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RESEARCH ARTICLE

Simultaneous adsorption of Remazol brilliant blue and Disperse orange dyes on red mud and isotherms for the mixed dye system

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Abstract The paper presents the adsorption of Remazol brilliant blue (RBB) and Disperse orange 25 (DO25) dyes from aqueous solution of the mixture of dyes onto concentrated sulphuric acid-treated red mud (ATRM). First-order derivative spectrophotometric method was developed for the analysis of RBB and DO25 in mixed dye aqueous solution to overcome the limitations arising due to interference in the zero-order spectral method. The optimum conditions to maximize RBB adsorption favoured the adsorption of RBB, and those for DO25 favoured DO25 adsorption from the mixed dye aqueous solutions. Presence of a second dye always inhibited the adsorption of a target dye. The uptake and percentage adsorption of each of the dyes onto ATRM from the aqueous solution of the mixture of dyes decreased considerably with increasing concentrations of the other dye showing the antagonistic effect. Monocomponent Langmuir isotherm fitted the mixed dye adsorption equilibrium data better than the monocomponent Freundlich isotherm. However, monocomponent models are suitable for the fixed concentration of the other dye. Modified

Langmuir isotherm model adequately predicted the multi-component adsorption equilibrium data for RBB-DO25-ATRM adsorption system with a good accuracy and is more generic from the application point of view.

Introduction

Dyes are used in many industries such as food, paper, rubber, plastics, cosmetics, leather and textiles. A large amount of highly coloured wastewater containing artificial dyes is generated from these industries. Today, there are more than 10,000 dyes available commercially and used for various applications in these industries. Industrial wastewaters containing dyes, if discharged into nearby streams and rivers without suitable treatment, may lead to severe impacts. Azo dyes are known as one class of important pollutants in wastewater (Karatas et al. 2012). Aromatic rings in azo dyes are toxic and mostly non-biodegradable. These dyes can be applied to synthetic fibres such as polyester, nylon, acetate, cellulose and acrylic. Reactive dyes are typically azo-based chromophores combined with different types of reactive groups. Reactive dyes pose serious environmental problems, because these particular type of dyes can display low fixation to cellulosic fibres (Koyuncu 2012). Disperse dyes are widely used in variety of industries, such as textiles, paper and leather. Disperse dyes are non-ionic aromatic compounds, toxic to aquatic organisms and carcinogenic and mutagenic to humans (Wang 2012). Hence, the waste water containing these dyes must be treated prior to the discharge in order to overcome the environmental impacts.

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Normally, industrial wastewater treatment involves pre-treatment, primary treatment, secondary treatment and tertiary treatment composing of certain specific physical, chemical and biological processes. One of the widely used physico-chemical method for colour removal is the adsorption process. Adsorption is a well-known equilibrium separation process for water treatment (El-Naas et al. 2017; Liu et al. 2015; Dabrowski and Piaseczny 2000) and an effective method for dye removal applications (Liu et al. 2015; El Haddad et al. 2013; Chowdhury et al. 2013). Use of industrial solid wastes as adsorbents for adsorption of dyes from water (Maderova et al. 2016) can often be considered as a favourable alternative. Red mud emerges as an unwanted by product during alkaline leaching of bauxite in Bayer process, which is used for the production of alumina from bauxite. About 500,000 m^3 of strongly alkaline (pH 12–13) red mud slurry is dumped annually into specially constructed dams around Aluminium plant (Tor and Cengeloglu 2006). Studies on the use of red mud as an unconventional adsorbent for water and wastewater treatment processes (Namasivayam and Arasi 1997; Altundogan et al. 2000; Tor et al. 2009; Sahu et al. 2015; Prajapati et al. 2016) are motivated by the fact that red mud is a fine grained mixture of oxides and hydroxides, capable of removing several contaminants (Gupta et al. 2004). Many industrial situations involve the discharge of effluents that contain a mixture of several dyes. In the application of adsorption for treatment of coloured wastewater, the solution normally contains mixture of many dyes rather than a single one. Presence of other dyes in a solution may affect the adsorption of the targeted dye on the adsorbent. The interactions between compounds may mutually enhance (synergetic effect) or inhibit (antagonistic effect) the adsorption capacity (Turabik 2008). In recent years, considerable information has been collected for the adsorption of single component dyes by various adsorbents and limited data is available on multi-component dye adsorption (Noroozi et al. 2008). Sellaoui et al. (2016a) have observed an inhibition effect between the adsorbed molecules for multi-component systems. Thus, understanding the interference in terms of antagonistic and synergetic effect of other dyes on the adsorption of a target dye is very important.

In case where interaction effect exist between the components from the mixture, equilibrium data obtained from single component aqueous systems is not adequate. Equilibrium adsorption isotherms play an important role in the predictive modelling that is used for the design and analysis of multi-component adsorption systems. Various multi-component isotherm equations have been developed by various researchers for adsorption of solutes like metals and dyes (Sellaoui et al. 2016b; Noroozi et al. 2008). The design of adsorption units must be based on mixed dye equilibrium data and adsorption studies on aqueous solution containing the mixture of dyes (Turabik 2008).

For single solute systems, Langmuir and Freundlich isotherms have been the most common adsorption models (Gupta et al. 2004). However, single component equilibrium models are applicable only at specified initial concentration of the other dye. This limits their application for aqueous solution of mixture of dyes at various concentrations. Many models have been published in literature to describe the equilibrium relationship between solute and adsorbent in both single and multi-component systems. Since the interaction of one component with the other components in a mixture may be synergistic, antagonistic or non-interactive, the adsorption results cannot be predicted accurately on the basis of single-component studies (Aksu et al. 2002).

The predictions of multi-component equilibrium conditions are complicated due to the interaction and competition effects between the components involved (Noroozi et al. 2008; Noroozi and Sorial 2013). Several competitive multi-component adsorption models have been proposed to describe the antagonistic interaction between the adsorbed quantity of one component and the concentrations of all other components, either in solution or already adsorbed at equilibrium. These isotherms range from simple models related to the individual isotherm parameters only (non-modified adsorption models) to more complex models related to the individual isotherm parameters and to correction factors (modified adsorption models) (Bellot and Condoret 1993; Esposito et al. 2001). For its simplicity, the modified Langmuir model remains the most widely used isotherm for multi-component systems (Noroozi and Sorial 2013). The monocomponent Langmuir model can be extended to describe a competitive multi-component adsorption system (Bellot and Condoret 1993). Another multi-component isotherm model commonly used is the empirical extended Freundlich model.

The present work reports the batch adsorption of RBB and DO25 dyes from single and mixed dye aqueous solutions onto concentrated sulphuric acid-treated red mud (ATRM). It also reports the development of first-order derivative spectrophotometric method for the analysis of simultaneous presence of RBB and DO25 dyes in the mixed dye aqueous solution. The test of validity of mono- and multi-component isotherm models to represent the equilibrium relationship for the RBB-DO25-ATRM adsorption system is also reported.

