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Competitive adsorption of reactive dyes from solution: Equilibrium isotherm studies in single and multisolute systems

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Abstract

Experimental data of the adsorption of reactive dyestuffs onto Filtrasorb 400 activated carbon (FS400) were determined in an equilibrium isotherm study. As most industrial wastewater contains more than one pollutant, an investigation into the effect of multisolute systems (using the unhydrolysed form of the reactive dyes) on the adsorption capacity was undertaken. Equilibrium isotherm models were employed to describe the adsorption capacities of single, binary and ternary dye solutions. The results of these analyses showed that adsorption of reactive dyes from single and multisolute systems can be successfully described by Langmuir, and Redlich–Peterson equilibrium isotherm models. Experimental data indicated that competitive adsorption for active sites on the carbon surface results in a reduction in the overall uptake capacity of the reactive dyes investigated.

Keywords: Reactive dyes; Competitive adsorption; Langmuir isotherm

1. Introduction

Waste effluent from the textile industry can be particularly problematic due to the presence of colour in the final effluent. This colour on entering the waterways is highly visible and thus undesirable. Conventional treatment facilities are often unable to remove certain forms of colour, particularly arising from reactive dyes due to their high solubility and low biodegradability. The failure of conventional physiochemical methods as a technique for treating reactive dye waste could be overcome by adsorption. Hence, adsorption is recommended as a viable means for reactive dye removal [1,2].

Reactive dyes are characterised by nitrogen-to-nitrogen double bonds, azo bonds (N=N), and used mainly for dyeing cellulose fibres. The colour of the azo dyes is due to this azo bond and associated chromophores [3]. The dyes are first absorbed onto the cellulose and then react with the fibre. The reaction occurs by the formation of a covalent bond between the dye molecule and the fibre. The reactive systems of these dyes react with ionised hydroxyl groups on the cellulose substrate [4]. However, hydroxyl ions present in the dye bath due to alkaline dyeing conditions compete with the cellulose substrate, resulting in a percentage of hydrolysed dyes which can no longer react with the fibre [5] and [4].

Activated carbon adsorption is widely used in the chemical process industries and is playing important role in cleaning up plant effluent and municipal wastewater. Within literature a numerous number of research papers have considered adsorption processes for single component systems. However, due to complexity of the textile effluent and the variability of the dyeing process little successes have been reported in using this technique as a full scale process to decolourise textile wastewater [1,6–9]. Hence, this study was undertaken to address the problems associated with multi component adsorption from aqueous solutions. This is essential for accurate design of adsorption systems as the effect of multicomponent interactions in the process effluent may cause deterioration in the adsorption capacity of activated carbon for dyestuffs.

2. Experimental

2.1. Carbon and dyes

Filtrasorb 400 activated carbon (FS400) was used as obtained from manufacturers (Chemviron) without any chemical or phys-

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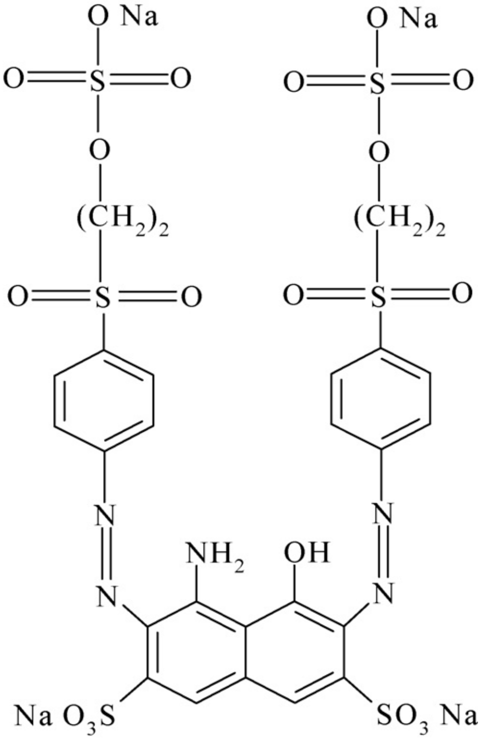

Fig. 1. Chemical structure of reactive black B.

ical treatment. The following surface properties were provided: surface area 1100 $m^2 g^{-1}$, bulk density 0.425 $g cm^{-3}$, moisture content 2.0% and iodine number 1050 $mg g^{-1}$. Three reactive dyes were used for this investigation; namely, Remazol reactive yellow (RRY), Remazol reactive black (RRB) and Remazol reactive red (RRR) supplied from (Bayer, Frankfurt, Germany). The chemical structure of these dyes is protected by manufacturers and only that of reactive black is given (Fig. 1). The pH of the entire dye concentration for all three dyes is less than 6. The working dye solutions were prepared from standard concentrated solutions (33–55%, w/w) as received from the manufacturer. The dyes under investigation were completely soluble in water and show moderate pH solution values (4.5–5.0) in distilled water at 1000 $mg dm^{-3}$ concentration (the upper range of adsorption isotherms). Standard solutions were prepared and the λ_{max} was determined for each dye. Values of 410, 520, 597 nm were obtained for R. yellow, R. red and R. black, respectively.

