RESEARCH ARTICLE

IMPACT OF IONIC INTERACTIONS ON THE MECHANISM OF THE PHOTOCATALYTIC REDOX REACTION OF TOLUIDINE DYE WITH DIETHYLTHIOUREA

Masooda QADRI[1] ,Shazia Nisar[2] , Nasreen Fatima[3]
Photochemistry Research Lab., Department of Chemistry University of Karachi, Karachi-75270, Pakistan

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Abstract

This investigation covers the interaction of the unreacted dye wastewater with various inorganic anions and cations like Cl^-, Br^-, I^- and NO_3^- CO_3^-, SO_4^{2-} , K^+ , Na^+,Ca^{2+} , Mg^{2+}, Co^{2+} , which are an open threat to the environment because it results in many non degradable complex polymer formation. Currently wide spread researches are in progress for the development of de-coloration techniques for the control of textile industries effluents. Our Study is focused on the decoloration / redox /encoring , abilities of different cations and anions at various important coperational parameters in the bleaching of the TB with DETU, . These are vital chemicals of textile dye industry effluent and should be addressed properly before disposal. The kinetics and mechanism study for decolorization and reduction of Toluidine blue (TB) with DETU in acidic medium were monitored at λ_{max} = 625 nm by observing the diminution in TB concentration using spectrophotometer. Kinetics of decolorization of dye was followed spectrophotometrically at different operational variables. Influence of addition of dye into reaction mixture retarded the bleaching processes which got enhanced by the addition of , DETU . Whereas the added salts showed a ripple of different behavioral aspects , which could be predicted on the basis of their interactions with the super active free Radicals .The variations of ionic strength of the medium in which the reaction was monitored and observed in NaCl salt solutions .It was found that variations had moderate effect on dye decolorization . Decoloration showed the following order for salts , $Na^+ > K^+ > Ca^{2+} \approx Mg^{2+}$,Na^+ ion being strong electrolyte delivered appreciable contribution on the dye decoloration ,Ca^{2+} and Mg^{2+} ions formed hydroxide precipitates , whereas Co^{2+} formed polycomplex with DETU . The tested anions showed that the dye decoloration was more prominent in presence of anions and followed the order $I^- > NO_3^- > HCO_3^- \approx Cl^- > SO_4^{2-}$ .The aspects with I^- ion were exceptional ,it exhibited brilliant photocatalytic performance.

Introduction

Toulidine Blue is an imperative basic metachromatic dye .It one of the important member of Phenothiazine dyes and exhibits photosensitizing property [Hoffman ,M.Z.,1979] . Photocatalytic Toluidine dyes are easily reduced to their light amber tinge , leucoforms by using mild-reducing agents and are decolorized completely by reduction

in photocatalytic process.This study is performed in aqueous medium where the dye aggregation happens resulting into the formation of dimerization of the dye [.Gabrielli , D.S. ,2004] and as the dye concentration increases and temperature decreases dye aggregation also enhanced and the rate of decolorization get less effected [Kumar ,S. K., 2009] ,as strong hydrated ions would decrease the available solution water and induce aggregations which would block the passage of light and exposure to photons decrease.But these hamperings were ignored at the stake of electron transfer redox reactions ,which are more facilitated in aqueous medium.The dye concentrations were also kept in low range $2x10^{-5}$ M to avoid these problems.The salt ions present in the effluents show quenching property to the dye aggregations [Furukh, M.A.,2012] **.**Photocatalytic destructive effect has also been observed to have increased in the presence of salts [Rupa, A.V. , 2007] . The dye decoloration enhances in the presence of many ions [Simoyi, R.H. , 1994]. Studies have been conducted on the effect of metal ions ($Cu^{2+,}$ $Fe^{3+,}$ $Zn^{2+,}$ $Al^{3+,}$ $Cd^{2+)}$ on the photo degradation of several dyes such as sulfo-rhodamine B (SRB), alizarin red (AR), and malachite green (MG) in aqueous TiO_2 in visible range. Ionic strength dependence indicated complex formation by monocationic and anionic species in solution. Kinetic evidence for a specific catalytic effect by binding of alkali metal ions to oxidant was also reported [Khan , M. N. and Sarwar, A.2001].