Material and methods

Red mud and dye

Red mud (composition: Fe_2O_3—42%, Al_2O_3—20%, TiO_2—9%, SiO_2—10–12%, Na_2O—4–5%) was obtained from Hindalco Aluminium Industry, Belgaum, India. Remazol brilliant blue (RBB) dye and disperse orange 25 (DO25) dye were gifted by Campbell Knitwear Ltd., Belgaum, India. The

chemical structure for RBB dye is presented elsewhere (Ratnamala et al. 2012) and that of DO25 is shown in Fig. 1.

Preparation of adsorbent

Red mud was washed thoroughly with distilled water, filtered and dried at 110 °C for 24 h. The red mud was treated with concentrated acid according to the methodology presented elsewhere (Ratnamala et al. 2015). This concentrated acid-treated red mud sample is known as ATRM.

Preparation of aqueous solution of the dyes

One thousand milligrammes per litre of stock solutions of RBB and DO25 in distilled water was prepared separately. The aqueous solution of desired concentration of a single dye was prepared by suitably diluting a known volume of 1000 mg/L of the dye stock solutions in distilled water. To prepare the aqueous solution of mixture of RBB and DO25, desired volume of the stock solution of each of the dyes was diluted to 100 mL with distilled water to get the desired concentration of each of the dyes in a mixed dye solution.

Analysis of dye concentration in aqueous solution of a single dye

The dye concentrations in aqueous solutions of a single dye were analysed by measurement of the absorbance of the solutions at 608 nm for RBB and 475 nm for DO25, using a pre-calibrated UV–Vis bio-spectrophotometer (Elico BL-198).

Analysis of RBB and DO25 concentrations in mixed dye aqueous solutions

The single dye aqueous solutions of RBB and DO25 with known initial concentrations of 50 and 130 mg/L were prepared, and the zero-order absorption spectra of these single dye aqueous solutions were recorded between 400 and 650 nm and are presented in Figs. 2 and 3. As it can be observed from Figs. 2 and 3, the wavelength for maximum absorption (λmax) of RBB and DO25 was determined as 475 and 608 nm, respectively. For the simultaneous analysis of RBB and DO25 dyes in an aqueous solution of the two dyes, the mixed dye aqueous solution containing 50 mg/L of RBB and 130 mg/L of DO25 were prepared and zero-order absorption spectra were recorded between 400 to 650 nm (Fig. 4). As it can be observed from Fig. 4, the spectra for RBB and DO25 show two peaks at 475 and 608 nm. However, in comparison of Figs. 2 and 3 with Fig. 4, it is observed that the absorbance values with dual dye spectra at 475 and 608 nm are different than those in the corresponding single dye spectra. This is due to overlap of the absorbance by both the dyes, indicating the interference between the zero-order spectra of RBB and DO25
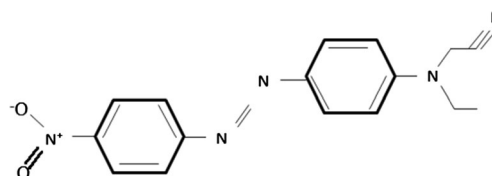

Fig. 1 Structure of disperse orange 25 dye

dyes. Hence, their concentrations in the mixture could not be determined by direct absorbance measurement at λmax. Therefore, it was not possible to determine the concentration of RBB and DO25 dyes in mixed dye solutions by directly measuring the absorbance using spectrophotometer at their corresponding λmax.

Zero-order method of analysis for the measurement of dye concentrations in a single dye aqueous solution may not be suitable for measurement of dyes in mixed dye solutions, if the dyes interfere with each other in analysis. Derivative spectro-photometry is an analytical technique of great utility for resolving mixtures with overlapping spectra. The derivation of zero-order spectrum can lead to separation of overlapped signals, which reduces the effect of spectral background interferences caused by presence of other compounds in a sample (Ojeda and Rojas 2004; Karpińska 2004). Thus, the simultaneous analysis of RBB and DO25 dyes were carried out using the first-order derivative spectrophotometric method (Turabik 2008; Douissa et al. 2014).

Derivative spectrophotometric method was used in the present work for simultaneous analysis of RBB and DO25 dye in mixed dye solutions, using zero crossing point of first-order derivative spectra. The variations of first-order derivative absorption spectra of RBB and DO25 in single and mixed dye solutions with wavelength are presented in Fig. 5. As it can be observed from Fig. 5, the first-order derivative spectra of RBB and DO25 dyes in single dye solution and mixed dye solutions showed that RBB absorbance can be determined at 550 nm in the presence of DO25, where the derivative of absorbance of DO25 is zero and DO25 dye can be determined at 480 nm in the presence of RBB, where the derivative of absorbance of RBB dye is zero (Fig. 5). The calibration equations for RBB and DO25 dyes at these individual wavelengths (550 and 480 nm) were separately obtained to determine the concentration of each dye in mixture.

Thus, to determine the dye concentrations in mixed dye aqueous solutions, UV–Vis bio-spectrophotometer (Elico BL-198) was calibrated at 550 nm for RBB and at 480 nm for DO25. The concentrations of RBB and DO25 in unknown samples with mixture of these dyes in aqueous solutions were measured by measurement of absorbance after suitable dilution using UV–Vis spectrophotometer at 550 nm for RBB analysis and at 480 nm for DO25 analysis followed by determination of concentration using the corresponding calibration followed by multiplication with dilution factors.

Fig. 2 Zero-order absorption
spectra for RBB
(concentration = 50 mg/L)
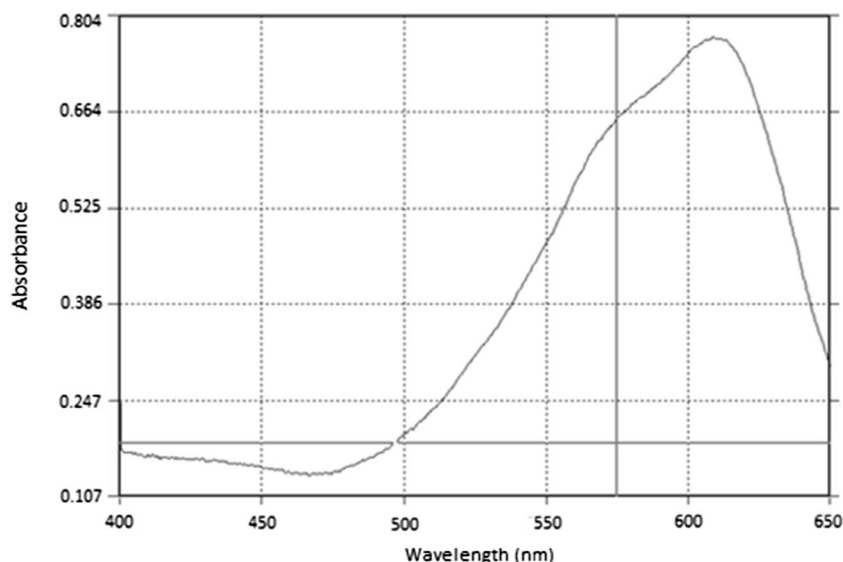
Batch adsorption studies with mixed dye aqueous solutions

