Desalination and Water Treatment
www.deswater.com

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doi: 10/5004/dwt.2012.3107

44 (2012) 261–268
June

Photocatalytic decolorization kinetics and adsorption isotherms of a mixture of two anionic azo dyes: Reactive Red 120 and Reactive Black 5

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Received 13 July 2011; Accepted 05 December 2011

ABSTRACT

Industrial effluents contain a number of dyes. In order to understand photocatalytic treatment in such conditions, there is a need to study a mixture of dyes. Present paper compares the adsorption isotherms, and photocatalytic decolorization of two anionic dyes Reactive Red 120 (RR120) and Reactive Black 5 (RB5) in single dye solution to that of in their mixture. Both dyes show adherence to Langmuir adsorption isotherms in single dye solution. Adsorption characteristics of RB5 dye are strongly affected in presence of RR120 in mixture studies. There seems to be competition for adsorption sites on catalyst surface between RR120 and RB5. RR120 shows higher affinity towards catalyst surface during adsorption studies. Subsequent photocatalytic degradation studies shows desorption and decolorization of individual dye components. RR120 shows desorption during photocatalysis. Pseudo first order decolorization characteristics of RR120 was found to be affected for catalyst load higher than 0.25 g l^{-1}. In dye mixture, decolorization rate constant (k_{app}) for RR120 with 0.25 g l^{-1} catalyst load was found to be 0.0109 min^{-1} while for RB5 it was 0.005 min^{-1}. For dye mixture k_{app} was found to be the average of k_{app} for single dye solutions.

Keywords: Reactive red 120; Reactive black 5; Dye mixture; Photocatalysis; TiO_2; Adsorption isotherms

1. Introduction

Dyes are used by many industries like textile, paint, leather and food industry [1]. Textile sector is main user of azo group of dyes, for dying natural fiber mainly. Azo dyes are characterized by the presence of one or more azo bonds (–N = N–). These dyes represent 50% of worldwide dye production. More than 15% of the dye remains unfixed at the end of the dying process [2]. This results in generation of huge amount of toxic effluents.

A number of physical and chemical techniques have been reported for the removal of dye compounds such as adsorption on activated carbon, biodegradation [3], ozonation [4], and advanced oxidation processes (AOPs) such as Fenton and photo-Fenton catalytic reactions [5,6], H_2O_2/UV processes [7], TiO_2 photocatalysis [8]. Most of the processes except AOPs are either ineffective in treating these toxic effluents and/or are merely resulting in transfer of toxicity from effluent to huge amount of solid waste. On the other hand, various AOPs offer the possibility of complete destruction of these toxic compounds without generating solid waste. Among the AOPs, heterogeneous photocatalytic oxidation using TiO_2 has been extensively studied [8–10] and found to be potentially advantageous. Photocatalytic oxidation leads to complete and fast mineralization of a

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wide range of compounds to CO_2, water and inorganic ions [11–13].

When TiO_2 surface is irradiated with UV radiation, the valance band electrons of TiO_2 are excited and jump to conduction band. This results in generation of an electron-hole pair. Minimum energy required for generation of an electron–hole pair is 3.2 eV. This electron-hole pair results in different oxidation and reduction reactions unless recombination of electron-hole pair occurs. Major reaction during photocatalytic degradation of dyes can be expressed as follows [14]:

$$\mathrm{TiO_2 + h\nu(UV) \leftrightarrow TiO_2(e^-_{CB} + h^+_{VB})} \tag{1}$$

$$\mathrm{TiO_2(h^+_{VB}) + H_2O \rightarrow TiO_2 + H^+ + OH^*} \tag{2}$$

$$\mathrm{TiO_2(h^+_{VB}) + OH^- \rightarrow TiO_2 + OH^*} \tag{3}$$

$$\mathrm{TiO_2(e^-_{CB}) + O_2 \rightarrow TiO_2 + O_2^{-*}} \tag{4}$$

$$\mathrm{O_2^{-*} + H^+ \rightarrow HO_2^*} \tag{5}$$

$$\mathrm{Dye + OH^* \rightarrow \text{deg radationproducts}} \tag{6}$$

$$\mathrm{Dye + h^+_{VB} \rightarrow \text{oxidationproducts}} \tag{7}$$

$$\mathrm{Dye + e^-_{CB} \rightarrow \text{reductionproducts}} \tag{8}$$

Various AOPs depend upon application of hydroxyl radical for oxidizing the pollutant. In case of TiO_2 based photocatalytic degradation oxidation and reduction reaction based upon Eqs. (7) and (8) are important since cationic dyes get adsorbed over catalyst surface in acidic pH conditions. Photocatalytic degradation with single pollutant in solution has been studied extensively [7,15–21].

It has been observed that industrial effluents contain a number of dyes. Only few studies related to simultaneous decolorization of more than one dye have been reported [22–26]. Studies made by Sahel et al. reported the simultaneous decolorization of Procion Red MX-5B and Remazol Black 5 [24]. Bergamini et al. studied simultaneous decolorization of three reactive azo dyes [25]. Present work deals with the adsorption and subsequent decolorization kinetics of RR120 and RB5 in single dye solution as well as in their mixture. The objective of the study is to compare the adsorption and subsequent photodegradation behavior of the two dyes in their single solution to that of their mixture. These two dyes have been chosen because (1) they have widely varying molecular weight and (2) different number of sulphonate groups.

A novel methodology to quantify each dye separately in dye solution has been also developed for the first time. Further studies compare the adsorption isotherms of two anionic dyes Reactive Red 120 (RR120) and Reactive Black 5 (RB5) in single dye solution to that in their mixture. Photocatalytic treatment of the dye mixture has been done, in order to optimize catalyst load. Individual dyes decolorization kinetics, in case of dye mixture, have been also studied. Finally decolorization kinetics of single dye solution has been compared with that of dye mixture.

2. Experimental

2.1. Dyes

RR120 dye (50–70% dye content, M.W. = 1469.98; λ_{max} = 524 nm) and RB5 (≈55% dye content, M.W. = 991.82, λ_{max} = 594 nm) were procured from Sigma Aldrich. Dyes were used without further purification. Solutions of dye were prepared in distilled water. The structure of dyes is shown in Table 1. The pH values of the solution were adjusted by using HCl and NaOH.

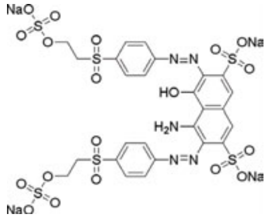
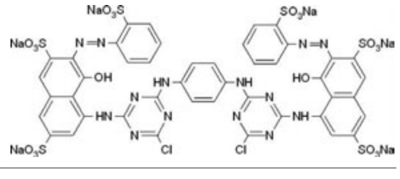
2.2. Photocatalyst

Degussa P25 TiO_2 was obtained from Degussa Company, Frankfurt, Germany. It has a BET surface area of 50 ± 15 $m^2\ g^{-1}$ and is 80% in anatase crystal form and 20% rutile with average particle size of 30 nm [27]. All other chemicals/reagents were of analytical grade.

2.3. Photoreactor

A batch type bench scale photocatalytic reactor system was fabricated for conducting experiments. The set up consisted of a batch reactor placed on a platform under UV tubes housed in a box. The tube box (4′ × 2.5′ × 2.5′) used was made up of galvanized aluminum sheet and fitted with 8 UV black tubes of 40 W each, fitted in parallel on the top of the reactor as shown in Fig. 1. The UV lamps emit radiation in the range of 300–400 nm, with the peak intensity at 350 nm. An exhaust fan is

Table 1
Structure and name of dyes

Dye description	Dye structure
Reactive Black 5 $C_{26}H_{21}Na_4N_5O_{19}S_6$	
Reactive Red 120 $C_{44}H_{24}Cl_2N_{14}O_{20}S_6Na_6$	