Materials and Methods
Preparation of Solutions
 STOCK SOLUTION OF DYE TOLUIDINE BLUE
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.
 STOCK SOLUTION OF DIETHYLETHIOUREA
0.1mol.dm^{-3} stock solution of DETU was prepared by dissolving 1.007 gm pure of it in 0.1 dm^3 of deionized water.
 STOCK SOLUTION OF HYDROCHLORIC ACID
4 mol.dm^{-3} standard freshly prepared solution of Hydrochloric acid was used as stock.
STOCK SOLUTION OF SODIUM CHLORIDE
0.1 mol.dm^{-3} standard solution of Sodium chloride was used as stock.
STOCK SOLUTION OF POTASSIUM CHLORIDE

0.1 mol.dm^{-3} standard solution of Potassium Chloride was used.
STOCK SOLUTION OF MAGNESIUM CHLORIDE

0.1 mol.dm^{-3} standard solution of Magnesium Chloride was used as stock .
STOCK SOLUTION OF CALCIUM CHLORIDE

0.01 mol.dm^{-3} standard solution of Calcium Chloride was used as stock.
STOCK SOLUTION OF SODIUM BI-CARBONATE

0.01mol.dm^{-3} standard solution of Sodium Bi-carbonate was used as stock.
STOCK SOLUTION OF SODIUM CARBONATE
0.01 mol.dm^{-3} standard solution of Sodium Carbonate was used as stock.
 STOCK SOLUTION OF COBALT CHLORIDE
Stock solution of 0.1 mol.$dm^{-3}$was used .
STOCK SOLUTION OF POTASSIUM NITRATE
stock solution of 0.1 mol.$dm^{-3}$was used .
STOCK SOLUTION OF SODIUM SULPHATE
stock solutions in range of   0.1mol.dm^{-3} were prepared.
STOCK SOLUTION OF POTASSIUM PHOSPATE
stock solutions in range of   0.1mol.dm^{-3} were prepared.
STOCK SOLUTION OF SODIUM ACETATE
stock solutions in range of 0.1mol.dm^{-3} were prepared.
All solutions were prepared by using standard methods [Mendham ,J., 2000].

KINETIC MEASUREMENTS

Each kinetic run was made by keeping one reactant varied and the others taken 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 [Qadri, M. , 2012].

DATA ANALYSIS OF THE EXPERIMENTS

The Beer-Lambert's law (A = εbc),was followed and   The absorption coefficient of Toluidine blue in aqueous medium was determined at 625nm , ε =0.202 /1x10^{-5} =2.02x10^{4} mol^{-1} dm^{3}cm^{-1} .Rates of the reaction were determined by the plot of A verses time and log A vs time be linear with a slope $k_{obs}/2.303$,where k_{obs} is a pseudo first order rate constant were determined .

Results and discussion

Mechanism of dye decolorization with DETU in acidic medium:

The Toluidine blue shows photo sensitivity towards solar energy photons and easily acquires excited state Equation 1 ,this excited state interacts with the environmental oxygen molecules and transfer the energy in form of florescence phenomena which visible in UV range .Consequently the excited dye induces singlet oxygen super radical formation Equation 2 ,these radicals interact with other oxygen molecules and generate in aqueous medium radical ions (ROS) like OH˙, $O_2^{.-}$ and H_2O_2 which are very aggressively strong oxidizing species . These radicals strike the DETU molecule and oxidized it into aminoiminoalkane sulphinic acid Equation(3) [Furukh, M..A.. ,2012] . The sulphinic acid reduces the dye molecule and sulphates are formed during this steps of the reaction Equation 4 consequently TB transformed into very light amber colored leuco form of the dye ,which is the reduced form of the dye .The oxygen anion radical in the presence of acidic medium ,attack the dye skeleton and detach the chromophores ,this process causes the decolorization of the dye molecules Equation (5) .

