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COMPARATIVE STUDY OF PHOTOKINETICS OF REDUCTION OF TOLUIDINE BLUE AND RED MCT DYES WITH N-ALLYLUREA

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ABSTRACT

The reaction of two dyes , Toluidine blue (TB) and Red MCT dyes (reactive red monochlorotriazine dyes – MCT)with N-allylurea (AU) has been studied in an unbuffered aqueous , acidic and basic medium at λ_{max}625nm and 535nmfor TB and Red MCT respectfully. The kinetics were investigated at various operative parameters including concentration of dyes and reductant , variation of pH and ions .The reaction was first order with respect to Red MCT and second orderwith respect to reductant,and the rate law is suggested to be -d/dt [Red MCT] = k [Red MCT][AU]^2[H$^+$]^2 .Whereas the reaction wasfirst order with respect to TB and reductantand the rate law is suggested to be -d/dt [TB] = k [TB$^+$][AU][OH$^-$]. In the reduction reaction of TB with AU, the cations showed suppressed effect. The reduction reaction of TB and AU under different cations showed following order Na^+>K^+>Ca^{2+}>Mg^{2+}behavior whereas in the presence of anions the dye decoloration was more prominent and showed following order HCO^{3-}>CO_3^{2-}>Cl^-.The reverse trend was shown with red MCTand AU reduction system ,which was enhanced in the presence of cations .The cationshowed order Na^+>K^+> $Mg^{2+} \cong Ca^{2+}$,whereas the influence of anions was not appreciable and the order was HCO^{3-}~CO_3^{2-}>NO_3^->Cl^-.Reduction kinetics was also studied at different temperatures and activation parameters were evaluated for a Red MCT-AU reactionand TB-AUreaction.The values of parameters obtained for Red MCT reaction and TB-AU reaction are :energy of activation (E_a=6.458kJ.mol^{-1} and 8.129 kJ.mol^{-1}), enthalpy change ($\Delta H^{\neq}$= -49.160 kJ.mol^{-1} and -54.323 kJ.mol^{-1}), entropy change ($\Delta S^{\neq}$=-163.993 J.mol^{-1}.K^{-1} and -148.920J.mol^{-1}.K^{-1}), and Gibbs energy change ($\Delta G^{\neq}$ = -0.290kJ.mol^{-1} and -9.945 kJ.mol^{-1}) respectively. Mechanisms of interaction of related ions involved in dye bleaching and reduction is proposed

Key words: Toluidine blue (TB), Red MCT(monochlorotriazinereactive dyes), allylurea (AU),decolouration,activation parameters.

INTRODUCTION

Reactive Dyes like Red MCT are extensively used in Textile industries (Nebojša and Ivanka, 2009) and generated enormous amount of coloured water .Wastewater discharged from these industries contains highly toxic un-reacted dye material which has imposed serious health problems to ecology of troposphere. Monochlorotriazine dyes produce remarkable and fast colours with a huge variety of shade and these dyes are superior to the other dyes in the way that they form covalent bond between carbon atoms of the dye reactive group and atoms of the cotton fabric hydroxyl groups under alkaline condition (Tam *et al*., 1997).The dyes haloheterocycle group reacts with cellulose fiber of the cloth through nucleophilic substitution mechanism . The significant parameters which affect the fixation of the dye are temperature, salt concentration and alkali concentration .Reactive dyes when released into waste water of rivers and streams destroy the delicate life cycle of organisms of water (Lewis and Vo, 2007).

Dyes waste water generated from the textile industry carries lot of dye supportive material used in fabrication. Their side reactions are dangerous and lethal for main stream. Therefore study was undertaken for monitoring the possiblereaction associated with wastewater .The paper will cover the reaction kinetics , mechanism and interaction of probable cations and anions in waste water .Allylurea is used to increase the affinity of fiberinthe absorption of the dye.This research is to focus attention on dye wastewater containing allylurea(AU) and other toxic metals ions which are commonly used in the dying process(Mills and Hoffmann, 1993; Dhale and Mahajani, 1999; Missmann*et al.,* 2006). TB and reactive dyes like Red MCT are water soluble,due to their stability they maintain their visibility and require high quantity of salts and alkali to have best performance ,their industrial waste has high intensity of these ions Baoub*et al.,* (2001).

Materials and Methods

All reagents obtained from E-Merck and were used as received.The experimental work was divided into various sessions,which includes preparation of solutions,kinetic studies and data analysis.All solutions are prepared in de-ionized water and are diluted before use. Kinetics is monitored on a UV-Visible Spectrophotometer.

Preparation of solutions

Preparation of stock solution of dye (TB): Stock solution of dye was 5x10^{-4} mol.dm^{-3} and it was prepared by dissolving TB (M.W = 305.8 $gmol^{-1}$) 0.01529 g in 0.1dm^3 of deionized water.

Preparation of stock solution of Red MCT Dye: 1.44x10^{-4} Stock solution of the dye (M.W =736$gmol^{-1}$)was prepared by dissolving0 .110g in 0.1$dm^3$of deionized water.

Preparation of stock solution of allyl urea ($C_4H_8N_2O$):0.1mol.dm^{-3} stock solution of Allyl urea ($C_4H_8N_2O$) was prepared by dissolving 1.007 gm pure allyl urea in 0.1 dm^3in 0.1dm^3 of deionized water.

Preparation of stock solution of hydrochloric acid (HCl):4 mol.dm^{-3} standardfreshly prepared solution of Hydrochloric acid (HCl) was used as stock.

Preparation of stock solution of sodium hydroxide (NaOH):1 mol.dm^{-3} standard stock solution of Sodium hydroxide (NaOH) was used as stock .

Preparation of stock solution of sodium chloride (NaCl):0.1 mol.dm^{-3}standard solution of Sodium chloride (NaCl) was used as stock.

Preparation of stock solution of Potassium Chloride (KCl):0.1 mol.dm^{-3} solution of Potassium Chloride (KCl) was used.