2.2. Isotherms of single and mixed dye systems

Concentration variation equilibrium isotherms for single, binary and tertiary mixtures were carried out at $20 \pm 2\,°C$ by shaking 0.050 g of adsorbent in 50 cm^3 of an aqueous solution of pre-selected dye concentration range (0–1000 $mg dm^{-3}$) in sealed glass bottles in a temperature controlled shaker (L.H. Engineering Co. Ltd., England). The experimental conditions for adsorption tests were summarised in Table 1:

Table 1
Initial system conditions for equilibrium adsorption isotherms

Adsorption system	Carbon mass (g) (±0.001 g)	Dye initial concentration range (in $mg dm^{-3}$)
Y	0.050	Y: 0–1000
Y (with B)	0.050	Y: 0–500 B: 0–500 (1:1 ratio)
Y (with R)	0.050	Y: 0–500 R: 0–500 (1:1 ratio)
Y (with B & R)	0.050	Y: 0–333 B: 0–333 R: 0–333 (1:1:1 ratio)
B	0.050	B: 0–1000
B (with Y)	0.050	B: 0–500 Y: 0–500 (1:1 ratio)
B (with R)	0.050	B: 0–500 R: 0–500 (1:1 ratio)
B (with Y & R)	0.050	B: 0–333 Y: 0–333 R: 0–333 (1:1:1 ratio)
R	0.050	R: 0–1000
R (with Y)	0.050	R: 0–500 Y: 0–500 (1:1 ratio)
R (with B)	0.050	R: 0–500 B: 0–500 (1:1 ratio)
R (with Y & B)	0.050	R: 0–333 Y: 0–333 B: 0–333 (1:1:1 ratio)

Note: Y stands for RRY, B stands for RRB, and R stands for RRR. Y (with B) stands for the adsorption isotherm of reactive yellow in the presence of reactive black. All isotherms (nine isotherms) were conducted at 30 °C and pH 7.00, maximum initial concentration = 1000 $mg g^{-1}$.

Constant agitation (100 rpm) was maintained throughout the experiments. In order to determine when adsorption equilibrium had been reached, liquid phase samples were taken at intervals between 1 and 5 weeks. After 3 weeks of shaking samples were removed and filtered through 0.45 μm Millipore cellulose nitrate filters and subsequently analysed for post adsorption concentrations using a Unicam spectrophotometer at the maximum wavelength for each dye. The equilibrium concentrations were determined by converting the optical densities (densities above 1.00 were diluted) to concentration using a pre-determined linear calibration graph. All isotherms were done in duplicate and results are reported as an average of these. Blanks were also included. These procedures gave reproducible results and were found to agree within 4%. The method described by Al-Duri et al. [10] was used to estimate the concentration of dyes in binary and tertiary systems. The absorptivity constant for each dye was determined from the absorbance measurements of the dye at specific concentration. Concentration absorbance curves were then constructed by plotting absorbance of each single dye against dye concentration. The slope of the linear regression curves gave the value of the absorptivity coefficients for each dye at its wavelength of maximum absorption and at the wavelength of maximum absorption (absorption at λ_{max}) for the other two dyes. These constants were then used to determine the value of the unknown dye concentration for the three dyes in binary and tertiary mixtures by solving simultaneous linear equations.

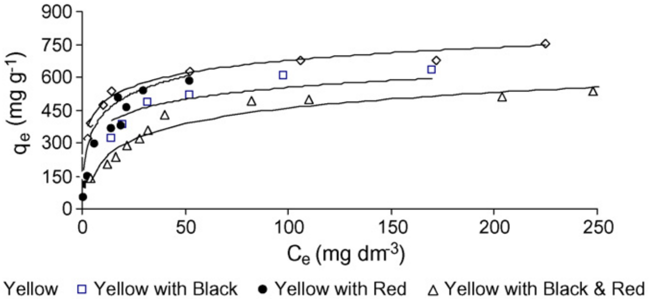

Fig. 2. Equilibrium adsorption isotherms for the adsorption of reactive yellow from single, binary, and ternary solutes systems onto FS400.