PROBABLE MECHANISM OF OF TOLUIDINE BLUE DECOLORIZATION

Equation (5)
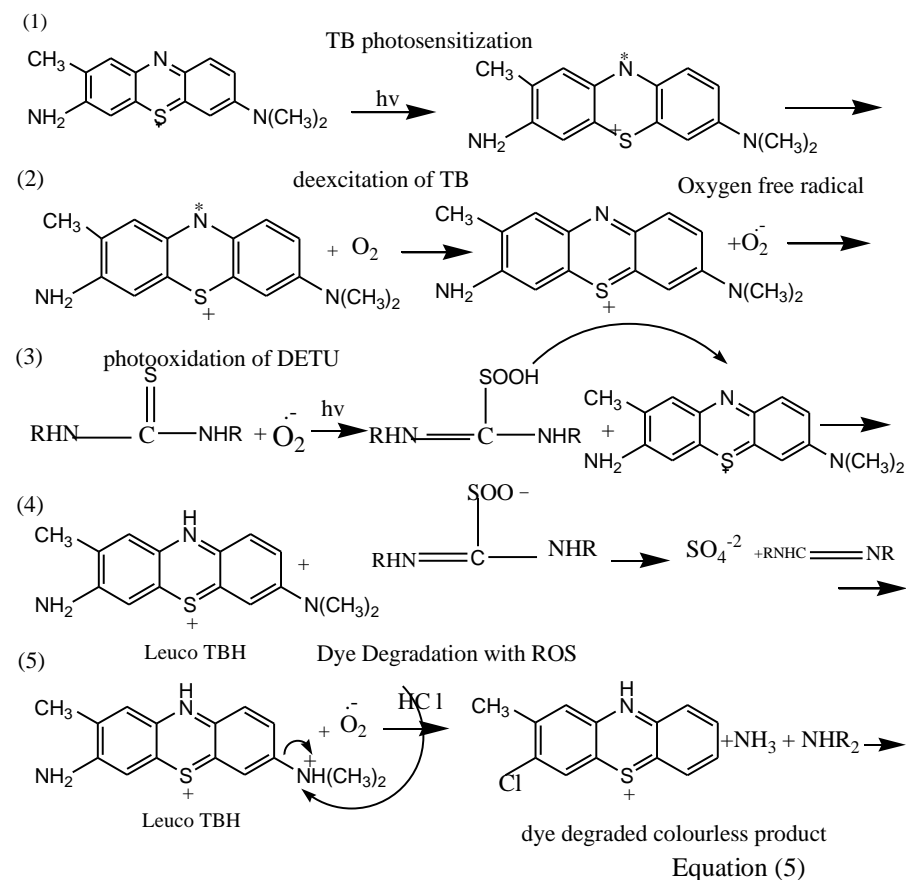
Controlling Factors in the decolorization process

There are several controlling conditional parameters that govern this process

(1)Electron and energy transfer in the excited state state controls the efficiency of photo induced process ,it influence the visible spectral behavior of the dissolved dye molecule .

(2) Solvent Polarity and its hydrogen bonding capacities . the dye deactivates according to the nature of solvent and its dielectric constant . Metachromacy is the characteristic features of TB in aqueous medium .The dye aggregation happens in aqueous medium and results in the formation of dimerization of the dye molecules .The resulting polymerization of the dye molecule reduces the formation of free radicals by dye stimulation in the presence of light and the decolorization phenomena is inhibited .

(3)Temperature of the reaction system also effect the process as the life time of the dye excitation depends on temperature due to the intermolecular charge transfer.