Preparation of stock solution of Magnesium Chloride ($MgCl_2$):0.1 mol.dm^{-3} solution of Magnesium Chloride ($MgCl_2$) was used as stock.

Preparation of stock solution of calcium chloride ($CaCl_2$):0.01 mol.dm^{-3} solution of Calcium Chloride ($CaCl_2$) was used as stock.

Preparation of stock solution of sodium bi-carbonate ($NaHCO_3$):0.01mol.dm^{-3} solution of Sodium Bi-carbonate ($NaHCO_3$) was used as stock.

Preparation of stock solution of sodium carbonate (Na_2CO_3):0.01 mol.dm^{-3} solution of Sodium Carbonate (Na_2CO_3) was used as stock.

Preparationof stock solution of cobalt chloride ($CoCl_2$): Sample solutions of concentrations 1x10^{-2} to 5x10^{-2} mol.dm^{-3} were used from stock solutions of0.1 mol.dm-^{3}.

Preparation of stock solution of potassium nitrate (KNO_3): Sample solutions of concentrations 1x10^{-2} to 5x10^{-2} mol.dm^{-3} were used from stock solutions of 0.1 mol.dm-^{3}.

These solutions were prepared by using standard methods in the literature (Jeffery*et al.*, 1989).

Kinetic measurements

Kinetics was monitored by keeping one reactant varied and the others as constant. Kinetic runs were pursued by measuring the absorbance of a mixture of thermostatic solutions as a function of time at regular 60 s intervals up to 10 min. The absorption spectrum of TB and Red MCT dye were scanned for absorption maximum (λ_{max}) at a wavelength of 625nm and 535nm respectively (Wong*et al.*, 2005).

Analysis of the data

According to the Beer-Lambert's law (A = εbc), the absorbance A of a dilute solution is proportional to its concentration *c,* and path length b. Under the experimental conditions, the TB concentration obeys the Beer-Lambert law. A linear plot of logA vs time indicates the pseudo first-order dependence of the rate on dye concentrationand the slope of the ln k vsln [AU] plot will be equal to the order of the reaction with respect to N-allylurea(Lilani*et al.*, 1986)

Results and Discussion

The dyes decolouration with AU was investigated initially in aqueous medium and the reduction was found to be slow in aqueous medium . The reduction of dyes with reductant was studied in aqueous medium at variousreductant, dyes concentrations and temperature . The rate constants were determined at constant concentration of reductant and dyes i.e. 1x10^{-2}mol dm^{-3} and 2.0x10^{-5}mol dm^{-3} in aqueous medium. Since the rates of the reduction with reductant in aqueous media are very low ,therefore reduction was monitored at high and low pH, by adding varying amount of HCl and NaOH.

The dyesdecolouration was studied at various pH with allylurea. The reduction rates and the extent of decolourationare reported in Tables(Nebojša and Ivanka, 2009;Tam, *et al*., 1997;Lewis and Vo, 2007;Mills and Hoffmann, 1993; Dhale and Mahajani, 1999; Missmann*et al.*, 2006) and represented plots are given in the Figures(Nebojša and Ivanka, 2009; Tam, *et al*., 1997; Lewis and Vo, 2007; Mills and Hoffmann, 1993; Dhale and Mahajani, 1999; Missmann*et al.*, 2006; Baoub*et al.*, 2001; Jeffery*et al.*, 1989;Wong, *et al.*,2005). The time dependence of the absorbance isplotted to be linear and the slope of the line is equal to the rate constant for different concentrations of dyes, AU, H^+ and OH^- ions. The rate constant data obtained for varied concentrations of allylurea with fixed concentrations of HCl, NaOH and the dye and varied concentrations of dyes with fixed concentrations of HCl, NaOH and AU were presented in the Tables 1,2and a representative graphs are shown in Figures1-6. First order rate constant (*k*) was obtained using the linear regression method. It was visualized that the dye decoloration is directly related with the allylurea concentration.

The kinetics of the redox reaction of TB and Red MCT with AU suggest that it dependson the concentration of AU and the dye molecules. No change was observed without AU (Mill and Maybe, 1988)

The value of rate constants k $=1.0\text{x}10^{-3}$ $mol^{-2}L^{2}s^{-1}$ for TB-AU and k $=1.39$ mol^{-2} L^{2} s^{-1} for Red MCT – AU respectively were determined .

Effect of dye concentration on reaction rate

The dye decolouration with regard to TB was first order with allylurea ($1\text{x}10^{-2}$mol.L^{-1})in basic medium ($1\text{x}10^{-2}$mol.L^{-1}NaOH solution)and first order with Red MCT dye with allylurea ($1\text{x}10^{-2}$mol.L^{-1})in acidic medium($1\text{x}10^{-2}$mol.L^{-1}HClsolution) respectively. The kinetics of the redox reaction of TB and RED MCT with AU suggest that the reaction depends on the concentration of dyes.

A plot of k verses dye concentration in presence of basic medium and acidic medium respectively for AU showed that dye decoloration is effected by varied concentration of TB and Red MCT. This reflects the fact that dye decoloration was dependent on the dye concentration as shown in figure3. A plot of k_{obs} vs [TB] in presence of AU was presented in the figure1, in which linear regression analysis proved that reaction followed first order kinetics and the R^2 values 0.828 also reflects a significant correlation in between dye and the process of reduction.whereas the plot of k_{obs}vs [Red MCT] was shown in figure 2 interprets the mechanism of the reaction to be followed by first order kinetics .

Effect of reductant concentration on reaction rate

The dye decoloration with respect to AU was first order regarding TB ($2\text{x}10^{-5}$mol.L^{-1}) in basic medium ($1\text{x}10^{-2}$mol.L^{-1} ,NaOH solution) and second order regarding Red MCT dye ($2\text{x}10^{-5}$mol.L^{-1}) in acidic medium ($1\text{x}10^{-2}$mol.L^{-1}HCl solution) respectively. The kinetics of the redox reaction of TB and RED MCT with AU suggests that the reaction depends on the concentration of allylurea,as shown by figures 4,5 and 6 .