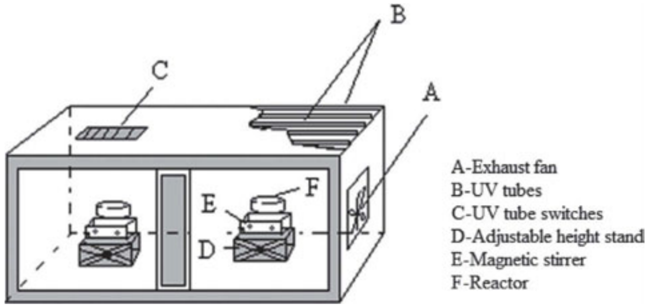


Fig. 1. Photoreactor.

fitted on the sidewall of the setup to maintain a constant temperature by air circulation.

2.4. *Dye concentration measurement*

RB5 and RR120 have peak absorbance values at 594 and 524 nm, respectively. Measurment of dye concentration for single dye solution was based upon their absorbance at their respective peaks as per existing methodology [18]. Absorbance values were measured by Perkin Elymer Lambda 35 UV-Visible spectrophotometer. However, to measure dye concentration of individual dyes in a solution of two dyes, values at single wavelength does not suffice because response at each wavelength is affected due to the presence of other dyes. Absorbance value at 524 and 594 nm for solution of known concentration with varying dye ratios were taken and multiple regression method was employed to develop equations for measuring concentrations of individual dyes [28]. Statistical analysis of the multiple regression model equation was done to validate the calibration.

2.5. *Adsorption on TiO_2 suspension*

The adsorption studies of both the dyes were done as single dye solution as well as in mixture. For adsorption study of single dye, 100 mg l^{-1} solution was taken. For adsorption study of dye mixture, equal amount of both dyes with equal concentration (100 mg l^{-1}) were mixed. Various amounts of catalyst were added to 200 ml of solutions in different flasks. The pH of this mixture was adjusted to 3 using HCl. Then flasks were magnetically stirred in the dark for 30 min to attain equilibrium between dye and TiO_2. Later, the samples were withdrawn and diluted in the ratio 1:1 with distilled water. Further samples were centrifuged at 14,500 rpm for 15 min. Absorbance at 524 nm and/or at 594 nm was taken as per requirement. The solution pH in all the cases was adjusted to three.

2.6. *Photocatalytic experiment*

A cylindrical Borosil glass vessel of 500 ml capacity was used as the photocatalytic reactor. Photocatalytic exposure was done for a period of 60 min. For all experiments, the area to volume ratio (A/V) of the reactor was kept at 0.201 $cm^2\ ml^{-1}$ and pH at 3. A magnetic stirrer was used to keep the reactor contents well mixed, so that the TiO_2 stayed suspended. The samples were withdrawn from reactor and centrifuged at 14,500 rpm for 15 min to separate suspended catalyst particles.

3. Results and discussion

3.1. *Calibration of two dyes in mixture*

In the absorbance spectra of mix dye, it was observed that the value of absorbance at 524 nm gets affected due to additional absorbance by other dye (Fig. 2). Thus, in case of unknown mixture, it is not possible to measure accurately individual dye concentration using a single wavelength. Various mixtures with varying dye ratios were made for calibration purpose. Absorbance values at 524 and 594 nm were taken. Multiple regression method was used for calibration purpose [28]. The final equations to determine individual dye in mixture of dyes are:

$$\text{RR120 concentration (mg/l)} = 46.937{*}\lambda_{524} - 22.362{*}\lambda_{594} \tag{9}$$

$$\text{RB5 concentration (mg/l)} = 43.754{*}\lambda_{594} - 1.371{*}\lambda_{524} \tag{10}$$

where $\lambda_{524,}$ and λ_{594} represent absorption values at 524 and 594 nm, respectively. It may be noted that negative terms in the Eqs. (9) and (10) removes the interference from other dyes in proportion to their concentration.