Batch adsorption experiments were carried out with 100 mL of mixed dye aqueous solutions with different concentration combinations (Tables 1 and 2) of RBB and DO25 in 250 mL conical flasks containing desired quantity of ATRM. Initial pH was adjusted to the desired level with 1 N NaOH or 1 N HCl solutions. The solution was agitated at constant speed of 145 rpm and at 30 °C temperature till the equilibrium condition was reached. These experiments were conducted at different initial concentrations of RBB (50, 70 and 90 mg/L) and at each of fixed initial DO25 concentrations (130, 150 and 170 mg/L) as shown in Table 1 and at conditions of pH and temperature previously optimized for maximum adsorption of RBB (temperature 32 °C and initial pH 1) and DO25 (temperature 37 °C and initial pH of solution 4). A constant ATRM dosage of 2.05 g/L (optimum for 105 mg/L RBB) and 0.88 g/L (optimum for 189 mg/L DO25) were used for experiments with RBB and DO25 respectively. The optimum values used in these experiments were obtained by conducting experiments designed as per central composite design (CCD) of design of experiments (DoE) strategy followed by optimization using response surface methodology (RSM) for adsorption of RBB (Ratnamala 2015) and for adsorption of DO25 (Ratnamala 2015) Adsorption experiments were also conducted with single dye aqueous solutions at conditions shown in Tables 1 and 2.

Fig. 3 Zero-order absorption
spectra for DO25 (Initial
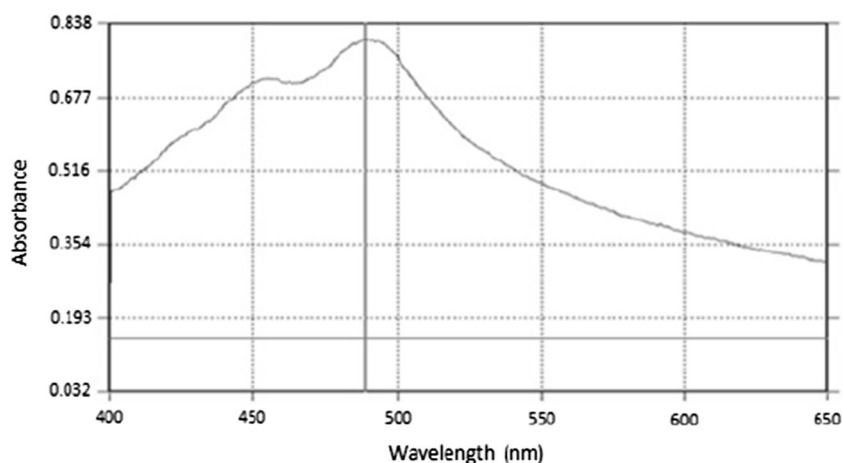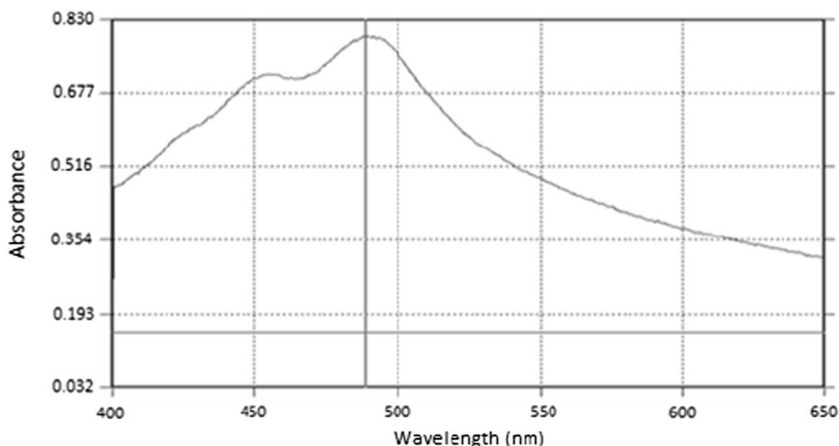concentration = 130 mg/L)

Fig. 4 Zero-order spectra of mixture of RBB (concentration = 50 mg/L) and DO25 (concentration = 130 mg/L)

The samples were withdrawn after the attainment of equilibrium, centrifuged and the absorbance of supernatant was measured at 550 and 480 nm for of RBB and DO25 respectively using UV bio-spectrophotometer. The equilibrium concentrations of each dye in the solution were then determined. Percentage adsorption of RBB and DO25 at equilibrium and adsorption capacities (q_e) were calculated using Eqs. (1) and (2) respectively.

$$\%\text{Adsorption of dye} = (C_o - C_t) \times 100 / C_o \tag{1}$$

$$q_e = (C_o - C_e)/m \tag{2}$$

where C_o, C_e and C_t are the initial concentration, equilibrium concentration and concentration at any time t of the dye, m is the ATRM dosage in g/L and q_e is the equilibrium dye uptake.

Application of monocomponent and multi-component isotherm models for adsorption of RBB and DO25 from mixed dye solutions on ATRM

In the present work in order to determine the valid isotherm model for adsorption of dyes from the aqueous solution of mixture of RBB and DO25 on ATRM, two different approaches were used.
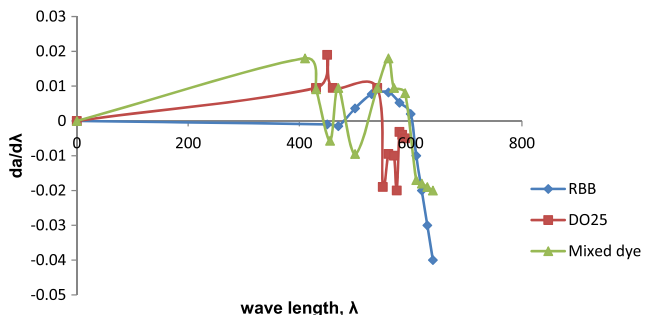

Fig. 5 First-order derivative spectra for RBB, DO25 and mixture of RBB and DO25 dyes

Approach 1. Monocomponent models were tested using the data from studies on mixture of dyes Eqs. (3) and (4) (Qiao et al. 2009; Turabik 2008)

Approach 2. Multi-component models were tested using the data from studies on mixture of dyes Eqs. (5) and (6) (Qiao et al. 2009; Turabik 2008; Noroozi et al. 2008; Al-Degs et al. 2009)

Approach 1

The equilibrium data for RBB and DO25 obtained from the batch experiments conducted for adsorption of these dyes on ATRM from mixed dye aqueous solutions at conditions optimized for RBB and DO25 adsorption were fitted onto Langmuir Eq. (3) isotherm (Qiao et al. 2009; Turabik 2008) and Freundlich Eq. (4) isotherm (Qiao et al. 2009; Turabik 2008), the monocomponent equilibrium models using the linearized form.

$$q_e = \frac{Q_o b C_e}{1 + b C_e} \tag{3}$$

$$q_e = k C_e^{1/n} \tag{4}$$

In Eqs. (3) and (4), q_e is the dye uptake on ATRM at equilibrium in milligrammes per gram and C_e is the equilibrium concentration in milligrammes per litre. In Langmuir isotherm model Eq. (3), Q_o is the monolayer adsorption capacity in milligrammes per gram and b is the Langmuir constant. In Freundlich isotherm model Eq. (4), k is the adsorption capacity (mg/g) and n is an empirical parameter which is an indicator of adsorption intensity or the bonding energy between the adsorbent and the adsorbate molecules. The validity of these models was tested by fitting the equilibrium data using curve fitting tool box of MATLAB 2013a, and the parameters(Q_o, b, k and n) of the models were evaluated.