(4) pH of the medium has an influence in this photocatalysis as the rapid decay of the dye is observed in acidic medium ,due to the formation of dicationic dye from the reaction of monocationic dye molecule in the excited state with DETU in the presence of hydrogen ions .This indicates that in the reaction of dye in excited state, the additional protons are located on nitrogen atom of the ring and not on terminal amine groups .

(5) Impact of additive ions in the dye decolorization process is prominent .The aggregation scenario has found to be effected by the presence of salts. The aggregation of the dye molecules in aqueous system is reduced by the added charge groups and electrolytes like BF_4 , KI , NaCl , SO_4^{2-}, PO_4^{2-} etc in the dye atmosphere ,which increases the electrostatic repulsions , attraction processes, increase the electropilic nature of the dye ,**Table 1**.
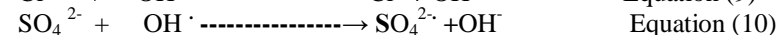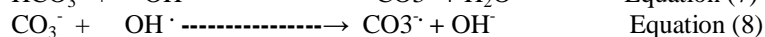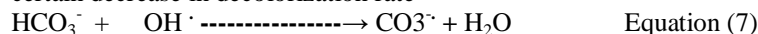
(i)Effect of Cations in the dye decolorization

The $Na^+$and K^+ metal ions have a moderate influence on the reduction of dye , The mechanism of dye reduction in the presence of these cations ,could be explained on the basis of their chemical reactions in the reaction mixture. Most likely, Na^+ and K^+ ions get reduced by OH^* radicals and form the soluble hydroxides in aqueous medium [Azmat,R. ,2011].The above reactions have slightly appreciably decoloration with Na^+ and K^+ as compared with the other cations (heavier cations) which may be attributed to the formation of alkali hydroxide. This supports the dye reduction related to the production of more hydroxyl ions. Similarly, the presence of $Ca^{2+}$and Mg^{2+} showed decrease in percent decolorization and also precipitates which indicates that these ions in dye reduction trap the OH^* radical later form the insoluble hydroxides, due to which less decolorization of dye was observed [Azmat,R., 2011].The behavior of Co^{2+} ions was a different story, as red colored layers formation in the case of Co^{2+} were observed which is due to the comlpexation of the Co (II) with DETU in the presence of Chloride ions ,consequently reduced the dye decolorization process by the adherence of dye on metal surface , provide (Co----N) active sites and censor the formation of singlet oxygen ,DETU behaves as organic ligand which exhibits electron donor Sulpher sites . These ligands surround the Co(II) ions in tetrahedral structural geometry .Chromium ions have also seen to follow same trend [Askalani , P. and Baily, R.A.1969].

   Co^{+2} + 2 DETU +2 Cl^- --------→ Co (DETU)$_2$ Cl$_2$ complexes   Equation (6)
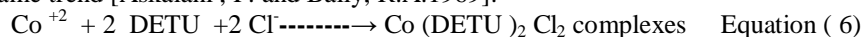
 Mg^{2+} and Ca^{2+} metal ions showed negligible contribution to the decolorization.

(ii)Effect of Anions in the dye decolorization

 These ions being rich of electrons attract the hydroxyl free radicals Equation (7,8,9 ,10) [Patri ,B.G. and Watts ,R.J. 2011], in the presence of these ions $OH^.$ radicals are trapped according to the below reactions which cause a certain decrease in decolorization rate

HCO_3^- + $OH^.$ ----------------→ $CO3^-$ + H_2O Equation (7)

CO_3^- + $OH^.$ ----------------→ $CO3^-$ + OH^- Equation (8)

 Cl^- + $OH^.$ ----------------→ Cl^- + OH^- Equation (9)

SO_4^{2-} + $OH^.$ ----------------→ SO_4^{2-} +OH^- Equation (10)

Study of SO_4^{2-} and PO_4^{3-} led to the concept that metachromacy of the dyes could be interpreted as the electroadsorption of the dye cation to ionogenic sites of the negative ions Equation (11) [Bergeron ,J.A. and Singer , M.1958] .Dye can have a resonance shifting of positive charge , SO_4^{2-} and PO_4^{3-} ions can push away the water molecules , the interactions occur at auxochromic dye groups ,consequently the dye aggregations decrease which leads to decolorization of dye .Therefore these anions facilitate the dye bleaching [Bergeron ,J.A. and Singer , M. 1958].