Statistical parameters related to this calibration are given in Table 2, which suggest a good fit of calibration data.

Previous studies on photocatalytic degradation of dyes mixture have used absorbance at single wavelength

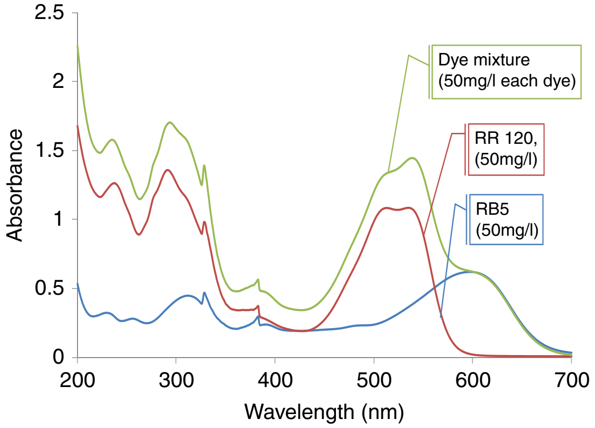


Fig. 2. UV-vis spectra of RR120, RB5 and dyes mixture.

Table 2
Statistical parameters related to calibration of both dyes in mixture

	Eq. (9)	Eq. (10)
No. of points	5	5
Degree of freedom	3	3
Residual sum of squares	0.1372	1.774
Adjusted R square	0.99997	0.99976

to quantify dye concentration [23–25]. However as explained previously additional absorbance caused by presence of other dyes cannot be ignored. The calibration made in such case can give actual results only if the dye concentration ratio does not vary during study. However in the intended application this ratio cannot be kept constant due to competitive adsorption and preferential degradation of one dye over the other. So the multiple regression based calibration is the option.

Additional techniques to measure dye concentration in case of dye mixture like MCR-ALS [22] and first order derivative of spectrum [26] have been also used. These techniques also attempt to remove interference from other dyes but are mathematically more rigorous.

3.2. Adsorption isotherm studies

RR120, and RB5 are both anionic dyes. Sulphonate groups in these dyes are supposed to be negatively charged. The TiO_2 surface can be charged negatively or positively according to pH of its solutions. For pH less than point of zero charge pH (pH_{pzc}), the TiO_2 surface is positively charged and for pH more than pH_{pzc}, it is negatively charged. Point of zero charge pH (pH_{pzc}), for TiO_2 is 6.8. Thus adsorption is favored in acidic pH conditions due to attraction between dye and catalyst surface. So adsorption and further photcatalytic degradation studies were performed at pH 3.

3.2.1. Adsorption isotherms of single dye solutions

Fig. 3 shows adsorption equilibrium for RR120 and RB5 when the solutions were made with single dyes. RR120 dye shows maximum adsorption of 50 mg g^{-1} while RB5 shows 25 mg g^{-1} adsorption. The adsorption equilibrium characteristics of both dyes are of typical L-1 shape [29]. There is clearly seen a difference in maximum adsorption quantity for both dyes. This can be interpreted from the fact that the two dyes have different molecular structure. The molecule of RR120 contains six number of sulphonate groups, while RB5 has four groups per molecule. Thus, RR120 shows higher adsorption per gram of catalyst. Another reason for this difference is the difference in purity of the dyes. The non dye content might be also getting adsorbed, which cannot be measured by spectrophotometer based study.

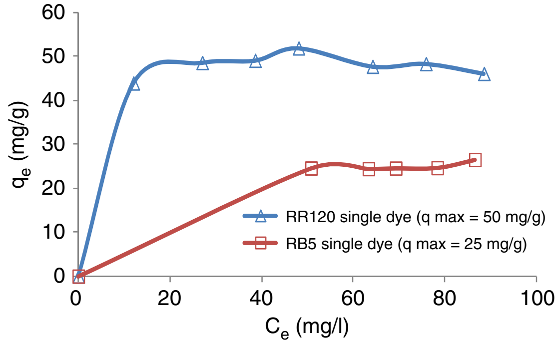


Fig. 3. Adsorption equilibrium of RR120 and RB5 dyes in case of single dye solutions (at pH 3).