Table 1 Effect of initial concentration of RBB on dye uptake on ATRM in the absence and presence of DO25 with ATRM dosage of 2.05 g/L (optimum conditions for RBB: temperature 32 °C, pH 1)

Initial concentration, RBB (mg/L)	Initial concentration, DO25 (mg/L)	C_e, RBB (mg/L)	C_e, DO25 (mg/L)	q_e, RBB (mg/g)	q_e, DO25, (mg/g)
50	0	0.05	–	24	–
70	0	1	–	34	–
90	0	1.8	–	43	–
50	130	10	39	20	44
70	130	16	46.1	26	41
90	130	24	60	32	34
50	150	13	55	18	46
70	150	18.75	62	25	43
90	150	27.5	73	30	38
50	170	14.2	67.5	16	50
70	170	22	72.5	23	48
90	170	32	84.5	28	42

Approach II

The equilibrium data (equilibrium concentrations and uptakes) for RBB and DO25 obtained from the batch experiments conducted for adsorption of these dyes on ATRM from mixed dye aqueous solutions at RBB and DO25 optimized conditions were fitted onto multi-component competitive modified Langmuir isotherm (Turabik 2008; Douissa et al. 2014) written for RBB-DO25 system as Eqs. (5) and (6) and extended Freundlich (Turabic 2008) isotherm for multi-component equilibrium adsorption written for RBB-DO25 system as Eq. (7) and (8) using curve fitting tool box of MATLAB 2013a.

Thus, for RBB-DO25 system, modified Langmuir isotherms are given as Eqs. (5) and (6) respectively for adsorption capacity of RBB and DO25

$$q_{e_{RBB}} = \frac{Q_{RBB} b_{RBB} \left(\frac{C_{e_{RBB}}}{\eta_{RBB}} \right)}{1 + \left(\frac{b_{RBB} C_{e_{RBB}}}{\eta_{RBB}} \right) + \left(\frac{b_{DO25} C_{e_{DO25}}}{\eta_{DO25}} \right)} \quad (5)$$

$$q_{e_{DO25}} = \frac{Q_{DO25} b_{DO25} \left(\frac{C_{e_{DO25}}}{\eta_{DO25}} \right)}{1 + \left(\frac{b_{RBB} C_{e_{RBB}}}{\eta_{RBB}} \right) + \left(\frac{b_{DO25} C_{e_{DO25}}}{\eta_{DO25}} \right)} \quad (6)$$

C_{eRBB} and C_{eDO25} are the residual concentrations of RBB and DO25 in the mixture at equilibrium; q_{eRBB} and q_{eDO25} are the adsorbed quantity of RBB or DO25 per gramme of adsorbent at equilibrium, respectively. b_i and Q_i (for i = RBB or DO25) were obtained from the Langmuir isotherm equation for corresponding single dye solutions, and η_{RBB} and η_{DO25} are the Langmuir correction coefficient of the component estimated from competitive adsorption data.

The extended form of Freundlich isotherm model restricted to aqueous solution of binary dye mixtures (Turabik 2008) is presented as Eqs. (7) and (8) for adsorption of RBB and DO25 respectively and this isotherm model contains six parameters (x_{RBB}; y_{RBB}; z_{RBB} and x_{DO25}; y_{DO25}; z_{DO25}) which are the extended Freundlich adsorption constants for RBB and DO25 in the mixed dye solution.

$$q_{eRBB} = \frac{k_{RBB} C_{eRBB}^{1/(n_{RBB}+x_{RBB})}}{C_{eRBB}^{x_{RBB}+y_{RBB}} C_{eDO25}^{z_{RBB}}} \quad (7)$$

$$q_{eDO25} = \frac{k_{DO25} C_{eDO25}^{1/(n_{DO25}+x_{DO25})}}{C_{eDO25}^{x_{DO25}+y_{DO25}} C_{eRBB}^{z_{DO25}}} \quad (8)$$

k_{RBB}, k_{DO25} and n_{RBB}, n_{DO25} are the Freundlich isotherm parameters derived from the corresponding individual Freundlich isotherm equations for RBB and DO25.

Table 2 Effect of initial concentration of DO25 on dye uptake on ATRM in the absence and presence of RBB with ATRM dosage of 0.88 g/L (optimum conditions for DO25: temperature 37 °C, pH 4)

Initial concentration, DO25 (mg/L)	Initial concentration, RBB (mg/L)	C_e, DO25 (mg/L)	C_e, RBB (mg/L)	q_e, DO25 (mg/g)	q_e, RBB (mg/g)
130	0	4	–	143.2	–
150	0	9	–	160.2	–
170	0	20	–	170.5	–
130	50	51.76	18.85	89	35
150	50	70	24.6	90.8	29
170	50	85.2	25.9	96.4	27
130	70	59.45	32	80	43
150	70	75	37.8	85	37
170	70	92.7	40.35	88	34
130	90	64	48	75.8	48
150	90	87.85	52.15	71	43
170	90	101.15	56.35	78	38

The validity of these models were tested using the good-ness of fit in terms of R^2 values, and the model parameters (x, y and z for Extended Freundlich isotherm model and η for modified Langmuir isotherm model) were evaluated.

Results and discussion

Effect of initial dye concentration on the adsorption of RBB and DO25 from mixed dye aqueous solution using ATRM

The effect of presence of one dye on adsorption of another dye on ATRM in aqueous solution of RBB-DO25 dye mixture system was studied. The adsorption studies were carried out at optimum conditions obtained through response surface methodology (Ratnamala 2015) for each of the dyes. Table 1 presents the values of equilibrium concentrations, adsorption capacities and percentage adsorption of RBB and DO25 obtained from the batch adsorption experiments conducted at different initial concentrations of RBB (50, 70 and 90 mg/L) and fixed initial DO25 concentrations (130, 150 and 170 mg/L) at optimum conditions of pH and temperature (initial pH 1 and temperature 32 °C) for maximum adsorption of RBB with a constant ATRM dosage of 2.05 g/L. Table 2 presents concentrations, adsorption capacities and percentage adsorption of RBB and DO25 at equilibrium obtained from batch adsorption experiments conducted at different initial concentrations of DO25 (130, 150 and 170 mg/L) and at fixed initial RBB concentrations (50, 70 and 90 mg/L) at optimum conditions of pH and temperature (initial pH 4 and temperature 37 °C) for maximum adsorption of DO25 with a constant ATRM dosage of 0.88 g/L.

The results in Table 1 indicate the increase in adsorption (uptake) capacities (q_e) of ATRM for RBB from 24 to 43 mg/g, with increase in the initial RBB concentration from 50 to 90 mg/L, in the absence of DO25 in solution. But in the presence of 130 mg/L of initial DO25, the uptake capacities of ATRM for RBB increased from 20 to 32 mg/g in the similar concentration range of 50 to 90 mg/L RBB. The RBB uptake with 50 mg/L initial concentration of RBB was 24 mg/g in the absence of DO25. However, on addition of DO25 at 130 mg/L, the uptake capacity of ATRM for RBB has decreased from 24 to 20 mg/g. The values q_e for RBB decreased with increase in DO25 concentration in mixed dye aqueous solution.