Equation (11)
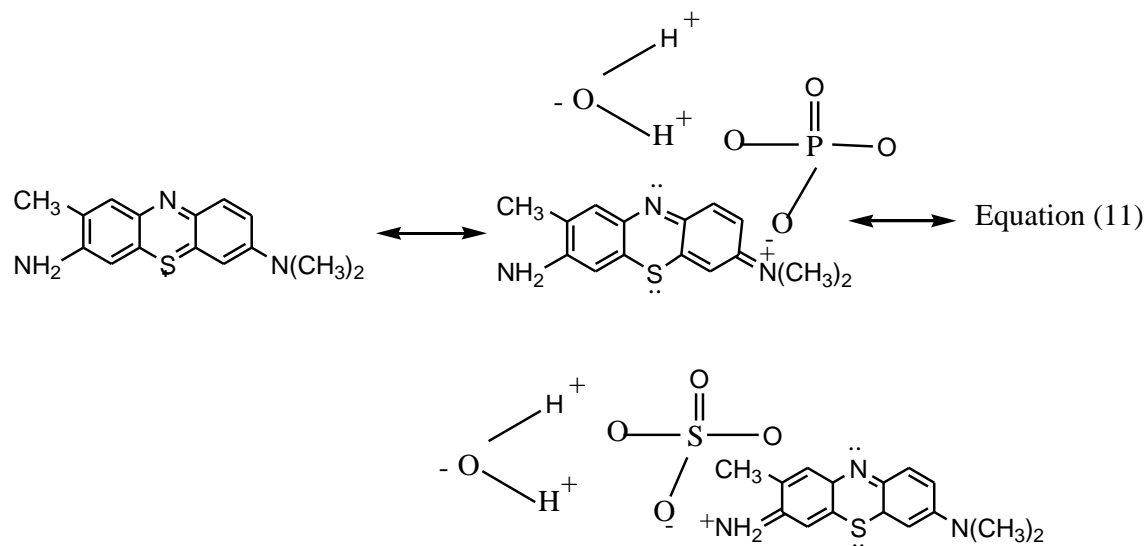
It showed that the dye decolorization took place variably in the presence of these anions without a shift in the wavelength, confirming the formation of leuco dye (TBH) . A comparison of the literature supports the mechanism of the reduction in the presence of added anions [Patri ,B.G. and Watts ,R.J. 2011]. The CO_3^{2-} and HCO_3^- have also observed to increase the reduction rate as these get excited according to the reactions Equation (7,8) [Patri ,B.G. and Watts ,R.J. 2011] and enter in a reduction reaction 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 , as indicated in equations(7, 8 ,9)

The catalytic role of I^- ion was exceptional and the reaction took place so fast (micro seconds)that the rate of the reaction could not be monitored and instant decolorizating took place. Iodide ion plays the role of transferring electrons in the reduction process in acidic medium .

(6)Effect of ionic Strength variation on the bleaching of the dye:

Ionic strength of the reaction mixture was adjusted with NaCl salt solutions from 0.001-0 .6 mol.L^{-1} concentraion variations Table 2. Results show that higher ionic strength had an elevation impact on dye degradation.ie ,higher concentration of NaCl enhanced the dye degradation process .However in previous studies [Furukh, M.A.,2012] it was found that Cl^- ion has retarding effect on hydroxyl radical and less reactive chlorine $Cl^{.-}$ radical is generated , which decrease the rate of decolorization reaction. Na^+ ions however have shown to have facilitated the decolorization as more electrostatic interactions would minimize the intermolecular hydrogen bonds during the aggregation of dye molecules in aqueous medium.

