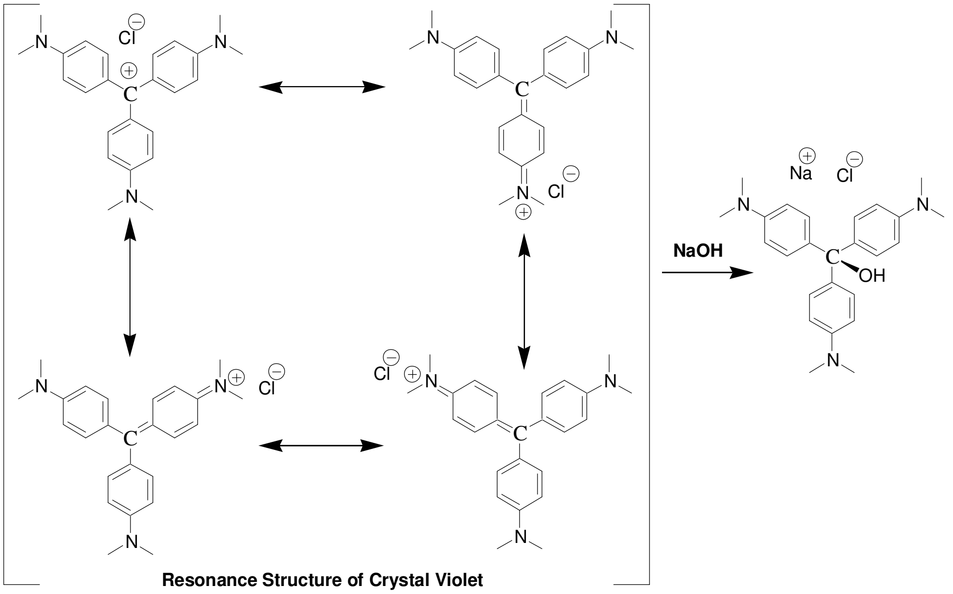

Fig. 2. Reaction of CV with hydroxyl ion.

For the both cases, the rate of the reaction is the rate of decrease of dye concentration which is as follows,

$-d[D]/dt = K[D]^{\alpha}[OH^-]^{\beta}$ (1)

When the order with respect to dye, *i.e.* $\alpha = 1$and $[OH^-] >> [D]$, then the reactions were performed under first order conditions by maintaining a large excess of alkali. At first the digital colorimeter ('Systronics' Make, Model No-841) was calibrated using 0.001% dye (CV & MG) solution to determine λ_{max}. Then 0.025(M) exact NaOH solution is prepared and a stock solution was made with the dye, exact NaOH and distilled water in optimum quantities. Then the reaction kinetics was recorded by monitoring the change in the absorbance of the malachite green (MG) and crystal violet (CV) at the absorbance maxima which was measured earlier, at the function of time. Then a study of salt effect on the alkaline hydrolysis of dye is done using 0.05(M) exact $NaNO_3$ & KNO_3 solutions. Kinetics of these solutions is studied by the same method in colorimeter. The rate constant values (K_{obs}) of the reaction are obtained from a plot of log(abs) vs. time. From this graph, values of log K_{obs} are calculated. Graphical plot of $\log K_{obs}$ vs. log[OH-] determines the order of reaction. Finding out the values of K from K_{obs} of each set of reactions, another graph of logK against $\sqrt{\mu}$ is plotted for each set and then slope is calculated.

II. RESULT AND DISCUSSION

Determination of λ_{max} of CV and MG: For calibrating the instrument (digital colorimeter), we use methanol:

water solution of 1:4 ratio as the blank solution and use 0.001% dye solutions as stock solution. Filter range of λ in colorimeter is from 420 nm to 720 nm. Using blank solution, at each filter set 100 and then we measure the transmittance value (% T) of stock solution at each filter. From the % T value, we measure the absorbance value using the formula as follows;

Absorbance (Abs) = 2 – Log (%T). Here, we found a peak at maxima at which % T value is lowest and absorbance value is highest. At this point, the corresponding value of λ is the λ_{max} of dye solutions.
The graphical plots of Abs vs. λ (nm) shows that they have more or less same λmax values (570-600nm) but absorbance values are different due to difference in structure.

