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Influence of Temperature and pH on the Stability and Colorimetric Measurement of Textile Dyes

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Abstract: Most of the textile dye removal techniques operate within temperature and pH ranges of 20-60 °C and 2-12, respectively. Both the pH and temperature have been reported to have significant effects on the efficiencies of the dye removal techniques. In this study, the effects of pH and temperature on the stability and color measurement (absorbance) of the textile dye remazol brilliant at different dye concentrations were investigated. Changing the pH from 1 to 13 and /or the temperature from 15 to 55 °C did not have any significant effect on the absorbance of the dye remazol brilliant blue at two concentrations (65 and 300 mg L^{-1}). The results showed the stability of the remazol brilliant blue in water under wide ranges of temperature and pH. However, the neutral compound $C_{22}H_{16}N_2Na_2O_{11}S_3$ is transformed to an ionic form with either negative charge $[C_{22}H_{15}N_2Na_2O_{11}S_3]^-$ under alkaline condition or positive charge $[C_{22}H_{15}N_2Na_2O_{11}S_3]^+$ under acidic condition. The formation of ionic form of the dye will facilitate its removal by various removal techniques. The results showed that a standard curve can be constructed at ambient conditions (a pH of 7 and a temperature of 25 °C) and used to determine the concentration of the dye using the colorimetric method.

Key words: Remazol brilliant blue, reactive dye, pH, temperature, colourimetric measurement, absorbance, stability

INTRODUCTION

Textile processing operations are considered an important part of the industrial sector in both developing and undeveloped countries. However, the textile industry is one of the most complex manufacturing industries. Various textile chemicals such as wetting agents, dyes, surfactants, fixing agents, softeners and other additives are used in wet processes (such as bleaching, dyeing and finishing) and as a result large volumes of highly polluted wastewater are produced[1-3]. The wastewater generated from the textile processing industries contains high amounts of suspended solids, dissolved solids, un-reacted dyestuffs (colour) and other auxiliary chemicals that are used in the various stages of dyeing and other processes[4]. Wastewater effluents from textile plants cause major water pollutantion problems. Strong colour of the textile wastewater is the most serious problem of the textile waste effluent. It has been estimated that more than 700,000 tonnes of dyes are used annually[5] of which over 15-20 % are left in the effluent during the dyeing process[6]. The presence of even small amount of dye in water (10–20 mg L^{-1}) is highly visible, aesthetically undesirable and affects the water transparency and in turn the photosynthetic activity in water bodies[7,8]. In addition to colouring of the receiving water, dyes in the water bodies such as rivers and lakes also undergo chemical and biological changes that consume dissolved oxygen resulting in fish kills and the distruction of other aquatic organisms. Some dyes possess toxicity that is hazardous to aquatic life and posses serious health problems to human[9]. Textile dyeing effluents are also known to cause extreme variations of pH, dissolved oxygen (DO), temperature, chemical oxygen demand (COD) and dissolved salts of the receiving water bodies[10-12].

Reactive dyes are the most common dyes used in the textile industry because of their bright colours, excellent colourfastness and ease of application[13,14]. Reactive dyes are the principal dyes used in the cotton industry which makes up 50% of the world's fiber consumption[15]. They exhibit a wide range of different chemical structures, primarily based on substituted

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aromatic and heterocyclic groups. A large number of reactive dyes are azo compounds that are linked by an azo group[16]. Many reactive dyes are toxic to some organisms and may cause direct destruction of aquatic life due to the presence of aromatic and metal chlorides[8]. It has been reported that some azo dyes are able to produce carcinogenic aromatic amines in the process of reductive degradation[17,18]. They are particularly challenging to textile wastewater managers because of their bright colours, high degree of colourfastness, resistance to aerobic biodegradation and the large amount of dye that is exhausted from the dye baths[15, 19]. Their high solubility, synthetic origin and complex aromatic molecular structure make their removal a very difficult task[20,21].

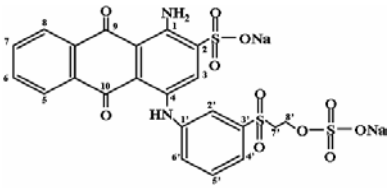
Removal of hazardous dyes from textile effluent is one of the important factors affecting the economic and environmental sustainability of the industry[21]. Traditional methods for treating textile dye wastewaters consist of various chemical, physical and biological processes. These include: coagulation and precipitation[22], adsorption[23] and aerobic and anaerobic biological processes[24,25]. More advanced treatment processes include: electro coagulation[26], ultrasonic decomposition[27], advanced chemical oxidation[28], electrochemical oxidation[29,30], photooxidation[29], nanofiltration,[31,32], colloidal gas aphrons[33], pre-dispersed solvent extraction[34], ozonation[35-38], supported liquid membrane[9,13,39] and liquid- liquid extraction[9,40]. Traditionally, the colourimetric measurement technique has been used to evaluate the effectiveness of these various dye removal methods. In this technique, the absorbance of influent and effluent are measured at the appropriate wave length using spectrophotometer and the removal efficiency is determined. A standard calibration curve is usually determined at ambient conditions. However, for most of the dye removal methods reported in literature, the pH and temperature of the effluent (Table 1) vary within the ranges of 2-12 and 20-60 °C, respectively. Although several of these authors emphasized the effects of temperature and pH on the effectiveness of these dye removal methods, no information is available in the literature on the effect of temperature and pH on the stability of the dyes in pure solutions. Therefore, there is a need to assess the impacts of pH and temperature on the colourimetric measurements of dyes in textile wastewater.