With Red MCT the reduction took place immensely in acidic medium ($1\text{x}10^{-2}$ mol.L^{-1} HCl solution). It was second order with respect to AU in acidic medium with constant conc. of Red MCT at $2\text{x}10^{-5}$ mol.L^{-1} and temperature 298 K as shown in figure 5, where as zero order in basic medium i.e: reduction was paralyzed in basic medium. For MCT and AU, a plot of k versus AU concentration in acidic medium showed immense effect on dye decolouration which reflected that the reaction was dependent upon the AU concentration as shown in figure 5, in which regression coefficient analysis proved that reduction with AU was enhanced by the concentration of allylurea and order of reaction was second order in acidic medium, the value of R^2 is 0.8 in acidic medium, which predicts high dependency. In basic medium the reaction was inhibited.

For TB and allylurea reaction, a plot of k vs AU was presented in figure 6. AU concentration variation is observed with constant concentration of TB ($2x10^{-5}$ $mol.L^{-1}$) at 298K. Linear regression analysis proved that dye reduction was increased by the concentration of AU and order of reaction was first order with AU concentration in basic medium. R^2 0.967value in figure 6 showed high significance on reduction of dye.

Effect of Acidic and basic medium on the rate of reduction reaction

The role of medium was significant in reduction phenomena. It was first order in alkaline medium for TB- AU and first order in acidic medium for Red MCT–AU couple.

Reduction of AU with TB occurred more rapidly in higher pH range , followed first order kinetics and the linear regression analysis showed a significant correlation coefficient of 0.92 and it followed first order kinetics in acidic medium R^2=0.804 for Red MCT as evident from Tables3 &4 and as shown by Figures 7 &8 respectively. Reason could be that reaction with TB, supplementary favorable alkaline medium may be attributed to the strong oxidizing power of the hydroxyl radical. The hydroxyl radicals react with the dye axochrome groups which commonly control the color of the dye or show affinity towards the CH_3 radical, resulting in demethylation with the production of the intermediate, which causes the bleaching of the dye (Uddin and Hasnain, 2002). This could also be the probable source of the initiation of dye decoloration at alkaline (pH 9) shown by Figure 7 .The zero order dependence of acidic medium for TB dye shows that the high concentration of protons or acidity obstructs the reaction .

In case of Red MCT dye, the reduction occurred in acidic solutions as shown in Table 4.The reaction suggested the formation of a complex ion formation as shown by equations (4) and (5) and a transient intermediate and protonated form of the dye as Red $MCTH_2$ species respectively and a simultaneous second order involvement of AU by A_{AC2} –type hydrolysis mechanism as shown in equations (Missmann*et al.,* 2006; Baoub*et al.,* 2001; Jeffery *et al.,* 1989; Wong, *et al.,* 2005)

Effect of various cations on dye reduction

The reaction kinetics of TB and red MCT was studied with varying initial concentrations of anions and cations which are commonly present in dye waste water solution. Analysis was performed in acidic (Red MCT) and alkaline(TB) medium to check the effect of these ions on the reduction of dyes .

The reduction of dyes was investigated with some inorganic metal cations (like Na^+, K^+, Mg^{2+} and Ca^{+2}) to verify whether these metals have some effects on dye decolourationas presented in Tables 5 . Experimental effects of cations were measured by varying the concentration of these ions at an alkaline pH for TB- AU and acidic pH for Red MCT–AU.

In TB-AU couple, cations like Na^+ and K^+ have a moderate influence on the reduction of TB, as illustrated in Tables 5 .Rate of dye reduction depends on moderate percent decoloration with Na^+ and K^+ as compared with the other cations, which may be attributed to the formation of alkali hydroxide. This supports the dye reduction related to the production of more hydroxyl ions. The presence of Ca^{2+} and Mg^{2+} showed less decrease in percent decolouration, which indicates that these ions in dye reduction search the hydroxyl group to form their hydroxides. Due to the less interaction of OH radical(probably due to large charge size of these metal ions) the less dye reduction is observed (Uddin and Hasnain, 2002) The general trend was $Na^{+}>K^{+}> Ca^{2+} \cong Mg^{2+}$.

In case of Red MCT it was observed that these cations showed enhanced effects on the reaction of AU with exceptionally good effect of Na^{+} ions. This may be related to the oxidation state of these metal ions ($Na^{+}>K^{+}> Mg^{2+} \cong Ca^{2+}$), as reported in Table 5 .

Influence of various anions on the reaction mechanism

The TB reduction was studied in the presence of anions such as HCO_3^{-}, CO_3^{2-}, $Cl^{-}$and SO_4^{2-} within the range of high pH. But low pH does not favor the reaction mechanism. These ions were considered because of their presence in the polluted water obtained from industries. It was observed that the dye reduction proceeds more rapidly at alkaline pH for TB compared to that at low pH .Results are reported in tables 5 , which shows that dye decoloration with AU was not enhanced by the presence of SO_4^{2-} ions. This is due to the common ion effect by sulphate ions presence in solution,formed during the decomposition of AU into urea and sulphateions .Cl^{-} ions have also found to lessen TB decoloration in the presence of AU, which may be due to the reaction of Cl^{-} ions with H^{+} obtained from the AU, which would eventually form HCl, resulting in the formation of less leuco form of TB. The CO_3^{2-} and HCO_3^{-} have also observed to increase the reaction rate as these get excited according to the reactions mechanism suggested (Uddin andHasnain, 2002) and enter in reaction sphere through de-excitation by releasing a photon during collision with the dye molecule resulting in the formation of a semi reduced dye, which later on is converted into a leuco dye by H-abstraction from the reductant molecule. This mechanism is also suggested for other anions, investigation suggested that percent decolouration increased in the presence of added anions and which may be due to the fact that the anions richness in electrons might lead to the reduction (Azmat*et al.*,2011; Mahadevan*et al.*, 1989; Muruganandham and Swaminathan, 2006; Snehalatha*et al.*,1997).