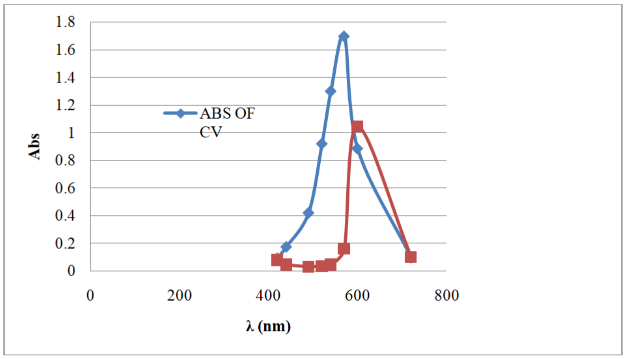

Fig. 1. Plot of absorbance against wavelength (λ).

Reaction rate & order: The absorbance values of solutions containing different concentrations of alkali and salts are measured. A constant initial dye concentration (0.001% *i.e.* 10^{-4}(M)) of CV & MG is considered. The concentration of NaOH is varied from 0.0025(M) to 0.0125(M) and that of KNO_3 and $NaNO_3$ solutions are varied from 0 to 0.04(M). The reaction temperature is 35°C *i.e.* 308K. It is found that the rate of reaction is first order with respect to alkali without addition of salts.

If the same experiment for the sets of different composition in which concentration of alkali varied, we will get the different K_{obs}. From equation (1),

$$K_{obs} = K.[OH^-]^{\beta}$$

Or, $$logK_{obs} = logK + \beta \log [OH^-]$$

Again, if we plot logK_{obs} against log[OH^-], we will get a straight line from its slope we will get β, i.e. order with respect to alkali.

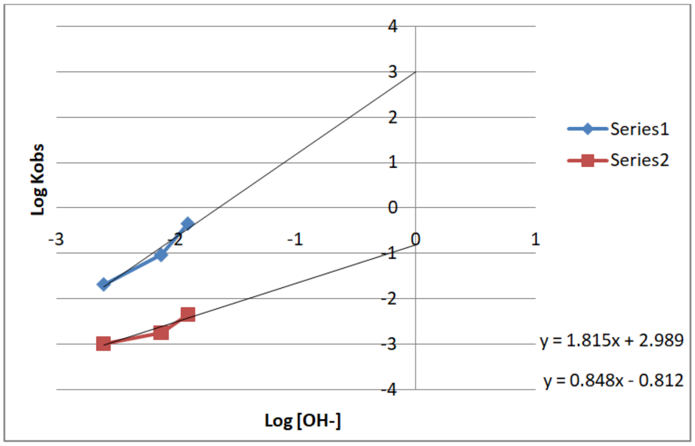

Fig. 2. Plot of Log Kobs vs. Log [OH-] for CV & MG.

From the above graph, we get the values of β for two different dyes (MG & CV) are 1.8 and 0.8.
The increase of concentration of OH^- ions results in increase of the reaction rate as shown above. The slope of both plots of log [OH^-] vs. log (K_{obs}) indicates that the reactions follow first order kinetics.

Effect of concentration of NaOH on observed rate constant: The value of K_{obs} can be determined according to the following formula-

The rate equation of the reaction of the dye with NaOH can be written as follows:

$$-\frac{d[D]}{dt} = K_{obs}[\mathrm{D}]$$

Integrating & applying proper limit,

$$-\int_{[D]_0}^{[D]} \frac{d[D]}{[D]} = K_{obs} \int_0^t dt$$

$$\text{Or,} ln\frac{[D]_0}{[D]_t} = K_{obs}.t$$

$$\text{Or, } log\frac{[D]_0}{[D]_t} = \frac{Kobs}{2.303}.t$$

Again we know, Absorbance α Molar concentration

$$\text{So, } log\frac{A_0}{A_t} = \frac{K_{obs}}{2.303}.t$$

$$\text{Or, } logA_t = logA_0 - \frac{K_{obs}}{2.303}.t$$

Hence, if we plot $logA_t$ vs. time (t), we will get a straight line with negative slope and positive intercept from which we can easily calculate the K_{obs}.