The aim of this study was to evaluate the impact of test conditions on the accuracy of colourimetric measurement of textile dye remazol brilliant blue.

Table 1: Ranges of pH and temperature reported for various dye removal techniques

Method of removal	pH	Temp.	References
Adsorption	2-10	25-30	Sanghi *et al*. [23]
Coagulation and precipitation	4-9	20-25	Liu *et al*. [22]
Elecro-coagulation	4-10	20-25	Alinsafi *et al*. [26]
Nonfiltration	10.5	20-25	Chakraborty *et al*. [41]
Aerobic and anaerobic	6-8	35-40	Beydilli *et al*. [24]
Advanced chemical oxidation	3-11	60	Arslan *et al*. [28]
Electrochemical oxidation	5-12	20-25	Lopez and Gutierrez [29]
Ozonation and electrochemical oxidation	7	35	Ehud *et al*. [42]
Supported liquid membrane	11	27	Muthuraman and Palanivelu [9]

Table 2: R 8001 Remazol brilliant blue R specification[44]

Synonym	Reactive Blue 19
Molecular Formula	$C_{22}H_{16}N_2Na_2O_{11}S_3$
Molecular Weight	626.54
CAS Number	2580-78-1
Colour Index Number	61200
MDL number	MFCD00001215
Molecular-structure	

The specific objectives were: (a) to evaluate the effect of pH and temperature on the absorbance, (b) to determine the mechanisms by which the pH and temperature influence the absorbance and (c) to develop a standard dye measurement procedure.

MATERIALS AND METHODS

Reagents: The chemicals used in this study included sodium hydroxide (NaOH), sulphuric acid (H_2SO_4) and remazol Brilliant blue dye (1-amino-4-[4-(1-sulfonyl-ethyl-2- sulfoxy)]-2-(9, 10-anthraquinone)-sulfonic acid; disodium salt). The 98.6 % NaOH (Ca # S 318-3) and 98 % H_2SO_4 (Ca #A 300 212) were obtained from a Fisher scientific (Fisher scientific, Montreal, Quebec, Canada). The remazol brilliant blue (dye content ~ 50%) was obtained from Sigma (R8001, Ca # 22-324-7, Sigma, Oakville, Ontario, Canada). The molecular structure of the dye is shown in Table 2.

Preparation of stock solutions: The remazol dye solution prepared in distilled deionized water at room temperature has a pH of 7. In order to prepare dye solutions with various pHs (1, 4, 10 and 13), the following equations were used to calculate the amount of NaOH or H_2SO_4 to be added to the distilled deionized water[43] :

Table 3: The required amounts of NaOH and H_2SO_4

pH	Ions	Calculated amount		Required Amount [(a)]	
		(mol/L)	(g/L)	(g/L)	
1	$[H3O^+]$	$1x10^{-1}$	0.00981 H_2SO_4	10.01	H_2SO_4
4	$[H3O^+]$	$1x10^{-4}$	0.004 H_2SO_4	0.01	H_2SO_4
10	$[OH^-]$	$1x10^{-4}$	4.0 NaOH	0.0041	NaOH
13	$[OH^-]$	$1x10^{-1}$	9.81 NaOH	4.06	NaOH

[(a)] based on 98 % H_2SO_4 and 98.6 % NaOH
H_2SO_4 molecular weight = 98.1 g mol^{-1}
NaOH molecular weight = 40.0 g mol^{-1}

$$pH = - \log [H_3O^+] \text{ for pH 1 and 4} \quad (1)$$

$$pH = - \log \frac{K_w}{[OH^-]} \text{ for pH 10 and 13} \quad (2)$$

Where:
$[H_3O^+]$ = the concentration of hydronium ions (mol/L)
$[OH^-]$ = the concentration hydroxide ions (mol/L)
$K_w = 1.0 \times 10^{-14}$.

The required amount of NaOH and H_2SO_4 are shown in Table 3. For the solution with pH value of 13, 4.06 g of electrolytic pellets of 98.6 % NaOH were placed in a 1000 mL volumetric flask and distilled deionized water was added to bring the solution to 1000 mL. The solution was mixed using a magnetic stirrer (120 MR, Fisher scientific, Ontario, Canada) to insure complete dissolution of the NaOH. From the above solution, 1 mL was transferred into a 1000 mL volumetric flask and distilled deionized water was added to bring the solution to 1000 mL. This solution contained 0.0041 g NaOH per litter and had pH of 10.

For the solution with pH value of 1, 5.44 mL of (10.01 g) of 98% H_2SO_4 were placed into a 1000 mL volumetric flask containing 500 mL distilled deionized water. Then, distilled deionized water was added to bring the solution to 1000 mL. For the solution with pH value of 4, 1 mL from the above solution was placed into a 1000 mL volumetric flask and distilled deionized water was added to bring the solution to 1000 mL. This solution contained 0.01 g L^{-1} H_2SO_4

The pH of the prepared solutions was measured using a pH meter (Accumet ® pH meter, 805 MP, Fisher scientific, Montreal, Quebec, Canada).

Experimental protocol: The effects of two factors (pH and temperature) with 5 levels each on the absorbance measurement of remazol brilliant blue were investigated. The five levels of pH were 1, 4,7,10 and 13 and the five levels of temperature were 15, 25, 35, 45 and 55 °C. The experiments were designed as 2^5 factorials with 3 replicates. This resulted in 75 treatments.