With Red MCT dye in acidic pH, the dye reduction was studied in the presence of anions such as HCO_3^{-}, CO_3^{2-}, Cl^{-}, NO_3^{-}within the range of low pH.. It was observed that the dye decoloration proceeds more rapidly. Results are reported in Table 5 which shows that dye decolouration was significantly higher in presence of NO_3^{-} ions in allylurea. This is probably due to the fact that anions being rich in electrons facilitate the electron transfer process.

Influence of temperature on the reaction rate and activation parameters

Temperature has been found to enhance the reaction rate immensely for both dyes with AU.The influence of temperature from (303-343K)was studied in alkaline (for TB)and acidic (for Red MCT) medium. The specific rate constant has been increased with the variations of temperature as shown in Table 6 and figures 9 & 10. Dyes were investigated at different temperatures, and activation parameters were evaluated for a Red MCT-AU reaction and TB-AU. The following values were obtained for AU-TB couple the energy of activation (E_a= 8.129 kJ.mol^{-1}), enthalpy change ($\Delta H^{\neq}$= -54.323 kJ.mol^{-1}), entropy change ($\Delta S^{\neq}$= -148.920 J.mol^{-1}.K^{-1}), and Gibbs energy change ($\Delta G^{\neq}$ = - 9.3945 kJ.mol^{-1}) respectively. The values obtained for AU-Red MCT couple were: energy of activation (E_a=6.458 kJ.mol^{-1}), enthalpy change ($\Delta H^{\neq}$= - 49.160 kJ.mol^{-1}), entropy change ($\Delta S^{\neq}$ = -163.993 J.mol^{-1}.K^{-1}) and Gibbs energy change ($\Delta G^{\neq}$ = -0.290 kJ.mol^{-1}) respectively. The negative value of $\Delta H^{\neq}$ showed that enthalpy is the driving force for the formation of complex product and the reactions are exothermic in nature while negative value of entropy for both the reduction reactions showed that entropy of product is greater than entropy of reactant. The negative value of $\Delta G^{\neq}$ indicates about the reaction is spontaneous with both the dyesand is enhanced with incremental temperatures.

Activation parameters were determined from the Eyring , Polanyi equation ,

$$k = k_B\, T/h\, e^{-\Delta G\neq/RT}$$

where ,$\ln k = -E_a/R\ .1/T + \ln A$,for activation energy

$$\ln k/T = - \Delta H^{\neq}\ /R\ .1\ /T + \ln k_B//h + \Delta S^{\neq}/R$$

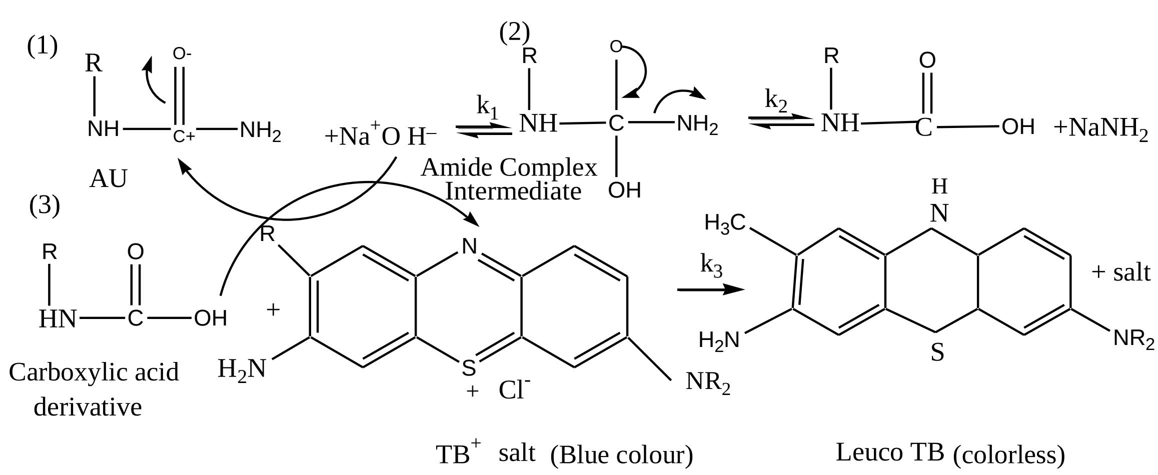
where slope = $- \Delta H^{\neq}\ /R$, intercept =$\ln (k_B /h) + \Delta S^{\neq}/R$

$$\Delta G^{\neq} = \Delta H^{\neq} - T\ \Delta S^{\neq}$$,for Gibbs free energy of activation

where h is the Planck ‛s constant and has the value of 6.625×10^{-34} J and T, the absolute temperature in K , k_B is the Boltzmann ‛s constant and has the value of 1.380×10^{-23} JK^{-1}

Probable mechanism of reduction of TB with AU by B_{AC2} –type

The reaction occur by base catalysednucleophilicacyle substitution mechanism B_{AC2}- type and proceeds via direct addition of OH^- to the carbonyl group ,this occurs because OH^- is stronger nucleophile than H_2O (Mill and Maybe, 1988).



Rate Law

The rate of the formation of leuco Toluidine blue could be expressed as follows by equations (1),(2) and(3) :

$[\text{LTB}] / dt = r = k_1 [\text{AU}] + k_2[\text{Amide}] + k_3[\text{TB}]$

whereas k_2 [Amide] is steady state , assoon it forms itdisappearsand the third step relieved H^+ for the formation of colourless dye, the leucoTB .