The uptake capacities of ATRM for RBB increased from 20 to 32 mg/g with an increase in RBB initial concentration from 50 to 90 mg/L in the presence of DO25 at 130 mg/L. The uptake capacities of ATRM for DO25 decreased from 44 to 34 mg/g with the increase in RBB initial concentration from 50 to 90 mg/L in the presence of DO25 at 130 mg/L. It can be also observed from Table 1 that the values of q_e for DO25 decreased with increase in RBB concentration.

Similar results were also obtained at optimum conditions for DO25 with fixed initial RBB concentration at different initial concentrations of DO25 (130, 150 and 170 mg/L). As it can be observed from Table 2, the adsorption capacities (q_e) of ATRM for DO25 increased from 143 to 170 mg/g, with the increase in initial DO25 concentration from 130 to 170 mg/L, in the absence of RBB in solution. But in the presence of 50 mg/L initial RBB, the adsorption capacities of ATRM for DO25 increased from 89 to 96 mg/g in the similar concentration range of DO25. It can be also observed from Table 2 that the values q_e for DO25 have decreased with increase in RBB concentration.

As observed from Tables 1 and 2, the uptake capacities of ATRM for RBB and DO25 are the maximum when these dyes are present solely in solution. But the uptake capacities decreased with the addition of second dye and also with the increased concentrations of the second dye. It shows the inhibitory effect of one dye on the adsorption of the other dye. In the mixed dye systems, when the initial concentration of the other dye was increased, the adsorption capacity of ATRM for the target dye has decreased. This trend was observed with both RBB and DO25 at both the optimum conditions. The equilibrium uptakes of RBB and DO25 in the aqueous solution of binary dye mixture decreased because of the presence of the other dye due to interaction between these dyes. The individual uptake for RBB and DO25 and total uptakes in mixed dye solution at optimum conditions for RBB are shown in Table 3. Table 3 also presents the dye uptake on ATRM from single dye aqueous solution. q_{total} shown in Table 3 is the sum of the individual dye uptake for RBB and DO25 from mixed dye solution.

As observed from Table 3, total uptake capacity of ATRM calculated for single dye aqueous solution of RBB (50 mg/L) and single dye aqueous solution of DO25 (130 mg/L) is 146 mg/g (24 mg/g for RBB from aqueous solution of RBB + 122 mg/g for DO25 from aqueous solution of DO25) but the total uptake capacity of ATRM for RBB and DO25 from the aqueous solution of mixture of these dyes (50 mg/L RBB and 130 mg/L DO25) is 64 mg/g (20 mg/g (RBB) + 44 mg/g (DO25)). Similar results were also observed in the case of experiments carried out at DO25 optimized conditions. As observed from Table 4, total uptake capacity of ATRM calculated for single dye aqueous solution of RBB (50 mg/L) and single dye aqueous solution of DO25 (130 mg/L) is 189.8 mg/g (46.6 mg/g for RBB from aqueous solution of RBB + 143.2 mg/g for DO25 from aqueous solution of DO25), but the total uptake capacity of ATRM for RBB and DO25 from the aqueous solution of mixture of these dyes (50 mg/L RBB and 130 mg/L DO25) from the mixed dye aqueous solution is 124 mg/g (35 mg/g (RBB) + 89 mg/g (DO25)).

Thus, it can be observed from Tables 3 and 4 that the summed dye uptake capacity of both the dyes on ATRM from

Table 3 Effect of initial concentration of RBB on total uptake of the dyes on ATRM in the absence and presence of DO25 at ATRM dosage of 2.05 g/L (RBB optimum conditions: temperature 31.65 °C, pH 1)

Initial concentration, RBB (mg/L)	Initial concentration, DO25 (mg/L)	q_e, RBB (mg/g)	q_e, DO25 (mg/g)	q_{total} (mg/g)
50	0	24	–	24
70	0	34	–	34
90	0	43	–	43
0	130	–	122	122
0	150	–	133	133
0	150	–	148	148
50	130	20	44	64
70	130	26	41	67
90	130	32	34	66
50	150	18	46	64
70	150	25	43	68
90	150	30	38	68
50	170	16	50	66
70	170	23	48	71
90	170	28	42	70

the mixed dye aqueous solution is lower than the sum of the individual dye uptake capacities from a single dye aqueous solution which indicates that there is an antagonistic effect of dyes in the adsorption process. This study revealed that RBB and DO25 exhibit antagonistic effect in their adsorption on ATRM from the aqueous solution of mixture of these dyes, thereby resulting in a lower uptake capacity from the mixed dye aqueous solution. The presence of one dye inhibited the adsorption of the other dye due to competitive adsorption.

The interactions of these dyes have mutually inhibited the uptake or adsorption capacity. The reduced capacities could be attributed to a combination of a number of factors. These include the following: (i) interaction between the dyes in solution; (ii) change in the adsorbent surface charge due to adsorption; (iii) competitive adsorption between the dyes for active sites on the adsorbent surface which can bind both RBB and DO25 where displacement effects replace the other dye from the adsorption sites (Allen et al. 1994; Hassanein and Koumanova 2012); and (iv) when one dye gets adsorbed on its active site, its non-functional group may block the active sites for the adsorption of other dyes.

Similar observations of a decrease in adsorption capacities of one dye in the presence of another dye have also been observed by Douissa et al. (2014) in their studies on the

Table 4 Effect of initial concentration of DO25 on total uptake of the dyes on ATRM in the absence and presence of RBB (DO25 optimum conditions: dosage 0.88 g/L, temperature 36.78 °C, pH 4)

Initial concentration, DO25 (mg/L)	Initial concentration, RBB (mg/L)	q_e, DO25 (mg/g)	q_e, RBB (mg/g)	q_{total} (mg/g)
130	0	143.2	–	143.2
150	0	160.2	–	160.2
170	0	170.5	–	170.5
0	50	–	46.6	46.6
0	70	–	63.6	63.6
0	90	–	77.7	77.7
130	50	89	35	124
150	50	90.8	29	119.8
170	50	96.4	27	123.4
130	70	80	43	123
150	70	85	37	122
170	70	88	34	122
130	90	75.8	48	123.8
150	90	71	43	114
170	90	78	38	116

adsorption of Acid Blue 25 (AB) and Direct Blue 86 (DB) using cellulose; by Turabik (2008) in the adsorption of Red 46 and Basic Yellow 28 using bentonite; by Al-Degs et al. (2009) in adsorption of reactive dyes using activated carbon; by Hassanein and Koumanova (2012) in adsorption of Basic Blue 3 (BB 3) and Basic Red 18 (BR 18) onto wheat straw (WS); by Regti et al. (2016) in the adsorption of Basic Blue 41 and Basic Yellow 28 using activated carbon; and by Gandhimathi et al. (2012) in the adsorption of Crystal Violet (CV), Methylene Blue (MB) and Malachite Green (MG) suing bottom ash as an adsorbent.