A volume of 500 mL of each of the five solutions with different pH values (pH = 1,4,7,10 and 13) were used. Three replicates were prepared for each pH solution. A total of 15 flasks were used. A water path (280, Precision Scientific, Winchester, VA, USA) was used to maintain a constant temperature. The water path temperature was adjusted to 15 °C. When the temperature reached, the desired value, the flasks were placed in the water path until the temperature of the solution reached the desired temperature (one hour was needed). An amount of 0.03 g of the dye was added to each flask. The flasks were kept in the water bath for additional 15 min. Samples were taking from each flask to measure the absorbance of the solution using spectrophotometer (Spectronic 601, Fisher scientific, Montreal, Quebec, Canada) at 475 nm. The same procedure was repeated for the other temperatures (25,35,45,55°C).

RESULTS AND DISCUSSION

Effects of pH and temperature on the absorbance of the dye: Figures 1 and 2 show the color measurements (absorbance) of remazol brilliant blue at different pH levels, temperatures and dye concentrations. Analysis of variance was preformed on the absorbance data using the SAS system (5 th ed, SAS, lastitrote inc, cery, North Carolina) as shown in Table 4. Duncan's multiple range test was also preformed on the data in order to test the differences among the levels of each factor as shown in Table 5.

The results showed that changing the pH from 1 to 13 and / or increasing the temperature from 15 to 55 °C did not seem to cause any significant changes in the absorbance of both dye concentrations (65 and 300 mg L^{-1}). There are no reports found in the literature on the effects of temperature and pH on the absorbance of dyes in pure solutions, except for two reports one on the thermal stability of cationic dyes (which are widely used in dyeing of acrylic fibers) and the other on the effect of pH on the fluorescent intensity of organic fluorescent dyes (used as traces to track spray deposit and drift during pesticide application).

Ma and sun[45] studied the thermal stability of six cationic dyes containing anthraquinone and quaternary ammonium salt structures (3 mono-substituted and 3 bi-substituted) using differential scanning colorimetric (DSC) and thermo gravimetric analysis (TGA) techniques. The dye samples were heated at 10°C min^{-1} in a nitrogen atmosphere. The DSC and TGA results showed that the dyes were stable below 190 °C but started to decompose between 205 and 400 °C resulting

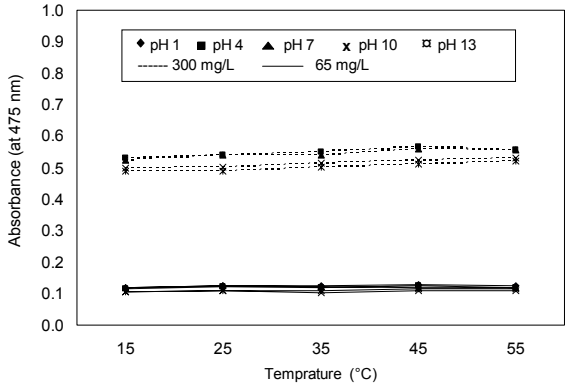


Fig. 1: Effect of temperature on the color measurement of remazol brilliant blue

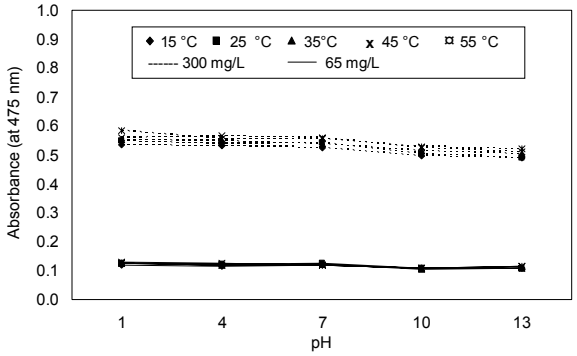


Fig. 2: Effect of the pH on the color measurement of remazol brilliant blue

in total weight losses of 20 %. No further weight losses were detected above 400°C. Since anthraquinone structures are thermally stable[46], the decomposition of the dyes was caused by their quaternary ammonium structure (QAS). The thermal decomposition of QAS is due to a de-alkylation reaction, a process regarded as the reverse of quaternization of tertiary amines[47,48].

Zhu *et al*.[49] studied the fluorescent intensity of several dyes (brilliant susfaflavine, fluorescein, pyranine, tinopal and eosin) commonly used as tracers for quantitative assessment of field spraying of pesticides under different pH conditions (6.9-10.4). The fluorescence of pyranine was the most sensitive to the solution pH, flowed by fluorescein and tinopal, while brilliant susfaflavine and eosin had a nearly constant fluorescent intensity over the pH range of 6.9-10.4. The fluorescence increased by 1.3, 1.25 and 3.0 times as the pH increased from 6.9 to 8.4 for fluorescein, tinopal and pyranine, respectively. No increases were observed above pH of 8.4.