The graph of log A_t vs. t for two dyes are as follows;

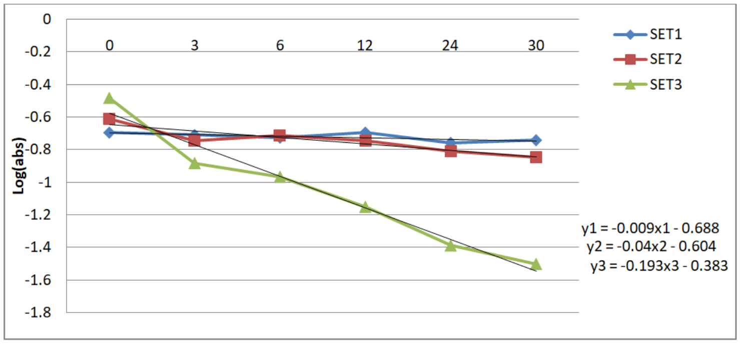

Fig. 3. Plot of Log A_t vs. t of CV.

Fig. 3 explain the nature of reaction with the variation of alkali concentration. For CV, when concentration of NaOH is 85%(v/v) w.r.t. dye, we get the nature of graph of log (abs) vs. time is more steeper than the other two sets where concentration of alkalis are 50%(v/v) & 75%(v/v).

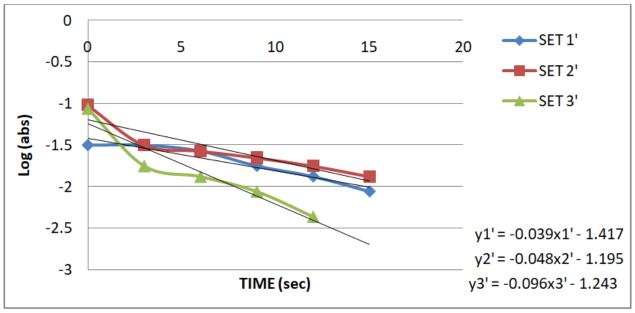

Fig. 4. Plot of Log A_t vs. t of MG.

Same kinetics is observed in case of hydrolysis of MG. We can calculate the K_{obs} values for alkaline hydrolysis of MG and CV from the plot of log (abs) vs. time. It is observed in both cases the value of absorbance decreases (%T increases) with increase of time *i.e.* extent of reaction completion.

Effect of ionic strength on the observed rate constant: The effect of ionic strength on the rate constants observed (K_{obs}) is determined by study ingreactions with different salt concentrations. The compositions of reaction mixtures are given in Table 1.

Table 1.

SET	CONC^N OF CV/MG (v/v)	CONC^N OF NaOH % (v/v)	CONC^N OF $KNO_3/NaNO_3$ % (v/v)	CONC^N OF H_2O % (v/v)
1.	10	10	0	80
2.	10	10	40	40
3.	10	10	80	0

Now, the value of ionic strength can be determined as follows:

The empirical rate equation between dye and alkali is,

$$Rate = k[D][OH^-] \qquad (1)$$

But when the reaction between dye and alkali takes place as follows;

$$D^+ + OH^- \overset{K}{\leftrightarrow} X \overset{k'}{\rightarrow} P$$

But from the above scheme,

$$Rate = k'[X]$$

Again, $k = \frac{a_X}{a_D a_{OH}}$

Or, $a_X = k\, a_D a_{OH}$;

Where, a_X = activity of complex, X

a_D = activity of dye

a_{OH} = activity of alkali

Or, $[X]f_X = K[D][OH]f_D f_{OH}$

Or, $[X] = \frac{K[D][OH^-]f_D f_{OH^-}}{f_X}$

Or, $Rate = k'\,K\,[D][OH^-]f_D\,f_{OH^-}/f_X$ (2)

Comparing (1) & (2),

$k = k'K\frac{f_D f_{OH^-}}{f_X} = k_0\frac{f_D f_{OH^-}}{f_X}$; where, k_0=k' K

Or, $logk = logk_0 + logf_D + logf_{OH^-} - logf_X$

Applying Debye Huckel limiting law for the very dilute solution i.e. $logf_i = -0.51Z_i^2\sqrt{\mu}$ for aqueous solution at 25°C we get-

$$logk = logk_0 - 0.51Z_D^2\sqrt{\mu} - 0.51Z_{OH^-}^2\sqrt{\mu} + 0.51(Z_D + Z_{OH^-})^2\sqrt{\mu}$$

$$= logk_0 + 1.02Z_D Z_{OH^-}\sqrt{\mu}$$

Where μ= the ionic strength of solution=$\frac{1}{2}\sum_j C_i Z_i^2$, Z_i= charge of i-th species, C_i= molar concentration of i-th species.