Therefore $d[\text{LTB}] / dt = r = k_1 [\text{AU}] + k_3 [\text{TB}]$

The rate Law of this reaction is ,

$-[\text{TB}^+] / dt = k_1 [\text{AU}] [\text{TB}^+][\text{OH}^-]$

Under excess conditions of AU and OH^- above equation reduces to

$-[\text{TB}^+] / dt = k^{'} [\text{TB}^+]$

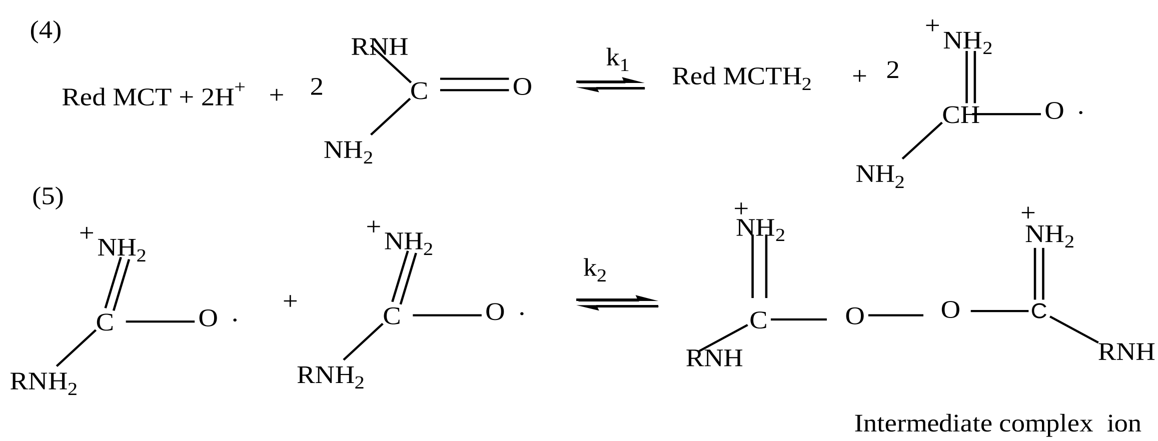
Where total rate constant of the reaction is $K = 1.0 \times 10^{-3}$ $\text{mol}^{-2}\text{L}^2\text{s}^{-1}$

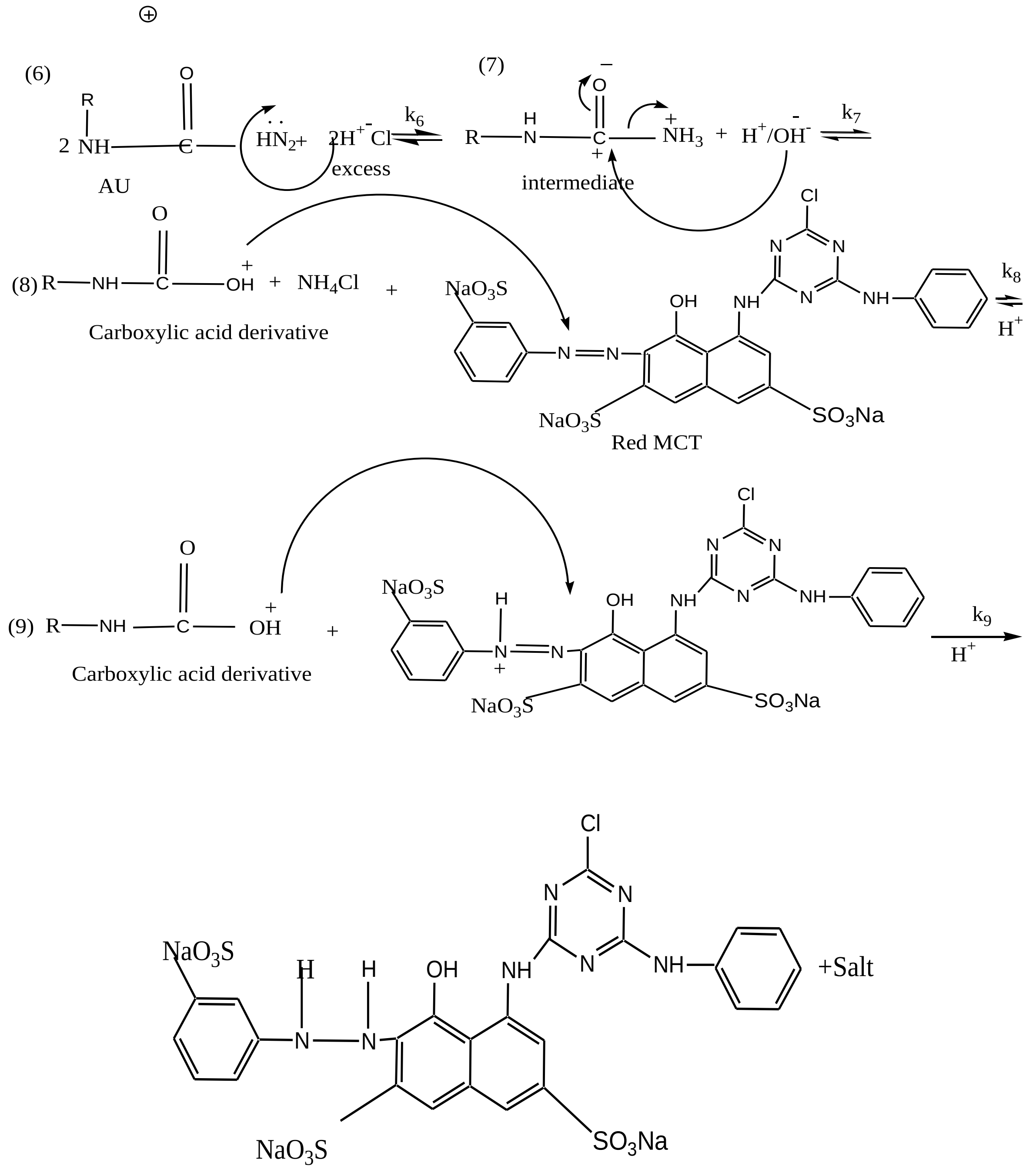
Probable mechanism of reduction of Red MCT with AU:

The observed order with AU is second order, and two steps suggested mechanism by equations (4) and (5) with simultaneous interaction of two molecules of AU to form an intermediate complex ion as the product of AU oxidation is considered (Lilani*et al.*,1986).