There is also limited information in the literature on the effects of pH and temperature on the stability of

Table 4: Analysis of variance

Source	DF	SS	MS	P
Total	149	6.53795		
Model	49	6.53788	0.13343	
C	1	6.48794	6.48794	0.0001
P	4	0.02770	0.00692	0.1311
T	4	0.00771	0.00193	0.3271
C*P	4	0.00811	0.00203	0.0001
C*T	4	0.00478	0.00120	0.0001
P*T	16	0.00098	0.00006	0.2191
C*P*T	16	0.00066	0.00004	0.3761
Error	100	0.00007	0.00000	

R^2 = 0.99, CV = 64.5 %, C= concentration, P= pH, T= temperature

Table 5: Differences among the levels of dye concentration, pH and temperature

Parameter	Level	No. of Obs.	Means	Dancan Grouping
pH	13	30	0.3066	A
	10	30	0.3106	A
	7	30	0.3327	A
	4	30	0.3342	A
	1	30	0.3403	A
Temperature (°C)	15	30	0.3146	A
	25	30	0.3200	A
	35	30	0.3242	A
	45	30	0.3317	A
	55	30	0.3339	A
Dye concentration	300	75	0.5328	A
(mg/L)	65	75	0.1171	B

Means with the same letter are not significantly different from each other at 95% confidence level.

natural pigments. Paik *et al*.[50] reported on the stability of blue pigments obtained from the fruit of *Gardenia jasminoides* under pH and temperature ranges of 5-9 and 60-90 °C, respectively. Several authors[51-53] reported on the stability of natural pigments produced by the *Monascus* fungi species at wide ranges of temperatures and pH levels.

Effects of pH and temperature on the structure of the dye: The molecular formula of remazol brilliant blue R dye [1-amino-4-[4-(1-sulfonyl-ethyl-2-sulfoxy)]-2-(9,10- anthraquinone)-sulfonic acid; disodium salt] is $C_{22}H_{16}N_2Na_2O_{11}S_3$. Remazol brilliant blue R is an aromatic compound that contains four benzene rings (three of which make anthraquinone) and amino, sulfonyl, ethyl, sulfoxy and sulfonic acid disodium salt groups as shown in Fig. 3. Anthraquinone is an aromatic organic compound, containing 3 benzene rings with two oxygen atoms double bonded to carbons 9 and 10. The amino groups are attached to carbons 1 and 4, sulfonyl and ethyl groups are attached to carbon 3′ and sulfonic acid disodium salts are attached to carbons 2 and 8′. In amino group, one atom of nitrogen is attached by covalent bonds two atoms of hydrogen, leaving a lone valence electron on the nitrogen which is

available for bonding to another atom. Sulfonyl group is an organic radical or functional group obtained from a sulfonic acid by the removal of the hydroxyl group. Sulfonyl groups can be written as having the general formula R-S(=O)$_2$-R', where there are two double bonds between the sulfur and oxygen. Ethyl group is an alkyl functional group derived from ethane (C_2H_6). Sulfonic acid is a hypothetical acid having the formula H-S(=O)$_2$-OH. This compound is a tautomer of sulfurous acid HO-S(=O)-OH, but less stable.

Under acidic condition (low pH), hydrogen ions (H^+) reacts with the amino group (NH_2) at carbon # 1 in the anthraquinone third ring of the dye structure to from NH_3. This results in the formation of the ionic form of the dye $[C_{22}H_{17}N_2Na_2O_{11}S_3]^+$ which has positive charge on the NH_3 group. This new ion is less stable. Therefore,two hydrogen atom from NH_3^+ are released in the form of hydrogen gas (H_2), resulting in the transfer of the positive charge to carbon # 4 as shown in Fig. 4[30].

$$C_{22}H_{16}N_2Na_2O_{11}S_3 + H^+ \rightarrow [C_{22}H_{17}N_2Na_2O_{11}S_3]^+ \quad (3)$$

$$[C_{22}H_{17}N_2Na_2O_{11}S_3]^+ \rightarrow [C_{22}H_{15}N_2Na_2O_{11}S_3]^+ + H_2\,(g) \quad (4)$$

Under alkali condition (high pH), the dye loses one hydrogen ion (H^+) from carbon # 7′ which reacts with a hydroxyl group (OH^-) from the alkaline media to from water (H_2O). This results in the transformation of the neutral compound to an ionic form having a negative charge at carbon # 7′ $[C_{22}H_{15}N_2Na_2O_{11}S_3]^-$. Electrons are then transferred from the adjacent sulfonyl group to carbon # 7′ resulting in a structure that has a sulfur carbon double bond (S=C) and a negative charge on the oxygen atom of the sulfonyl group as shown in Fig. 5[54].

$$C_{22}H_{16}N_2Na_2O_{11}S_3 + OH^- \rightarrow [C_{22}H_{15}N_2Na_2O_{11}S_3]^- + H_2O \quad (5)$$

The transformation of the dye from a neutral compound to an ionic form facilitates its removal from solutions by several removal techniques. However, the effectiveness of these techniques is influenced by the temperature and pH of the medium as reported by several authors.

Liversidge *et al*.[55] examined the use of linseed oil cake as an adsorbent for selected dyes. The enthalpy of adsorption was found to be endothermic and the adsorption capacity of the linseed cake for the dye decreased with increasing temperature.