The equilibrium data has been found to fit well in linearized form of Langmuir Eq. (11):

$$C_e/q_e = 1/b.q_m + C_e/q_m \tag{11}$$

A plot between C_e/q_e vs. C_e has shown a good fit for both dyes in single dye solution (Fig. 4). The equilibrium constants were determined by fitting the experimental data to the Langmuir equation to describe the adsorption of dye. The equilibrium constant for RR120 and RB5 thus obtained were 1.626 and 1.342 l g^{-1}, respectively.

3.2.2. Adsorption isotherms of dye mixture

Fig. 5 shows the combined adsorption equilibrium of total dye (RR120 and RB5) when adsorption study is done with mixed dye solution. Fig. 6 shows the adsorption equilibrium of single dyes when in mixed dye solution. It has been observed that value of q_{max} (40 mg g^{-1} in Fig. 6) for RR120 dye in dye mixture is close to q_{max} value of RR120 in single dye solution (50 mg g^{-1} in Fig. 3). his implies that RR120 dye is largely adsorbing over

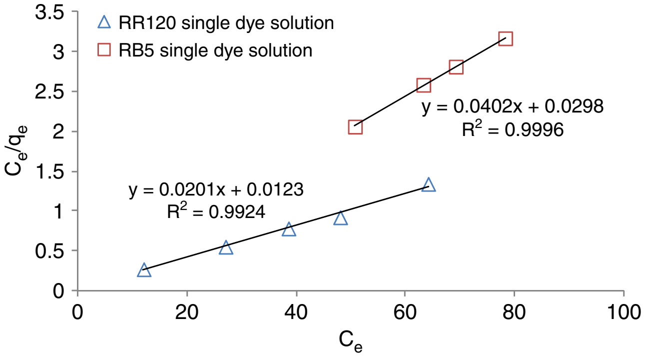


Fig. 4. Langmuir adsorption isotherms of RB5 and RR120 in case of single dye solutions.

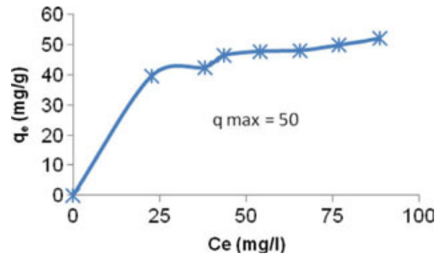


Fig. 5. Adsorption equilibrium for tota l adsorption of RR120 and RB5 dyes in dye mixture (at pH 3).

catalyst surface in case of dye mixture as well. In case of dye mixture there is seen a competition among dyes to occupy the active sites over catalyst surface. RR120 shows higher adsorption, which can be clearly observed in Fig. 6. The adsorption equilibrium of RR120 in dye mixture still shows typical L-1 shape [29]. However, RB5 adsorption equilibrium is strongly altered in presence of RR120. This also shows that competitive adsorption is taking place. Sahel et al. observed similar alteration in RB5 adsorption behavior, while studying mixture of Procion Red MX-5B and RB5 [24]. They concluded that this alteration in RB5 adsorption behavior was due to pH change resulting from mixing of dyes. Our studies rule out this reason, because our adsorption studies were made at constant pH. Our observation is that, the amount of RB5 adsorbed per unit catalyst weight was high at higher catalyst load only because under such conditions, residual concentration of RR120 was found limiting to compete with RB5. In other words the adsorption of RB5 was high only when the residual concentration of RR120 in solution was very small. Thus, it may be concluded that adsorption of RR120 occurs preferentially over RB5. Competitive adsorption can also be explained based upon free energy change associated with dyes. RR120 dye has higher value of equilibrium constant, so the associated decrease in free energy due to its adsorption is also higher. All chemical systems tend naturally toward states of minimum Gibbs free energy. So adsorption of RR120 occurs preferentially. Competitive adsorption of metanil yellow and reactive blue 15 dyes and remazol black 5 and remazol brilliant orange 3R dyes has also been reported in literature [30,31].