Rate Law of the decolorization reaction

$-d[TB^+]/dt = k [H^+] [TB^+]^0 [DETU]$

Figures 1,3 ,4 confirm the Rate Law

Rate constant of the reaction k $=1.0x10^{-1}$ $mol^{-1}.dm^{-3}.s^{-1}$

Figure 2 confirms the value of the rate constant of the acidic decolorization of TB with DETU , the moderate value of the rate constant show clearly that the reaction is fast in acidic medium [Qadri,M. , 2014]

TABLE 1 :IMPACT OF VARIOUS IONS ON THE RATE OF DECOLORIZATION REACTION OF TB WITH DETU IN

ACIDIC MEDIUM

Ions	Ions concentration mol.L^{-1}	Ratex10^4 TB mol$L^{-1}s^{-1}$	K_{obs}x10^4 s^{-1} TB	%decoration TB
Na^+	0.01	26.0	17.0	98.85
K^+	0.01	38.0	43.0	99.4
Mg^{2+}	0.01	-	-	-
Co^{+2}	0.01	-	-	-
Ca^{2+}	0.001	-	-	-
CO_3^{2-}	0.001	2.0	2.5	19.4
HCO_3^-	0.001	2.0	2.0	20.0
Cl^-	0.01	20.0	26.0	98.0
SO_4^{2-}	0.01	2.0	9.0	10.0
NO_3^-	0.01	39.0	2.0	98.20
PO_4^{-3}	0.001	32.11	30.0	47.0
CH_3COO^-	0.01	1.0	2.0	10.0

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

[HCl] =1.0×10^{-2} mol·dm^{-3},

TABLE2:EFFECT OF VARIATION OF IONIC STRENGTH OF NaCl IN THE PRESENCE OF TB DYE AND DETU

[TB]= $2x10^{-5}$ mol.dm^{-3}, [DETU] = 0.01 mol.dm^{-3}, Temperature = 298K

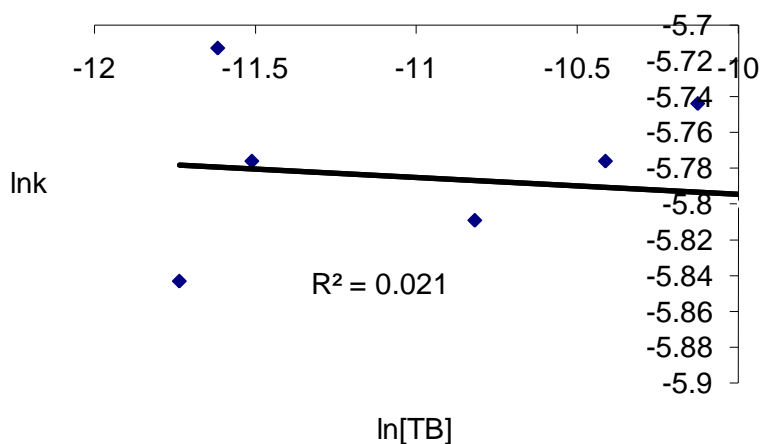| S.No	[NaCl] (mol.dm^{-3})	Ionic Strength	dx/dtx10^4 (mol.$dm^{-3}s^{-1}$)	K_{obs}x10^4 (s^{-1})	% Decoloration
01	0.001	0.011	21.0	30.0	70.52
02	0.01	0.02	21.05	30.11	85.420
03	0.1	0.11	21.06	34.2	86.740
04	0.2	0.21	21.1	34.2	86.911
05	0.4	0.41	22.0	36.0	88.435
06	0.6	0.61	22.7	36.1	88.411