Alok *et al*.[56] carried out an adsorption experiment using different concentrations of malachite green (MG) in the range of 1×10^{-5} to 1×10^{-4} M at a fixed pH of 5

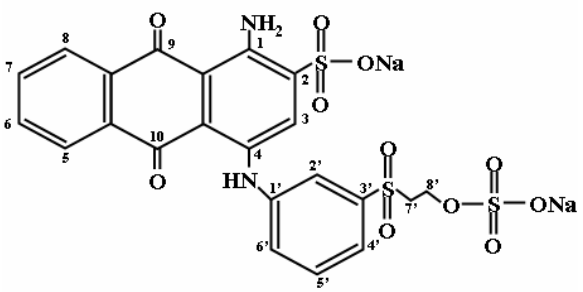


Fig. 3: The structure of remazol brilliant blue R dye

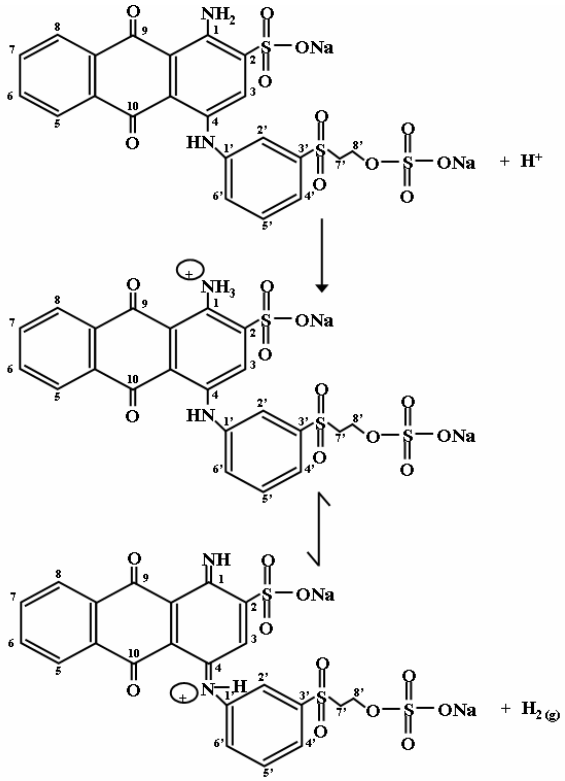


Fig. 4: Proposed mechanism for the effect of acidity (low pH) on the structure of remazol blue dye[30]

and different temperatures (30, 40 and 50 °C). The adsorption increased with increased in temperature, which indicated that the ongoing adsorption process is endothermic in nature.

Saquib and Muneer[57] evaluated a semiconductor mediated photocatalysed degradation of the dye remazol brilliant blue R under sunlight and an artificial light source, employing Degussa P25 and UV100 as photocataysts under pH values in the range of 3 - 11. The pH of the solution was adjusted before irradiation and was not maintained throughout the reaction. A decrease in the pH of the reaction mixture was observed

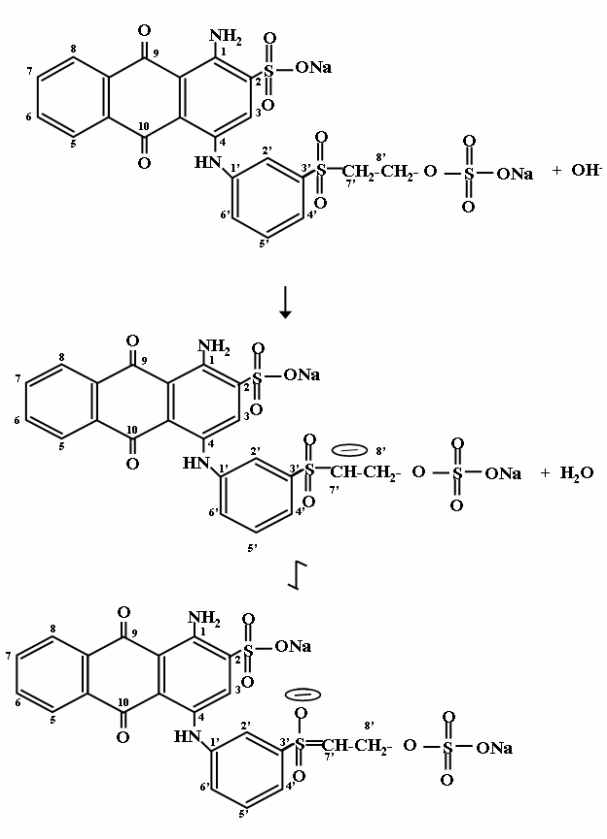


Fig. 5: Proposed mechanism for the effect of acidity (high pH) on the structure of remazol blue dye[54]

at the end of illumination. It was observed that under sunlight, the highest efficiency for the degradation of the dye was observed at pH 3, which slowly decreases with the increase in pH of the reaction mixture. On the other hand, when the reaction was carried out under UV light, higher efficiency was observed at pH 9, whereas the efficiency for the degradation of the dye at pH 3,5.2 and 11 was similar.

Patricia *et al*.[30] evaluated different electrochemical methods for the oxidation and degradation of reactive blue 4 in aqueous solution. The oxidation on glassy carbon electrode and reticulated vitreous carbon electrode occurred in only one step at $2.0 < pH < 12$ involving a two-electron transfer to the amine group leading to the amide derivative. Dye solution was not decolorized effectively in this electrolysis process. Nevertheless, the oxidation of this dye on $Ti/SnO_2/SbOx$ (3% mol)/RuO_2 (1% mol) electrode showed 100% of decolorization and 60% of total organic carbon removal in Na_2SO_4 0.2 M at pH 2.2 and potential of +2.4 V.