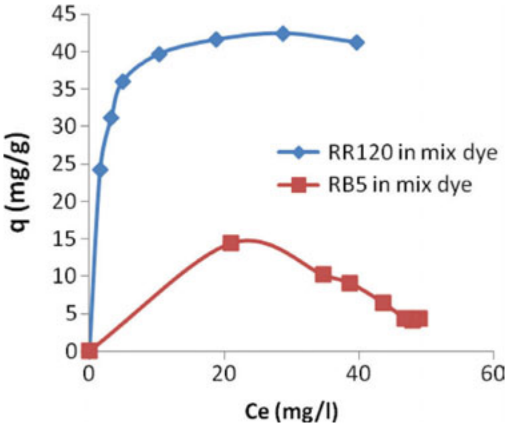


Fig. 6. Adsorption equilibrium of RR120 and RB5 dyes in dye mixture (at pH 3).

All the adsorption isotherms show an excellent fit to Langmuir isotherm except of RB5 in dye mixture (Figs. 7 and 8). RB5 isotherm data was also found not to fit in Freundlich isotherm.

The non applicability of Freundlich isotherm suggests that the adsorption of RB5 does have wide variation in heat of adsorption. Freundlich isotherm is expected to be applicable in case adsorption sites are distributed exponentially with respect to heat of adsorption.

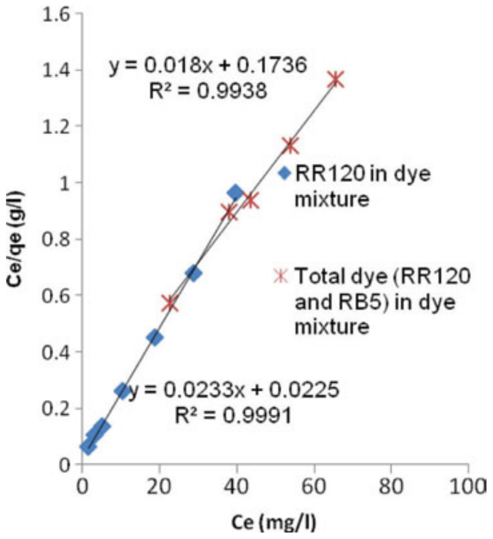


Fig. 7. Adsorption isotherms of RR120 and total dye (RR120 and RB5) in dye mixture.

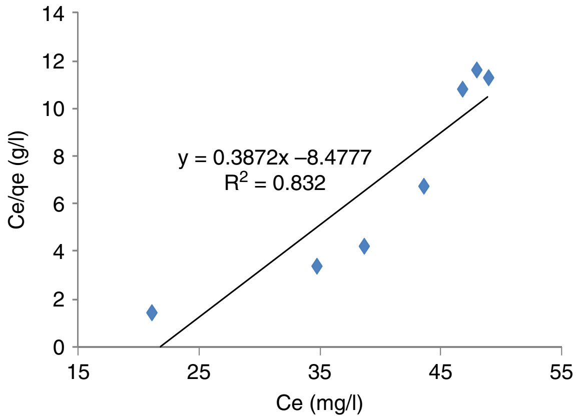


Fig. 8. Langmuir adsorption isotherm of RB5 dye in dye mixture showing a poor fit.