Figure 6 presents the effect of varying initial RBB concentrations at fixed initial DO25 concentration on percentage adsorption of RBB at RBB optimized conditions. It can be observed from Fig. 6 that the percentage adsorption of RBB decreases with increase in RBB concentration at fixed DO25 concentration. The percentage adsorption of RBB has also decreased with the increase in DO25 concentration at fixed RBB concentration.

Figure 7 presents the effect of varying the initial DO25 concentrations at fixed initial RBB concentration on percentage adsorption of DO25 at optimum conditions for RBB. It is observed from Fig. 7 that the percentage adsorption of DO25 has decreased with increase in DO 25 concentration at fixed RBB concentration and decreased with RBB concentration at a fixed DO25 concentration at the optimum conditions for RBB.

The similar experiments were also performed at optimum conditions for DO25. The variation in percentage adsorption of DO25 with initial DO25 concentrations in the absence and presence of RBB at optimum conditions for DO25 is as shown in Fig. 8. The variation in percentage adsorption of RBB with initial RBB concentrations in the absence and presence of DO25 at optimum conditions for DO25 is as shown in Fig. 9.

It is observed from Figs. 6, 7, 8 and 9 that the percentage adsorption of RBB and DO25 is the maximum when these dyes are present solely in solution. However, the percentage adsorption decreased with the addition of the other dye and also with the increased concentrations of the other dye. These results are similar for both RBB and DO25 optimum conditions. It shows the inhibitory effect of one dye on the adsorption of the other dye.
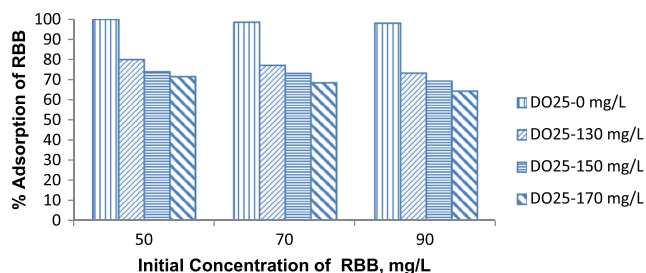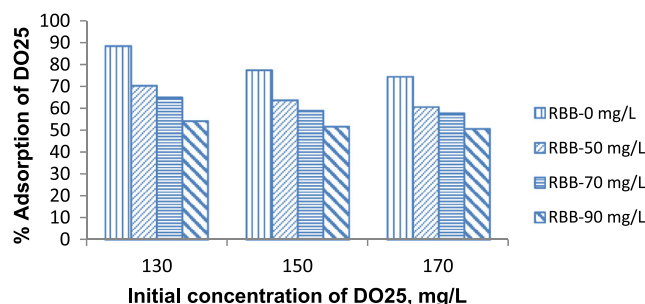

Fig. 7 Percentage adsorption of DO25 vs initial DO25 concentration at different RBB concentration at optimum conditions for RBB

The binary dye aqueous solution exhibited antagonistic (competitive) effect in adsorption of each of the dyes on ATRM, thereby resulting in a lower percentage adsorption as compared to adsorption from single dye aqueous solution. The percentage adsorption of RBB and DO25 in the binary mixture decreased because of the presence of the other dye due to the antagonistic interaction between these dyes. Similar results were also reported for the adsorption of Basic Red 46 and Basic Yellow 28, from aqueous solutions onto bentonite by Turabik (2008).

At optimum conditions for RBB adsorption, the percentage adsorption of RBB was higher as compared to the adsorption of DO25 dye in mixed dye system. Thus, the optimum conditions favoured the adsorption of RBB than that of DO25 from mixed dye system. Similar observations were also made when the batch experiments were carried out with aqueous solution of mixture of dyes in similar concentration combinations at optimum conditions for DO25. The percentage adsorption of DO25 is higher than that of RBB at DO25 optimum conditions.

For the adsorption of dyes, it is known that molecular characteristics of dyes and physico-chemical properties of adsorbents can affect the adsorption mechanism. Noroozi et al. (2008) have reported that the functional groups of dye and adsorbent play major role in adsorption. It may be said that, in a system with mixture of two dyes, at the optimum condition of one of the dyes (say dye1), as the rate of adsorption of dye 1 is higher than that of dye 2,

Fig. 6 Percentage adsorption of RBB vs initial RBB concentration at different DO25 concentration at optimum conditions for RBB
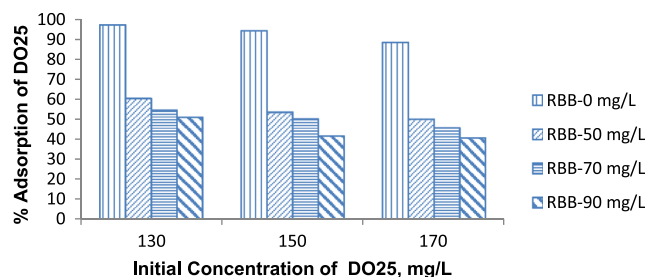

Fig. 8 Percentage adsorption of DO25 vs initial DO25 concentration at different RBB concentrations at optimum conditions for DO25
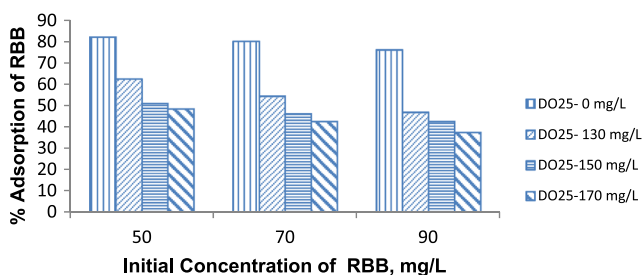
Fig. 9 Percentage adsorption of RBB vs initial RBB concentration at different DO25 concentrations at optimum conditions for DO25

dye 1 may be adsorbed on the surface faster as compared to dye 2. Once the functional group of dye 1 gets bound on to the surface of ATRM, the other non-functional part of the dye molecules may block the active sites for dye 2 on ATRM. This may be the reason for the lower percentage adsorption of dye 2 in the presence of dye 1 under optimum conditions of dye 1 or vice versa. For example, once the functional group of RBB gets bound on to the surface of ATRM due to adsorption, the other non-functional part of the RBB molecules may block the active sites for DO25 available in the neighbourhood on ATRM. This may be the reason for reduction of percentage adsorption and dye uptake of DO25 in the presence of RBB at optimum conditions of RBB.

Percentage adsorption and uptake of RBB are higher at RBB optimum conditions and those for DO25 are high at optimum conditions for DO25. However, RBB optimum conditions may be suitably adopted for treating the water contaminated with mixture of RBB and DO25 owing to favourably higher percentage adsorption of both the dyes taking place at optimum conditions of RBB.

Adsorption equilibrium for mixture of dyes (RBB and DO25) on ATRM

The equilibrium data obtained in the multi-component system (mixed dye aqueous solution) indicated how these components affected each others' adsorption equilibrium as compared to the results from single-component adsorption situation. In the present work in order to determine the valid isotherm model for adsorption of dyes from the aqueous solution of mixture of RBB and DO25 using ATRM, two different approaches were used: (i) testing of monocomponent models with the mixed dye system equilibrium data and (ii) testing of multi-component models with mixed dye system equilibrium data.