The other suggested mechanism involves the concept that carbonic acid derivatives like N-allyl urea are less reactive towards hydrolysis due to ground stabilization of carbonyl group by electron donating properties of nitrogen atom .The hydrolysis require acid catalysis the acid hydrolysis of AU occur through A_{AC2}-type mechanism (Mill and Maybe, 1988).This reaction occur in three steps ,in the first step AU is attacked by the proton donated by acid and a transient intermediate is formed which is readily transformed into carboxylic acid derivative which reduces dye in third and fourth steps as shown by equations (6) ,(7) , (8) and (9).

(4)




(6)
AU
excess
k6
(7)
intermediate
k7
(8)
Carboxylic acid derivative
Red MCT
k8
(9)
Carboxylic acid derivative
k9
+Salt

Reduced dye

Rate Law

The rate expression may be as follows according to first proposed mechanism:

-d [Red MCT]/dt = r = k_1 $[H^+]^2[AU]^2$ [Red MCT]+k_2[complex ion]

Under excess concentration conditions of $H^+$and AU , the equation reduces to

r = k' [Red MCT]

where $k' = \{ k_1[H^+]^2[AU]^2 + k_2$[complex ion]

The rate expression for second proposed mechanism:

-d [Red MCT]/dt = r = k_6 $[H^+]^2[AU]^2$ + k_7[transient intermediate]+ k_8 [Red MCT]

Since step (7) is steady state,therefore above equation got reduced to ,

-d [Red MCT]/dt = r = k_6 $[H^+]^2[AU]^2$ + k_8 [Red MCT]

where k_6 $[H^+]^2[AU]^2$ is a constant term under excess concentration conditions of H^+ and AU

The rate equation got reduced to,

-d [Red MCT]/dt = r = k_8' [Red MCT]