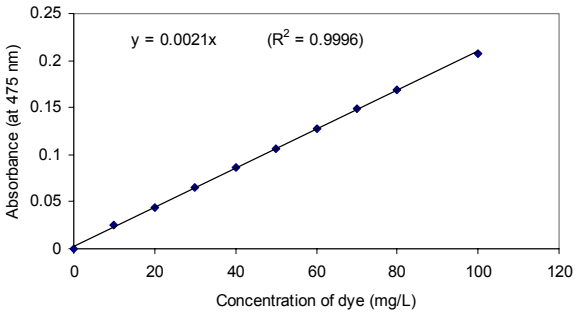


Fig. 6: Standard curve (pH = 7, temperature 25˚C)

Muthuraman and Palanivelu[9] conducted a laboratory study on supported liquid membrane (SLM) system for removal and recovery of textile dye from the aqueous solution using renewable, non-toxic, natural vegetable oils. The study was carried out at different pH levels (7-14). Dye transport rate increases with increasing the pH and maximum extraction (as well as maximum transport) was achieved at a pH of 11.0. However, at a pH value higher than 12, the dye transport and extract efficiency diminished.

Alok *et al*.[56] studied the Removal and recovery of malachite green (MG) from wastewater using an agricultural waste material (de-oiled soya). The process of adsorption of MG on de-oiled soya was highly pH dependent and a maximum uptake of the dye took place at a pH of 5. Beyond this pH, adsorbent attains the same maximum value.

Daneshvar *et al*.[58] investigated the effectiveness of biological decolorization of synthetic dye solution containing malachite green. Batch experiments were carried out at different initial dye concentrations (2.5–12.5 ppm), temperatures (5–35 ◦C) and pH values (2.5–10) using various types of algae (*Cosmarium*, *Chlorella*, *Chlamydomonas* and *Euglena*). The decolorization was dependent on the dye concentration, pH, type of algae and temperature, but the pH had the largest effect on dye removal. The optimal dye removal was achieved at a temperature of 25 °C, a pH of 10 and a dye concentration of 5 ppm using *Chlorella*.

Antonio *et al*.[59] used synthesized silica–aminopropyl (Sil–NH_2) to quantify the roles of temperature and pH in the adsorptions of blue and red remazol dyes in aqueous medium. The method was carried out at temperatures in the range of 25 -50 ˚C and pH values in the range of 3.0 - 6.0. The effect of pH on the absorbance of the dye (mg dye/g Si-NH_2)was more pronounced than the effect of temperature. The adsorption Gibbs free energies (ΔG) were influenced by

pH, dye concentration and temperature changes did not affect the ΔG values significantly.

Lopez and Gutierrez[29] conducted a study to optimize the electrochemical decolorization of textile effluents containing reactive dyes. The electrochemical decolorization was carried out at a pH levels in range of 5-12 and temperatures in the range of 20-25 °C. 100% of decoloization was reached at a pH of 5 in 1 min whereas at a pH of 9, a decoloization of only 12% was acheived.

Proposed procedure for colorimetric measurement of remazol brilliant blue: The results indicated that both the pH and temperature have no effects on the absorbance of the dye, thus affirming its stability under alkaline and acidic conditions within the temperature range studied (15-55 °C). Therefore, in order to determine the concentration of the remazol brilliant blue dye in a solution using the colorimetric techniques, a standard curve can be developed from the standard solution of remazol brilliant blue dye which can be prepared by dissolving 0.1 g of the dye in 1000 mL of distilled deionized water (pH= 7) at a temperature of 25 ˚C. Then, a set of 9 solutions with remazol blue dye concentrations of 10, 20, 30, 40, 50, 60, 70, 80 and 100 mg L^{-1} should be prepared. Finally, the absorbances of the prepared solutions can be measured (in triplicates) using spectrophotometer at 475 nm. The absorbance measurments are then plotted against the known remazol blue dye concentrations (mg/L) as shown in Fig. 4. A blank sample should be used to zero the spectrophotometer.

CONCLUSION

The effects of pH and temperature on the stability and color measurements (absorbance) of the dye remazol brilliant at different dye concentrations were investigated. Changing the pH from 1 to 13 and /or the temperature from 15 to 55 °C did not have any significant effect on the absorbance at both concentrations of remazol brilliant blue (65 and 300 mg L^{-1}). However, under acidic or alkaline conditions, the neutral compound $C_{22}H_{16}N_2Na_2O_{11}S_3$ is transformed to an ionic form with either negative $[C_{22}H_{15}N_2Na_2O_{11}S_3]^-$ or positive charge $[C_{22}H_{15}N_2Na_2O_{11}S_3]^+$, thereby facilitating its removal by various removal techniques. For evaluating the effectiveness of any dye removal technique using the colorimetric methods, a standard curve can be constructed at the ambient conditions (a pH of 7 and a temperature of 25 °C) and used to determine the concentration of the dye.

ACKNOWLEDGMENTS

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REFERENCES

1. Ademorotti, C.M.A., 1992. Studies of textile effluent discharges. Intl. J. Environ. Studies, 38: 291-296.
2. Navarro, V.A., 2001. Determination of wastewater Lc50 of the different process stages of the textile industry. Ecotoxicol. Environ. Safety, 48: 56-61.
3. Sheng, H.L. and M.L. Chi, 2003. Treatment of textile waste effluents by ozonation and chemical coagulation. Water Res., 27: 1743-1748.
4. Santhy, K. and P. Selvapthy, 2006. Removal of reactive dye from wastewater by adsorption on coir pith activated carbon. Biores. Technol., 97: 1329-1336.
5. Robinson, T., G. Mc Mullan, R. Marchant and P. Nigam 2001. Remediation of dyes in textile effluent a critical review on current technologies with a proposed alternative. Biores. Technol., 77: 247-255.
6. Carneiro, P.A., M.E. Osugi, J.J. Sene, M.A. Anderson and M.V.B. Zanoni, 2005. Evaluation of color removal and degradation of reactive textile azo dye on maroporous TiO_2 thin film electrodes. Electrochim. Acta, 49: 3807-3820.
7. Zbaida, S.,1995. The mechanism of microssomal azoreduction: predictions based on electronic aspects of structure activity relationship. Drug Metab. Rev., 2: 497- 516.
8. Papic, S., N. Koprivanac, A.L. Bozic and A. Metes, 2004. Removal of some reactive dyes from synthetic wastewater by combined Al(III) coagulation/carbon adsorption process. Dyes Pigments, 62: 291-298.