If we plot logk against √μ for sets of different composition with different ionic strength, we will get a straight line with positive intercept. From the slope, we can realise the nature of the reacting species.

Now, the plots of log (abs) vs. time for the effect of KNO_3 on the reaction of dye with NaOH are;

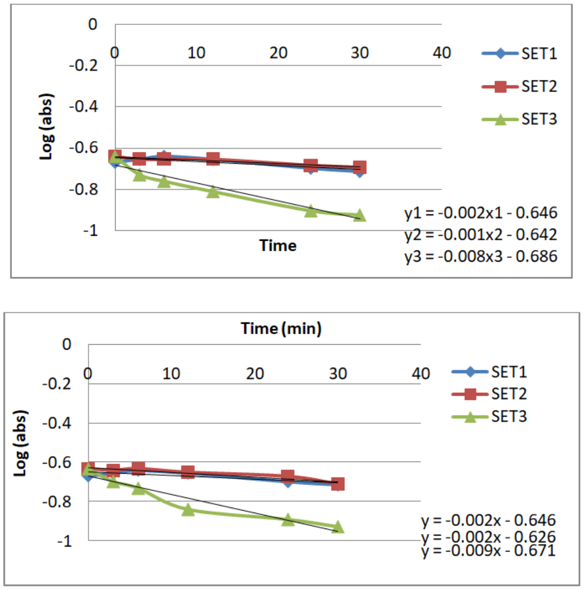

Fig. 5-6. Plot of Log (abs) vs. time for salts (KNO_3 & $NaNO_3$) effect of CV respectively.

The above figures show the kinetics of the reaction in presence of two different salts. The graph becomes steeper for the highest salt concentration i.e. 80 %(v/v). Hence, the reaction rate is highest in this set (set 3).

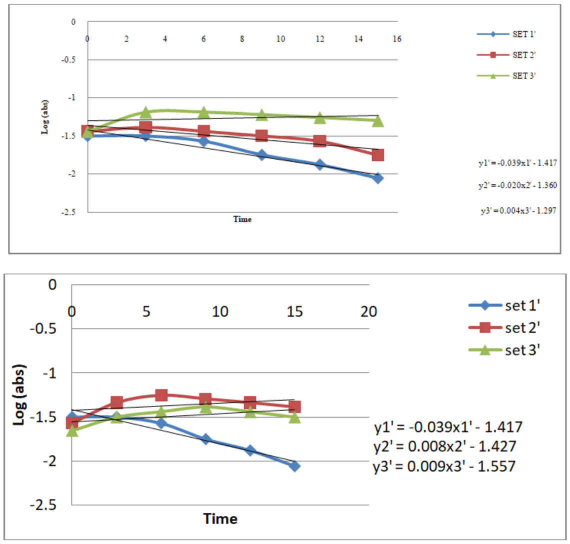

Fig. 7-8. Plot of Log (abs) vs. time for salts (KNO_3 & $NaNO_3$) effect of MG respectively.

These two graphs explain the behaviour of reaction rate of hydrolysis of MG dye in presence of two salts- $NaNO_3$ & KNO_3. Here in set-1 where no salts are added, the graph is steeper than other two sets where the concentrations of salts are 40% and 80% (v/v). This indicates the salts here suppress the reaction rate of hydroxylation of MG.

From the straight line intercept we can easily determine the k_0 value. From these values we can easily calculate the logk values from Debye Huckel limiting law.

Effect of ionic strength of dye solutions: When a plot of logK vs. $\sqrt{\mu}$ is drawn to see the salt effect of salts KNO_3 & $NaNO_3$ for CV dye solution, it found as follows:

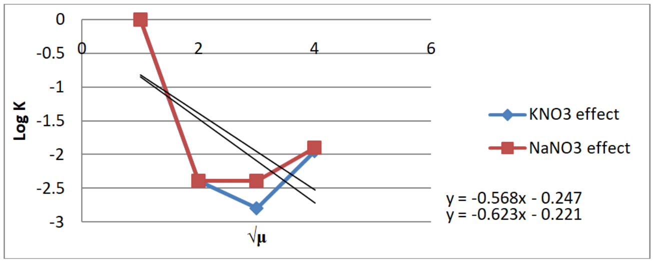

Fig. 9. Plot of Log K vs. $\sqrt{\mu}$ for CV.