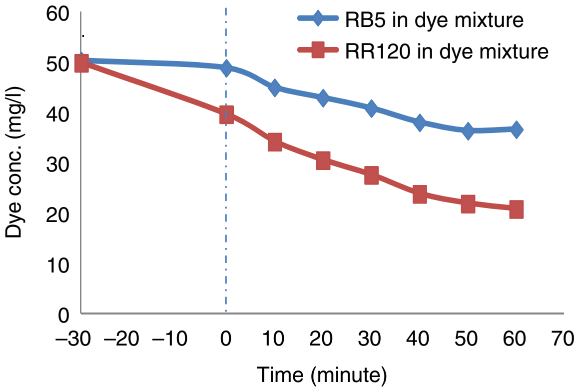


Fig. 9. Decolorization characteristics of RR120 and RB5 dyes in the mixture with 0.25 g l^{-1} as catalyst load (The time less than zero indicate the time for adsorption equilibrium without UV exposure.).

3.3. Photocatalytic decolorization kinetics

3.3.1. Photocatalytic decolorization kinetics of a dyes mixture

Equal amounts of RR120 and RB5 in equal concentration of 100 mg l^{-1} were mixed for dye mixture studies. This makes total concentration to 100 mg l^{-1} for dye but each dye concentration is reduced to 50 mg l^{-1}. Photocatalytic decolorization studies were performed on dye mixture with various amounts of catalyst.

Fig. 9 shows the decolorization characteristics of individual dyes in dye mixture with 0.25 g l^{-1} as catalyst load. When the kinetics of the photocatalytic decolorization reactions were studied, it was found that the correlation between ln (C/C_0) and the irradiation time was linear. This is a typical first-order reaction plot. The slopes of the lines give the apparent rate constant (k_{app}). The kinetic expression can be presented as follows:

$$\ln\left(\frac{C}{C_0}\right) = k_{app}t \qquad (12)$$

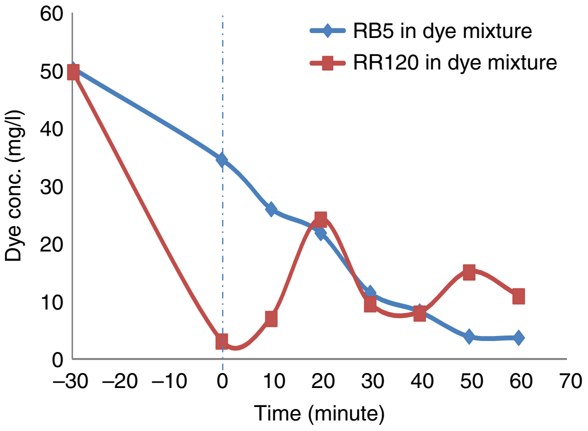


Fig. 10. Decolorization characteristics of RR120 and RB5 dyes in dye mixture with 1.5 g l^{-1} as catalyst load. (The time less than zero indicate the time for adsorption equilibrium without UV exposure.).

The data fits well with pseudo first order kinetics. Overall decolorization behavior taking both dyes into consideration is also found to be pseudo first order.

Fig. 10 shows decolorization of RR120 and RB5 in a dye mix with 1.5 g l^{-1} as catalyst load. It can be observed here that RR120 dye is getting desorbed during photocatalytic exposure with higher amount of catalyst. Desorption of red color from catalyst surface can be also observed with naked eye. Thus pseudo first order nature of RR120 decolorization kinetics is lost. Desorption of RR120 during photocatalysis suggests a weak attraction between catalyst surface and dye. Table 3 shows the decolorization rate constants for individual dye components in dye mixture as well as for combined dye in dye mixture.

It has been observed that pseudo first order decolorization kinetics of RR120 is limited to catalyst load up to 0.25 g l^{-1} only. However, pseudo first order decolorization kinetics of RB5 remains retained for higher catalyst loads. For 0.25 g l^{-1} catalyst load k_{app} value of RR120 is

Table 3
Pseudo first order decolorization rate constants for individual dyes RR120, RB5 and for total dye content (RR120 + RB5) in mix dye

Catalyst load (g l^{-1})	k_{app} for RR120 (min^{-1})	k_{app} for RB5 (min^{-1})	k_{app} (RR120 + RB5) (min^{-1})
0.25	0.0109	0.005	0.0074
0.5	[a]	0.0103	0.0105
0.75	[a]	0.0164	0.0195
1.0	[a]	0.0251	0.0199
1.25	[a]	0.0314	[a]
1.5	[a]	0.0401	[a]
2.0	[a]	0.0503	[a]

[a] Decolorization rate constant determination could not be done due to excessive desorption from catalyst surface during photocatalysis.