To check the consistency of the adsorption isotherm models and for the comparison between the models to determine the model with the best fit, average relative error (ARE) and root mean square error (RMSE) values were calculated using Eqs. (9) and (10) and compared in

addition to the determination of the coefficient of determination (R^2).

$$\mathrm{ARE}(\%) = \frac{100}{n} \sum_{i=1}^{n} \left[\frac{\left| q_{e,\exp} - q_{e,\mathrm{cal}} \right|}{q_{e,\exp}} \right]_i \qquad (9)$$

$$RMSE = \sqrt{\frac{\sum \left(q_{e,\exp} - q_{e,\mathrm{cal}} \right)^2}{n}} \qquad (10)$$

where $q_{e,\exp}$ and $q_{e,\mathrm{cal}}$ represent the amount of dye adsorbed per unit mass of the adsorbent (mg g^{-1}) at equilibrium determined experimentally and calculated, respectively. n is the number of observations in the regression model.

Application of monocomponent adsorption models to equilibrium data for aqueous solution of mixture of dyes

The single component adsorption isotherms can be applied to multi-component mixture by neglecting the effect of the other component. The studies on adsorption of RBB and DO25 on to ATRM from aqueous solution of binary dye mixtures were conducted. Thus, batch experiments were conducted by varying the initial concentration of the studied dye (dye 1) by keeping the initial concentration of the other dye (dye 2) constant at optimized conditions for each of the dyes.

The equilibrium concentrations and uptake obtained by experiments conducted with fixed DO25 concentration by varying RBB concentration at optimum conditions for RBB (Table 1) were fitted on to single component Langmuir Eq. (3) and Freundlich isotherm Eq. (4) models. The isotherm analysis was carried out at different initial concentrations of RBB (50, 70, 90 and 110 mg/L) constant DO25 concentrations (130, 150 and 170 mg/L) at optimum conditions for RBB. The experiments were also carried out in the absence of DO25.

Similarly, the equilibrium concentrations and uptake obtained by experiments conducted with fixed RBB concentration by varying DO25 concentration at optimum conditions for DO25 (Table 2) were also fitted on to Langmuir Eq. (3) and Freundlich isotherm Eq. (4) models. The isotherm analysis was carried out at different initial concentrations of DO25 (130, 150, 170 and 190 mg/L), in the absence of RBB (0 mg/L) and in the presence of fixed RBB concentrations (50, 70 and 90 mg/L) at optimum conditions for DO25.

The Langmuir isotherm constants were calculated from the slope and intercept of linearized plot ($1/q_e$ vs $1/C_e$) of Langmuir isotherm for each condition. The Freundlich isotherm constants were calculated from the slope and intercept of the linearized plot (ln q_e vs ln C_e) of Freundlich isotherm for each condition. The values of R^2, ARE and RMSE along with isotherms parameters for both the isotherms for RBB adsorption in absence and presence of DO25 at optimum conditions

Table 5 Effect of initial DO25 concentration on monocomponent isotherm parameters for RBB adsorption on ATRM at optimum conditions for RBB

Initial concentration of RBB (mg/L)	Initial concentration of DO25 (mg/L)	Langmuir model					Freundlich model				
		Qo (mg/g)	b	R^2	RMSE	ARE	k (mg/g)	n	R^2	RMSE	ARE
50	0	111	1.25	0.98	0.021	4.3	24.1	4.6	0.94	0.12	5.7
70											
90											
110											
50	130	52	0.68	0.99	0.08	3.4	7.4	2.13	0.93	0.094	4.1
70											
90											
110											
50	150	47	0.59	0.98	0.14	3.7	6.3	1.17	0.94	0.25	4.8
70											
90											
110											
50	170	40	0.46	0.97	0.22	2.34	5.25	2	0.95	0.39	3.5
70											
90											
110											

for RBB are presented in Table 5. Similarly, the R^2, ARE and RMSE values along with the isotherm parameters for DO25 adsorption, in the absence and presence of RBB at optimum conditions for DO25, are presented in Table 6. The Freundlich constants (k and n) and Langmuir isotherm parameters (Qo and b) were calculated for the adsorption of RBB and DO25 dyes from single and binary dye mixture solutions neglecting the interaction of other dye at optimized conditions for both RBB and DO25 and are presented in Tables 5 and 6. As observed from Tables 5 and 6, the values of R^2 being larger

and ARE and RMSE being smaller, the adsorption equilibrium for RBB for all the initial DO25 concentrations and the adsorption equilibrium for DO25 for all the initial DO 25 or RBB concentrations fitted the Langmuir monocomponent model better than the Freundlich monocomponent model.

As it can be observed, from Table 5, the maximum monolayer adsorption capacity (Qo) of ATRM for RBB is 111 mg/g in the absence of DO25 and then decreased from 111 to 40 mg/g with increase in DO25 concentration up to 170 mg/L. The same trends were observed at optimum conditions for

Table 6 Effect of initial RBB concentration on monocomponent isotherm parameters for DO25 adsorption on ATRM at optimum conditions for DO25

Initial concentration of DO25 (mg/L)	Initial concentration of RBB (mg/L)	Langmuir model					Freundlich model				
		Qo (mg/g)	b	R^2	RMSE	ARE	K (mg/g)	n	R^2	RMSE	ARE
130	0	116	1.5	0.95	0.0012	4.2	93	9.17	0.92	0.08	5.1
150											
170											
190											
130	50	95	0.04	0.96	0.09	3.4	64.7	3.74	0.93	0.12	4.0
150											
170											
190											
130	70	87.8	0.03	0.99	0.15	4.6	56.7	3.62	0.93	0.29	5.6
150											
170											
190											
130	90	68	0.03	0.98	0.22	2.5	54.2	3.44	0.94	0.31	3.2
150											
170											
190											

Table 7 Multi-component isotherm parameters of modified Langmuir adsorption and extended Freundlich isotherm models for simultaneous adsorption of RBB and DO25 onto ATRM

	Component	Modified Langmuir model parameters					Extended Freundlich model parameters					
		η_1	η_2	R^2	ARE	RMSE	x	y	z	R^2	ARE	RMSE
RBB optimum conditions (pH = 1, dosage = 2.05 g/L, temperature 31.6 °C)	RBB (1:RBB; 2:DO25)	3.33	1.11	0.93	8.01	2.04	0.0005	0.0001	0.4	0.63	16.9	4.09
	DO25 (1:DO25; 2: RBB)	2.1	0.83	0.84	4.92	2.44	0.019	0.106	0.302	0.61	6.15	2.94
DO25 optimum conditions pH = 4, dosage = 0.88 g/L, temperature 36.78 °C)	RBB (1:RBB; 2:DO25)	1.61	1	0.88	3.51	2.17	0.0003	0.0001	0.33	0.78	9.7	3.66
	DO25 (1:DO25; : RBB)	0.181	1	0.95	6.92	2.34	0.0001	0.0001	0.20	0.8	8.34	2.98

DO25 dye. From Table 6, it can be observed that maximum adsorption capacity of ATRM for DO25 is 116 mg/g in the absence of RBB and then decreased from 116 to 68 with increase in RBB concentration up to 90 mg/L. From Table 5, it can be observed that the k value for RBB is 24.1 mg/g in the absence of DO25, but decreased to 7.4 mg/g in the presence DO25 at 130 mg/L. Similarly from Table 6, it is observed that k value for DO25 is 93 mg/g in the absence of RBB, but decreased to 64.7 mg/g in the presence RBB at 50 mg/L. The k values significantly decreased in the presence of the other dye in the solution with increased concentration, indicating that the adsorption intensity of ATRM for each component in binary dye systems decreased with the increase in concentration of the other dye.