K_8' is Pseudo first order rate constant

The overall rate constant for the reaction k =1.39 mol^{-2} L^2 s^{-1}

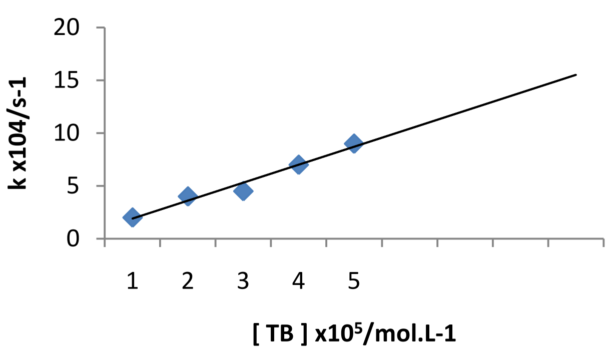


Fig. 1: The plot of kvs [TB], for AU in basic medium

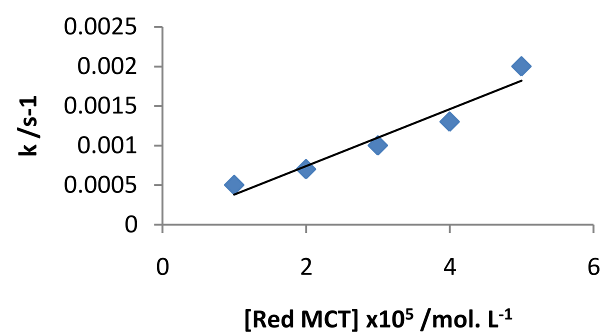


Fig. 2: The plot of kvs [Red MCT], for AU in acidic medium

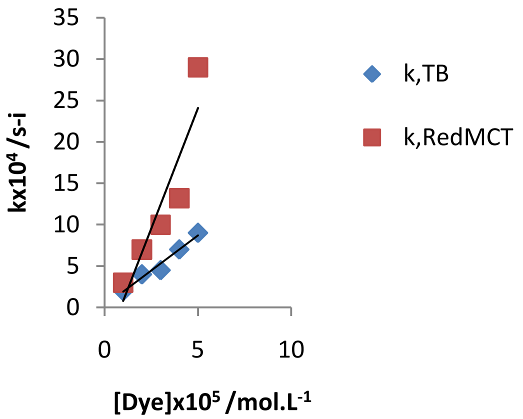


Fig. 3: The plot of kvs [Dyes], for AU as reductant in basic and acidic medium

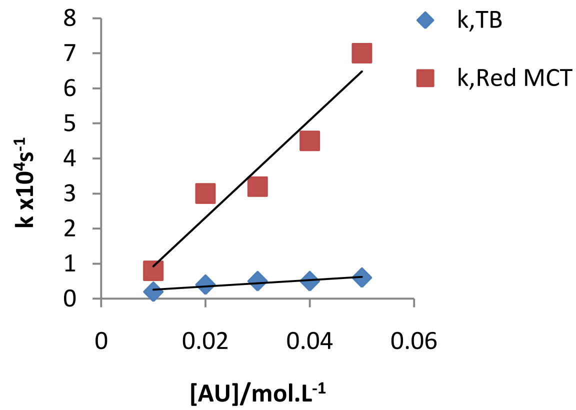


Fig. 4: The plot of kvs [AU], for TB and Red MCT in basic and acidic medium

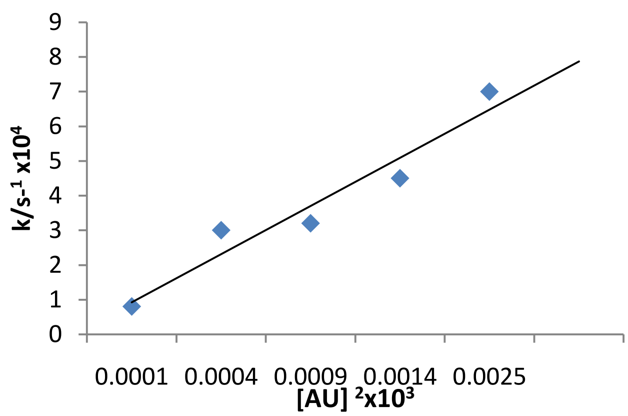


Fig. 5: The plot of kvs $[AU]^2$, for Red MCT in acidic medium

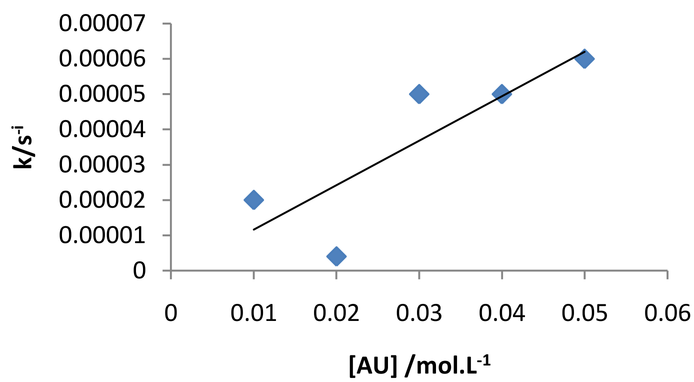


Fig. 6 : The plot of kvs [AU], for TB in basic medium

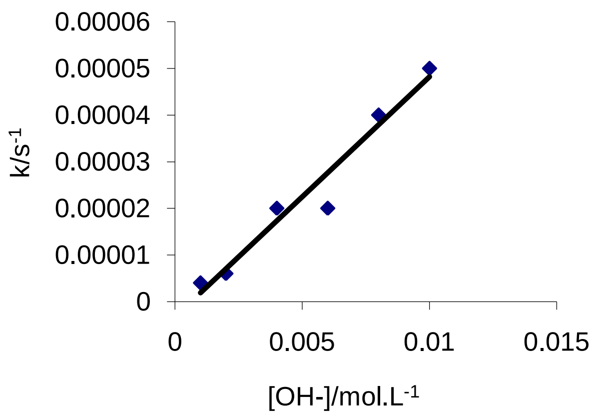


Fig 7: The plot of k vs $[OH^-]$ for the AU with TB

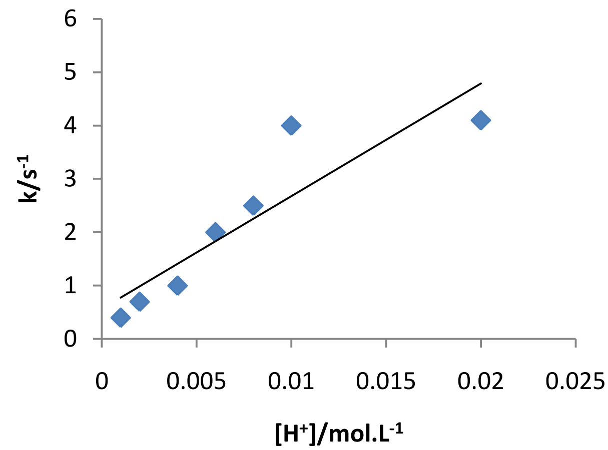


Fig 8: The plot of k vs $[H^+]$ for the AU with Red MCT

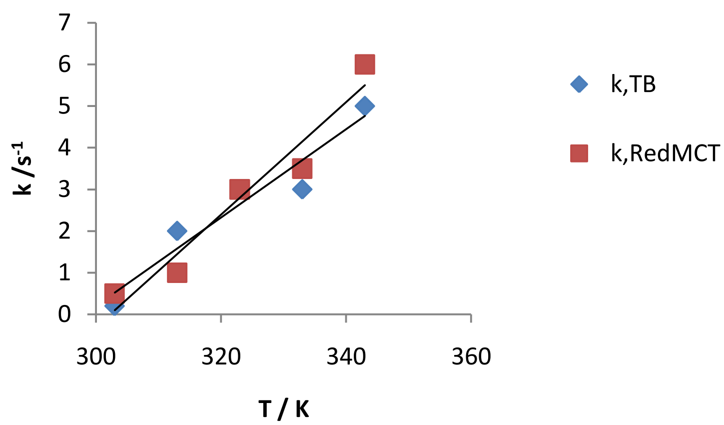


Fig 10: $[TB] = 2.0 \times 10^{-5}$ mol·L^{-1}, [Red MCT] $=2.0\text{x}10^{-5}$mol. L^{-1} $[AU] = 1.0 \times 10^{-2}$mol·L^{-1},[NaOH] $=1.0\times10^{-2}$mol·dm^{-3},[HCl] $=1.0\times10^{-2}$mol·dm^{-3}

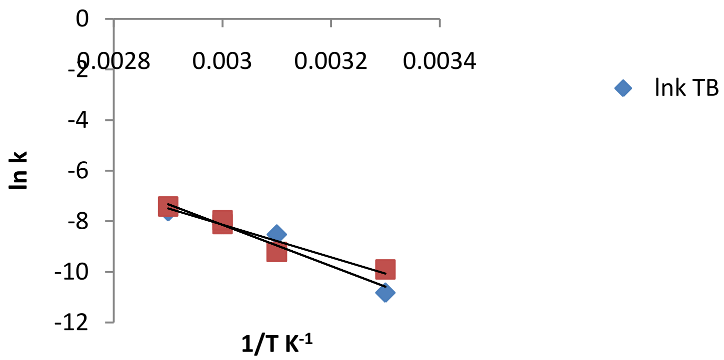


Fig 11: [TB] = 2.0×10^{-5} mol·L^{-1}, [Red MCT] =$2.0\text{x}10^{-5}$ mol L^{-1} , [AU] = 1.0×10^{-2}mol·L^{-1},[NaOH] =1.0×10^{-2}mol·dm^{-3},[HCl] =1.0×10^{-2}mol·dm^{-3}

Table 1: Comparative impact of TB and Red MCT conc. on the rate of reactions

[TB]x10^5 mol.L^{-1}	[RedMCT]x10^5 mol.L^{-1}	k x 10^4 s^1 TB (basic medium)	k x 10^{4}s^{-1} RedMCT (acidic medium)	%decoration TB	%decoloration Red MCT
1.00	1.00	2.0	3.0	24.0	30.0
2.00	2.00	4.0	7.0	16.0	34.5
3.00	3.00	4.5	10.0	17.8	34.0
4.00	4.00	7.0	13.2	17.8	41.0
5.00	5.00	9.0	20.0	25.0	45.2