Figure 1 : The plot of ln k_{sp} vs ln [TB] with DETU
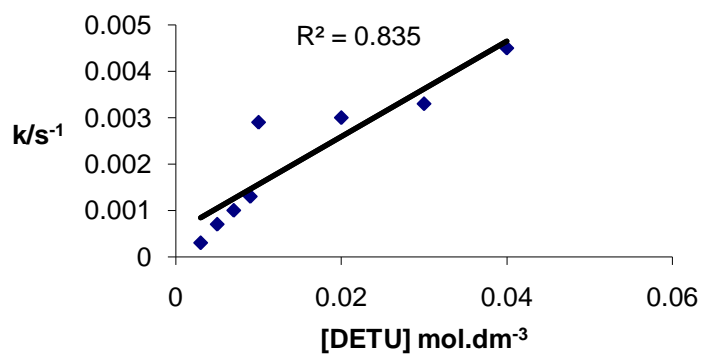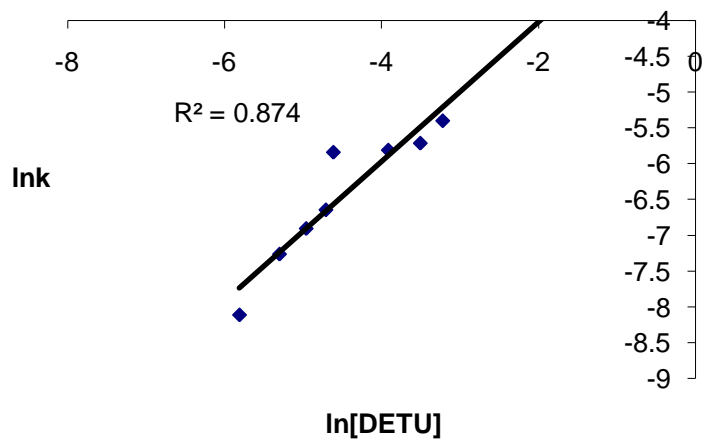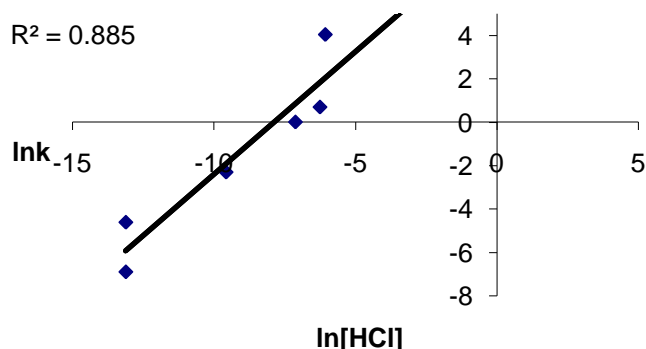

Figure2:A plot of k_{obs} vs [DETU] in acidic medium

Figure 3:The plot of ln k vs ln [DETU] in acidic medium

Figure 4**:**The plot of ln k vs ln H^+ concentration for reduction of TB with DETU

CONCLUSIONS

All cations and anions showed some decrease in percent decoloration, except in some exceptional cases. In presence of K^+, more percent decoloration was observed as compared to any other cations used. I^- ion showed cent percent decloration as compared to any other ion due to the reaction between H^+ and I^-. Dye reduction when monitored in presence of I^- it was found that reaction proceeds tremendously rapidly as compared to any other ion used in the reaction mixture which may be related with the iodine-Hydrgen reaction in acidic medium . These studies resulted in a general pattern of oxidation of thiourea that goes through successive oxygen transfer to the forms, sulfinic and sulfonic acids and, finally, sulfate ion. Same results were observed in the present investigation where oxygen gained by sulphur group of diethylthiorea due to which reaction was proceeded in a micro second and rate was not determined. This may be attributed with the autocatalytic reaction, of the both H+ and I− in the reaction between dye and DETU in an acidic medium. The presence of metal ions may result in polymerization or aggregation or complex formation or adsorption of the dye on the metal surface. This investigation on the whole involves the effect of different cations, anions on dye reduction process to develop a new oxidative technique with diethylthiourea.

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