The decrease in value of n with the increase in concentration of the other dye indicates that the adsorption of the dye under study is less favoured in the presence of increasing concentrations of the other dye. The value of n, which is significantly higher than unity, indicated that both RBB and DO25 dyes are favourably adsorbed on ATRM. Comparison of the maximum adsorption capacity from single dye solutions to that of binary dye solutions for both RBB and DO25 (Tables 5 and 6) shows that the maximum adsorption capacity for any given dye decreased with the presence of the other dye and also with the increase in the concentration of the other dye.

Generally, the adsorption capacities of each individual dye are proportionally less in the presence of another dye. This can be attributed to the interaction between the dyes on the solid surface, with non-equal competition attributed to the heterogeneity of adsorbent surface. Factors that affect the adsorption preference of a adsorbent for different kinds of adsorbates may be related to the characteristics of the binding sites (e.g. functional groups, structure, surface properties), the properties of the adsorbates (e.g. concentration, ionic size, ionic weight, molecular structure, ionic nature or standard reduction potential) and solution chemistry (e.g. pH, ionic strength). It is difficult to determine which factors affect the selective adsorption of ATRM. For that reason, the observed results may be

the consequence of combination of all the above factors (Turabik 2008).

It was found that monocomponent Langmuir model describes the adsorption of RBB and DO25 from mixed dye aqueous systems. However, monocomponent Langmuir model is applicable only at fixed initial concentration of the other dye. This appears to be a limitation in applicability of this model for mixed dye adsorption system.

Application of multi-component adsorption models to equilibrium data in mixed dye solution

The limitation of the monocomponent models can overcome by using multi-component adsorption equilibrium models which can be used to predict the equilibrium uptake of one dye at specified equilibrium concentrations of both the dyes, thus making it more generic in application. The equilibrium adsorption data (Tables 1 and 2) from mixed dye solution studies were then fitted onto multi-component models. Simultaneous adsorption of RBB and DO25 onto ATRM from binary mixture was investigated by conducting batch experiments at optimum conditions for each the dyes, and the data were fitted on to the multi-component modified Langmuir
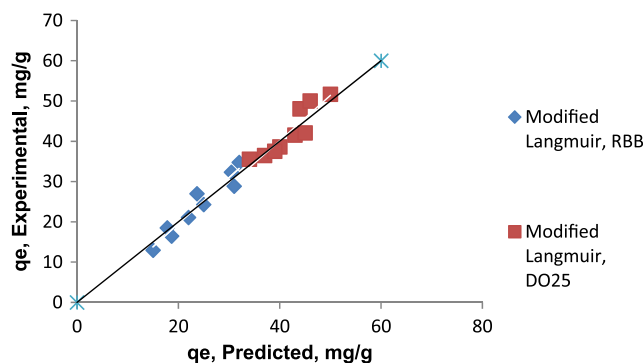

Fig. 10 Comparison of experimental and predicted q_e values from modified Langmuir model for adsorption of RBB and DO25 from mixed dye aqueous solutions at optimum conditions for RBB
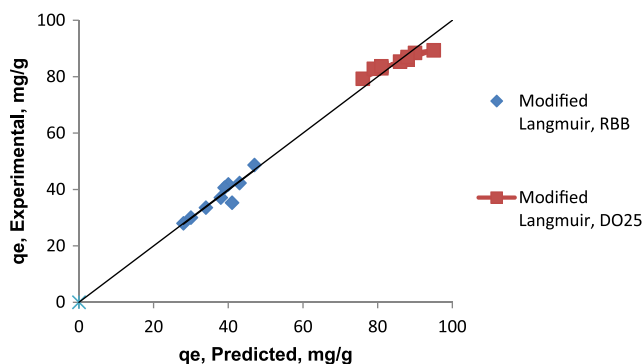
Fig. 11 Comparison of the experimental and predicted q_e values from modified Langmuir model for adsorption of RBB and DO25 from mixed dye aqueous solutions at optimum conditions for DO25

model Eqs. (5) and (6) and extended Freundlich Eqs. (7) and (8) isotherm models.

Using the monocomponent Langmuir constants (Q_o and b) and Freundlich constants (k and n) for each of the dyes with single dye solution given in Tables 5 and 6, the multicomponent modified Langmuir and extended Freundlich isotherm parameters were evaluated from the batch experimental data conducted at optimum conditions for RBB and optimum conditions for DO25 (Table 7). The model parameters at optimized conditions for RBB and DO25 adsorption, ARE, RMSE and the R^2 values are presented in Table 7.

The R^2 values obtained with modified Langmuir model are higher, and RMSE and ARE values are lower as compared to those obtained with extended Freundlich model as shown in Table 7, both under RBB optimized and DO25 optimized conditions. The modified Langmuir model fitted the data on adsorption of RBB and DO25 from mixed dye solutions reasonably well as compared to the extended Freundlich model as observed in Figs. 10 and 11 under the optimum conditions for RBB and DO25 dyes on ATRM, respectively. The better fit of the equilibrium data with modified Langmuir model as compared to extended Freundlich model suggests that the adsorption equilibrium for RBB-DO25-ATRM may better be described by modified Langmuir isotherm model.

Conclusions

In the present study, the adsorption of RBB and DO25 from the aqueous solutions of single dyes and mixture of the dyes on ATRM was studied. A method for spectrophotometric analysis of RBB and DO25 in aqueous solution of the mixture of these dyes was developed based on first-order derivative method, as these dyes were found to interfere with each other during the analysis by the conventional zero-order spectral technique. The adsorption of RBB on ATRM was favoured as compared to that of DO25. It was found that the adsorption of a dye was less favoured with increase in concentration of

the other dye and adsorption capacity of ATRM for a dye decreased with increasing concentration of the other dye. Thus, it is concluded that RBB and DO25 dyes exhibit antagonistic effect on adsorption onto ATRM. The adsorption of RBB was favoured at RBB optimum conditions and DO25 adsorption was favoured at optimum conditions for DO25 from the mixed dye aqueous solutions. However, RBB optimum conditions may be suitably adopted for treating water contaminated with mixture of RBB and DO25 owing to favourably higher percentage adsorption of both the dyes taking place at optimum conditions of RBB. It was found that monocomponent Langmuir model describes the adsorption of RBB and DO25 from mixed dye aqueous systems. However, Langmuir model being a single component model may be applicable only at fixed initial concentration of the other dye. This appears to be a limitation in applicability of this model for mixed dye adsorption system. It was found that the modified multi-component Langmuir model is applicable for prediction of the equilibrium data for adsorption of RBB and DO25 from mixed dye aqueous solutions and these models can be used to predict the equilibrium uptake of one dye at specified equilibrium concentrations of both the dyes, thus making it more generic in application.

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