Temperature = 298 K, [AU] = 1.0×10^{-2}mol·L^{-1}, [H$^+$] = 1.0×10^{-2}mol·L^{-1} , [OH$^-$] = 1.0×10^{-2} mol·L^{-1}

Table 2: Comparative impact of allylurea conc. on the rate of reactions

[AU]x10^2 mol.^{1}L^{-1}	K_{obs} x10^{4}s^{-1} TB (basic medium)	K_{obs} x10^{4}s^{-1} RedMCT(acidic medium)	%decoration TB	%decoloration Red MCT
1	0.2	0.8	10.65	10.70
2	0.4	1.0	6.61	6.50
3	0.5	2.0	24.00	23.00
4	0.5	2.5	25.02	25.00
5	0.6	7.0	24.00	25.00

Temperature = 298 K, [TB] = 2.0×10^{-5} mol·L^{-1}, [Red MCT] =$2.0\text{x}10^{-5}$mol., [H$^+$] = 1.0×10^{-2}mol·L^{-1} L^{-1} ,[OH$^-$] = 1.0×10^{-2} mol·L^{-1}

Table 3: Impact of basic medium on the rate of reaction of TB

[NaOH] mol.^{1}L^{-1}	k_{sp} x10^{4} s^{1} TB	%decoration TB
0.001	0.04	10.00
0.002	0.06	14.00
0.004	0.2	15.11
0.006	0.2	20.32
0.008	0.4	24.00
0.01	0.5	25.5
0.02	0.5	25.0

Temperature = 298 K, [TB] = 2.0 × 10^{-5} mol·L^{-1}, [AU] = 1.0 × 10^{-2}mol·L^{-1}

Table 4: Impact of acidic medium on the rate of reaction of Red MCT

[HCl] mol.^{1}L^{-1}	k_{sp} x10^{4} s^{-1} RedMCT	%decoloration Red MCT
0.001	0.5	9.12
0.002	0.7	11.64
0.004	1.0	16.99
0.006	2.0	18.91
0.008	2.5	20.91
0.01	4.0	25.0
0.02	4.1	26.0

Temperature = 298 K, [Red MCT] =2.0x10^{-5}mol. L^{-1} [AU] = 1.0 × 10^{-2}mol·L^{-1}

Table 5: Comparative impact of ions on the rate of reaction in basic and acidic mediums

Ions	Ions conc. mol.^{1}L^{-1}	K_{obs} x10^{4} s^{1} TB(basic medium)	K_{obs} x10^{3} s^{-1} RedMCT(acidic medium)	%decoration TB	%decoloration Red MCT
Na^{+}	0.01	10.0	7.0	16.0	31.0
K^{+}	0.01	8.0	4.0	11.0	20.0
Mg^{2+}	0.01	0.1	4.0	1.45	20.0
Co^{+2}	0.01	4.0	-	20.26	-
Ca^{2+}	0.001	0.3	4.0	2.00	21.0
$CO_3{}^{2-}$	0.001	2.0	2.5	19.4	2.0
HCO_3^{-}	0.001	2.0	2.0	20.0	2.0
Cl^{-}	0.01	10.0	1.0	6.00	1.0
SO_4^{2-}	-	-	-	-	-
$NaNO_3$		-	2.0	-	1.0

Temperature = 298 K, [TB] = 2.0 × 10^{-5} mol·L^{-1}, [Red MCT] =2.0x10^{-5}mol. L^{-1} [AU] = 1.0 × 10 $^{-2}$mol·L^{-1}, [NaOH] =1.0×10^{-2}mol·dm^{-3}, [HCl] =1.0×10^{-2}mol·dm^{-3},

Table 6: Comparative impact of temperature on the rate of reaction in basic and acidic mediums

Temperature/K	K_{obs}x10^{4}s^{1} TB(basic medium)	K_{obs} x10^{4}s^{-1} RedMCT(acidic medium)	%decoration TB	%decoloration Red MCT
303	0.2	0.5	25.89	6.85
313	2.0	1.0	27.64	29.17
323	3.0	3.0	27.31	35.00
333	3.0	3.5	33.69	41.50
343	5.0	6.0	34.14	54.70

[TB] = 2.0 × 10^{-5} mol·L^{-1}, [Red MCT] =2.0x10^{-5}mol. L^{-1} [AU] = 1.0 × 10 $^{-2}$mol·L^{-1},
[NaOH] =1.0×10^{-2}mol·dm^{-3}, [HCl] =1.0×10^{-2}mol·dm^{-3}

Conclusions

The main purpose of this research work is to focus on the oxidation reaction of the agent (AU) with the reactive textile and basic dyes (Red MCT and TB)respectively and consequences of the close association of these toxic dyes with these ions (cation and anions) are exclusively observed in industrial waste discharge in the water channels used by us .

Presence of the cationic salts in alkaline medium (pH 9) and acidic medium (pH 1) have found to increases the affinity of the basic and reactive dyes for the agent AU and theconsequent reduction was followed by intense decolourization .Increasing concentration of the dyes and the agent increases decolorization progressively .Presence of the cationic salts in this scenario, positively affects the dye exhaustion.However the acidic medium blocks the reduction reaction probably due to common proton effect which is triggered by the release of protons from AU for TBdye exclusively. Reverse situation is observed for Red MCT dye which favors acidic environment and strongly supports hydrolysis in acidic catalysis.Temperature has also found to enhance these reaction rates, consequently reactions of AU have occurred in the presence of high temperatures, which satisfies the Arrhenius Law.

Reaction of AU by Red MCT dye supersedes the TB dye mechanism as shown by the Tables (1,2,3,4,5,6) and the respective graphs .Therefore AUis a better reductant for Red MCT than TB as evidently demonstrated in this research.

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