2.18 times more than that of RB5. It may be noted that the q_{max} value of RR120 (50 mg g^{-1}) is twice to that of RB5 (25 mg g^{-1}) in case of single dye solution. This suggests that dye which has higher adsorption has also higher decolorization rate constant. Also the ratio of decolorization rate constant is proportion the ratio of their q_{max} values. Christopher et al. also observed in their study on single dye solution that photocalytic effect was increasing with increasing adsorption [32]. Our studies suggest that the observation is also valid in case of dye mixture.

3.3.2. Photocatalytic decolorization kinetics of a mixture of dyes vs. single dye solutions

In order to compare decolorization characteristics of single dye solution to the mixture of dyes, experiments were performed with 100 mg l^{-1} of both RB5 and RR120. The catalyst load was kept at 0.25 g l^{-1}. Decolorization rate constant of RR120 and RB5 were found to be 0.0083 and 0.0064 min^{-1} in case of single dye solution while for dye mixture the decolorization rate constant was 0.0074 min^{-1} (Table 3). The decolorization rate constant for dye mixture is found to be exactly the average of decolorization rate constants for single dyes. Thus, we may conclude that photocatalytic degradation efficiency of dyes is not affected due to presence multiple dyes in dye solution. However it may be noted in dye mixture degradation rate of RB5 is suppressed, while RR120 shows higher degradation rates. This can be explained again based upon the amount of adsorption in both cases.

4. Conclusions

Present study was about the adsorption and subsequent photoctalytic decolorization kinetics of reactive RR120 and RB5 in single dye solution as well as in their mixture. Additionally quantification of single dyes in solution has been made by a new method. The conclusions drawn are as below.

A novel methodology to quantify the dyes in the dye mixture solution has used for the first time. The method is based upon the multiple regression. Statistical results have been used to verify the calibration. It has been observed that this method is better choice when we study adsorption and photo degradation. This is because dye concentration ratio varies due to competitive adsorption and preferential photodegaradtion.

Adsorption studies of single dye solutions show that both dyes RR120 and RB5 show adherence to Langmuir adsorption isotherms, that maximum specific adsorption of RR 120 and RB5 is 50 and 25 mg g^{-1} respectively. Adsorption studies of dye mixture show that RR120 is preferential adsorbed than RB5, that both RR120 and total dye content follows Langmuir adsorption isotherm, that adsorption characteristics of RB5 are strongly altered.

Ratio of decolorization rate constants of dyes in case of single dye solution is found to be in proportion to their maximum specific adsorption values. Photocatalytic degradation studies of dye mixture suggest that RR120 degrades at higher rate for low catalyst load. However with increasing catalyst load the desorption of RR120 causes loss of pseudo first order decolorization characteristics. Release of dye due to desorption presents a technical problem in optimizing catalyst load in case of mix dye effluent. Primarily, it appears that photocatalytic degradation efficiency of dyes is not affected due to presence of multiple anionic dyes in dye solution.

Symbols

λ_X — absorbance at X nanometer wavelength
C_e — equilibrium dye concentration (mg l^{-1})
q_e — amount of dye adsorbed per gram of catalyst at equilibrium (mg g^{-1})
q_m — maximum amount of dye adsorbed per gram of catalyst (mg g^{-1})
b — adsorption equilibrium constant (l g^{-1})
C — dye concentration at instant t
C_0 — dye concentration at $t = 0$ (mg l^{-1})
t — time of reaction in minutes
k_{app} — pseudo-first-order rate constant (min^{-1})

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