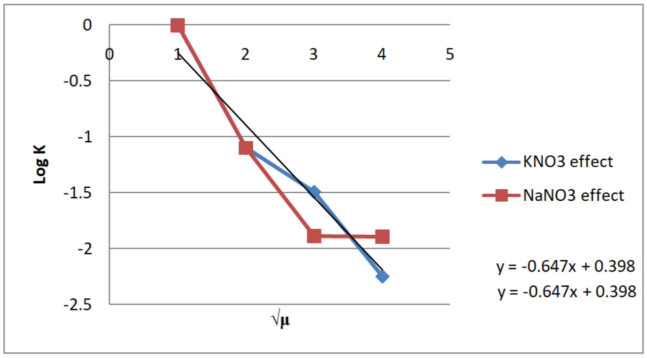

Fig. 10. Plot of Log K vs. $\sqrt{\mu}$ for MG.

And, the salt effect of salts KNO_3 & $NaNO_3$ for MG dye solution, it is found as follows:

So, in both CV and MG dye solution, KNO_3 and $NaNO_3$ shows salt effect with increase the value of ionic strength. The value of logK decreases correspondingly with increase the value of $\sqrt{\mu}$. We also found that for CV, the slope is positive but for MG, the slope is of negative value and more steeper.

Salt effect of silver salts (like $AgNO_3$ & AgCl) could not study due to appearance of precipitation of silver oxide (Ag_2O) for $AgNO_3$ & AgOH for AgCl. Another salt like NaCl, KCl have no effect on hydroxylation of CV & MG because the solution becomes colourless at the moment of addition of pinch of these salts and absorbance shown negative in colorimeter.

Determination of the stability of dye solution: A coloured solution shows its stability in colorimetric study until its colour is disappeared. Here, the stability study on MG solution is done during one and half month and it is found that solution becomes completely colourless and its transmittance (%T) value reaches at maxima. Hence, its absorbance value is lowest *i.e.* zero.

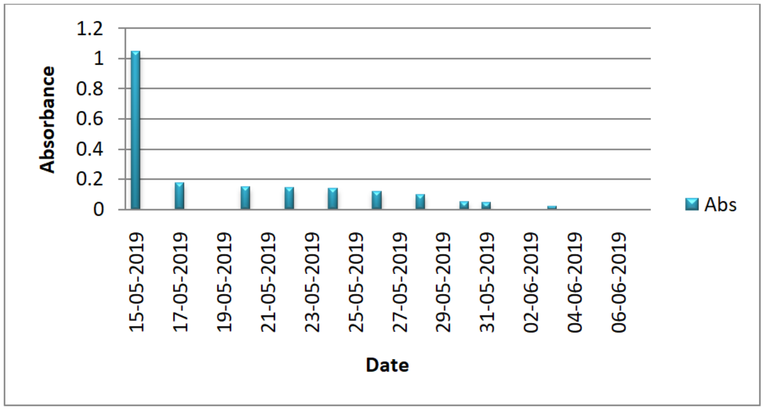

Fig. 11. Plot of abs vs. date for MG.

The stability of CV is higher than MG dye solution. So, colour discharge of it taken very long time than MG. Hence, the rate of reaction of CV is also comparatively higher than that of MG.

CONCLUSION

The present research work shows that the reaction mechanism of hydrolysis of MG and similar to that of hydrolysis of CV in alkaline medium. It is observed that 0.001% MG solution (solution made in 1:4 ethanol: water) is completely decolourised at 20 days (shown in Fig. 11) but it was reported that due to high stability of solution, CV takes infinite time for decolourisation. Some difference in reaction rate and kinetics is attributed for the structural difference of two dyes. More mechanistic studies on salt effect on hydroxylation of other organic dyes, their comparative studies and surface adsorbent effect are also our ongoing research. The present study offers new perspectives for exploring the potentials of these dyes to study the chemical kinetics and also toxicological properties.

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Conflicts of interest. None.

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