9. Muthuraman, G. and K. Palanivelu, 2006. Transport of textile dye in vegetable oils based supported liquid membrane. Dyes and Pigments, 70: 99-104.
10. Sevimli, M.F. and H.Z. Sarikaya, 2002. Ozone treatment of textile effluents and dyes; effect of applied ozone dose pH and dyes concentration. J. Chem0 Technol. Biotechnol., 77: 842-850.
11. Sevinmli, M.F. and C. Kinaci, 2002. Decolorization of textile by ozonation and Fenton's process. Water Sci. Technol., 45: 279-286.
12. Sheng, H.L. and M.L. Chen, 1997. Treatment of textile wastewater by chemical methods for reuse. Water Res., 31: 868-876.
13. Yang, X.Y and B. Al-Duri, 2001.Application of branched pore diffusion model in the adsorption of reactive dyes on activated carbon. Chem. Eng. J., 83: 15-23.
14. O'Mahony, T., E. Guibal and J.M. Tobin, 2002. Reactive dye biosorption by *Rhizopus arrhizus* biomass. Enzyme Microb. Technol., 31: 456-463.
15. Sarina, J.E.M., M.T. Brian and A.R.M. Reckhow, 2006. Evaluation of water treuse technologies for the textile industry. J. Environ. Eng., 3: 315-322.
16. Raymound, E.K. and F. Dunald, 1984. Encyclopedia of Chemical Technology. John Wiley, New York, USA.
17. Lee, J.W., S.P. Choi, R. Thiruvenkatachari, W.G. Shim and H. Moon, 2006. Evaluation of performance of adsorption and coagulation processes for the maximum removal of reactive dyes. Dyes and Pigments, 69: 196-203.
18. Sponza, D.T. and M. Isik, 2005. Toxicity and intermediates of C.I. direct red 28 dye through sequential anaerobic / aerobic treatment. Process Biochem., 40: 2735-2744.
19. Gahr, F., F. Hermanutz and W. Oppermann, 1994. Ozonation: an important technique to comply with new German laws for textile wastewater treatment. Water Sci. Technol., 30: 255-63.
20. Pandit, P. and S. Basu, 2002. Removal of organic dyes from water by liquide liquid extraction using reverse micelles. J. Colloid Interface Sci., 24: 208-214.
21. Mittal, A., L. Kurup and V.K. Gupta, 2005. Use of waste materials-bottom ash de-oiled Soya, as potential adsorbents for the removal of Amaranth from aqueous solution. J. Hazard. Mater., 117: 171-178.
22. Liu, R.L.H., H.-M. Chiu and R.Y.L. Yeh, 2003. Colloid interaction and coagulation of dye wastewater with extra application of magnetites. Intl. J. Environ. Studies, 59: 143-158.
23. Sanghi, R, B. Bhattacharya and W. Qual, 2002. Can. J. Forest Res., 38: 553.
24. Beydilli, M.I., S.G. Pavlostathis and W.C. Tincher, 2000. Biological decolorization of the azo dye reactive red 2 under various oxidation-reduction conditions. Water Environ. Res., 72: 698-705.
25. Liakou, S., U. Zissi, M. Kornaros and G. Lyberatos, 2003. Combined chemical and biological treatment of azo dye-containing wastewaters. Chem. Eng. Comm., 190: 645-661.
26. Alinsafi, A., M. Khemis, M.N. Pons, J. P. Leclerc, A. Yaacoubi, A. Benhammou and A. Nejmeddine, 2004. Electro-coagulation of reactive textile dyes and textile wastewater. Chem. Eng. Process., 44: 461-470.
27. Ge, J. and J. Qu, 2003. Degradation of azo dye acid red B on manganese dioxide in the absence and presence of ultrasonic irradiation. J. Hazard. Mater., 100: 197-207.
28. Arslan, I., I.A. Balcioglu and T. Tuhkanen, 2000. Treatability of simulated reactive dye-bath wastewater by photochemical and non-photochemical advanced oxidation processes. J. Environ. Sci. Health, 35: 775-793.
29. López-Grimau, V. and M.C. Gutiérrez, 2006. Decolorisation of simulated reactive dye bath effluents by electrochemical oxidation assisted by UV light. Chemosphere, 62: 106-112.
30. Patricia, A.C., E.O. Marly, E. Osugi, C.S. Fugivara, N. Boralle, M. Furlan and M. Zanoni, 2005. Evalution of different electrochemical methods on the oxidation and degradation of reactive blue 4 in aqueous solution. Chemosphere, 59: 431-439.
31. Van der Bruggen, B., I. De Vreese and C. Vandecasteele, 2001. Water reclamation in the textile industry: Nanofiltration of dye baths for wool dyeing. Indust. Eng. Chem. Res., 40: 3973 - 3978.
32. Koyuncu, I., 2003. Direct filtration of procion dye bath wastewaters by nanofiltration membranes: Flux and removal characteristics. J. Chem. Technol. Biotechnol., 78: 1219.
33. Roy, D., K.T. Valsaraj and S.A. Kottai, 1992. Separation of organic dyes from wastewater by using colloidal gas aphrons. Separation Sci. Technol., 27: 573-88.

34. Lee, D.W., R. Won and H.K. Yup, 2000. Removal of an organic dye from water using a predispersed solvent extraction. Separation Sci. Technol., 35: 1951-1962.
35. Snider, E.H. and J.J. Porter, 1994. Ozone treatment of textile wastes. J. Water Poll. Cont. Fed., 46: 886.
36. Beszedits, S., 1980. Ozonation to decolor textile effluents. American Dyestuffs Report, 69: 38.
37. Green, J.M. and C. Sokol, 1985. Using ozone to decolorize dyeing plant wastewater. American Dyestuff Report, 74: 67.
38. Gould, J.P. and K.A. Groff, 1987. Kinetics of ozonolysis of synthetic dyes. Ozone Sci. Eng., 9: 153.
39. Venkateswaran, P. and K. Palanivelu, 2006. Recovery of phenol from aqueous solution by supported liquid membrane using vegetable oils as liquid membrane. J. Hazard. Mater., 131: 146-152.
40. Kasuga, K. T.S. Hirose, T. Aiba, S. Takahashi and K. Hiratani, 1998. Transport of monosaccharide through a liquid membrane mediated by lipophilic alkalic earth metal complex. Tetrahedron Lett., 39: 699-702.
41. Chakraborty, S., S.D.E., J.K. Basu and S. Dasgupta, 2005. Treatment of a textile effluent: application of a combination method involving adsorption and nanofiltration. Desalination, 147: 73-85.
42. Ehud, N.L., S.P. David, A.M. Asce, J.E. Sarina, P.E. Ergas, A.M. Asce, R.A. David and A.M. Asce, 2006. Electrochemical oxidation and ozonation for textile wastewater reuse. J. Environ. Eng., 3: 324-330.
43. Atkins, P.W. and J.A. Beran, 1990. General Chemistry. W.H. Freeman and company, New York, USA.
44. Sigm-Aldrich, 2005. Advancing Science and Biotechnology, Sigma-Aldrich, Oakville, Ontario, pp: 2067.
45. Ma, M. and G. Sun, 2004. Antimicrobial cationic dyes: Part 2 - thermal and hydrolytic stability. Dyes and Pigments, 63: 39-49.
46. Gordon, P.F. and P. Gregory, 1983. Organic Chemistry in Color. Springe-Verlag, Berlin, Germany.
47. Bdazejowsk, J. and E. Kowalewska, 1985. Thermal decomposition of alkylammonium chlorides. Thermochim. Acta, 92: 811.
48. Rodd, E., 1951. Chemistry of Carbon Compounds. Volum 1. Part A. Elsevier Publishing Company, Amsterdam, The Netherlamds.
49. Zhu, H., R.C. Derksen, C.R. Krause, R.D. Fox, R.D. Brazee and H.E. Ozkan, 2005. Fluorescent intensity of dye solutions under different pH conditions. J. ASTM Intl., 2: 1-7.
50. Paik, Y.S., C.M. Lee, M.H. Cho and T.R. Hahn, 2001. Physical stability of the blue pigments formed from geniposide of Gardenia Fruits: Effect of pH, temperature and light. J. Agri. Food Chem., 49: 430-432.
51. Lin, T.F. and A.C. Demain, 1991. Effect of nutrition of *Monascus* sp. on fermentation of red pigments. Appl. Microbiol. Biotechnol., 36: 173-179.
52. Fabce, C.E., G. Goma and P.T. Blanc, 1993. Production and food application of red pigments of *monascus ruber*. J. Food Sci., 58: 1-5.
53. Lee, Y.K. and D.C. Cheu, 1995. Production of *Monascus* pigments by a solid liquid state culture method. J. Ferment. Biotechnol., 79: 516-518.
54. Nagendrappa, G., 2004. An epitome of K venkataraman's chemistry. Resonance, 12: 45-51.
55. Liversidge, R.M., G.J. Lloyd, D.A.J. Wase and C.F. Forster, 1997. Removal of basic blue 41 dye from aqueous solution by linseed cake. Process Biochem., 32: 473-477.
56. Alok, M., L. Krishnan and V.K. Gupta, 2005. Removal and recovery of malachite green from wastewater using an agricultural waste material, de-oiled soya. Separation and Purification Technol., 43: 125-133.
57. Saquib, M. and M. Muneer, 2002. Semiconductor mediated photocatalysed degradation of an anthraquinone dye, remazol brilliant blue R under sunlight and artificial light source. Dyes and Pigments, 53: 237-249.
58. Daneshvar, N., A.R. Khataee, M.H. Rasoulifard and M. Pourhassan 2006. Biodegradation of dye solution containing malachite green: Optimization of effective parameters using Taguchi method. J. Hazard. Mater., 3: 1-6.
59. Antonio, R.C., F.S.V. Eunice and S.S. Esdras, 2006. Interactions of anionic dyes with silica-aminopropyl: 1. A quantitative multivariate analysis of equilibrium adsorption and adsorption Gibbs free energies. J. Colloid and Interface Sci., 297: 22-30.