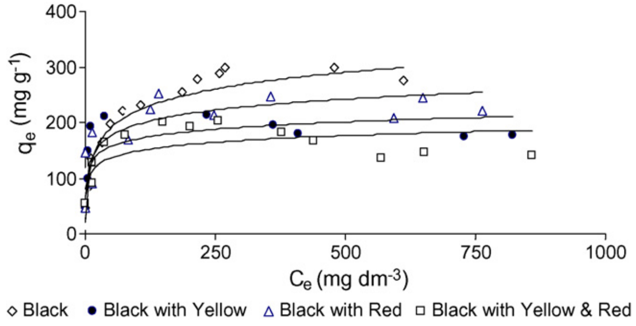

Fig. 3. Equilibrium adsorption isotherms for the adsorption of reactive black from single, binary, and ternary solutes systems onto FS400.

3. Results and discussion

3.1. *Adsorption of reactive dyes in single and multisolute solution*

In the application of adsorption for purification of wastewater the solution will normally be a mixture of many compounds rather than a single one. The interactions of these compounds may mutually enhance or mutually inhibit adsorption capacity [11].

In this study the effect of multisolute interactions on the capacity of activated carbon was investigated using binary and ternary mixtures of dyes having pre-fixed ratios. The initial results from these experiments are expressed as conventional plots of the liquid phase dye concentration versus solid phase dye concentration, as illustrated in Figs. 2–4. The adsorption data obtained were correlated to three commonly used equilibrium isotherm models: Langmuir (Eq. (1)); Freundlich (Eq. (2)); Redlich–Peterson (Eq. (3)) [12,13]:

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{a}{Q_{\max}} C_e \tag{1}$$

$$q_e = K_F C_e^{1/n} \tag{2}$$

$$q_e = \frac{K_R C_e}{1 + a_r C_e^b} \tag{3}$$

where C_e and q_e in Eqs. (1)–(3) are the solution and surface concentration for the dye, respectively. K_L and $Q_{\max}$ are Langmuir constants. K_F and n are Freundlich constants. K_R, a_r and b are Redlich–Peterson constants.

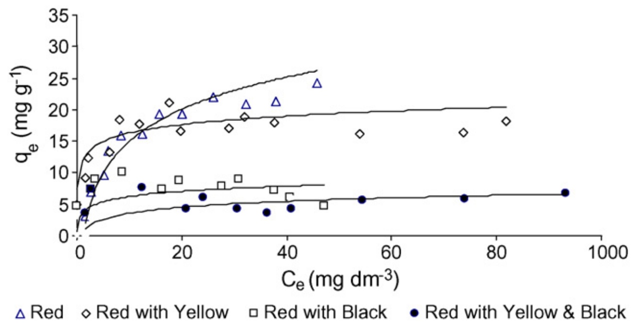

Fig. 4. Equilibrium adsorption isotherms for the adsorption of reactive red from single, binary, and ternary solutes systems onto FS400.

The models were each applied to adsorption data from single, binary and ternary systems. In adsorption in multisolute solutions, the above equations were applied to each solute neglecting the possible interference from other solute(s). The possible reduction in adsorption in multisolute solutions was evaluated by comparing the maximum adsorption from single solute solutions to that of multisolute solutions for each particular dye. It should be noted that any reduction in dye adsorption in binary and ternary systems were evaluated by comparison of the capacity in the single solute system with that of multisolute system. Such comparisons should only be made if the initial conditions are identical in single and multisolute systems. As illustrated in Table 1, the adsorption isotherms data in this study were determined under identical experimental conditions. The adsorption capacities for dyes in single and in multisolute systems are expressed by mass (mg g^{-1}) and rather than molar mass (mol g^{-1}) as the exact chemical structures of RRY and RRR are still to be released by the manufacturers. However, we are aware that it is more accurate to compare the capacities in terms of molar mass (mol g^{-1}) in competitive studies [13]. It should be noted that modified forms of Langmuir and Freundlich isotherm models, which describe competitive adsorption, have been used in this study [14]. Moreover, the isotherm models as described by Eqs. (1)–(3) have been used to simulate competitive adsorption systems [13,12,9].

The results of fitting of Eqs. (1)–(3) to adsorption data of single and multisolute systems are presented in Table 2. Table 2 also contains the maximum adsorption capacity (Q) of activated carbon for reactive dyes from single and multisolute solutions.

The activated carbon showed an uptake capacity of 714 mg g^{-1} for reactive yellow followed by 278 mg g^{-1} for reactive black and 213 mg g^{-1} for reactive red (Table 2). A reduction in individual dye adsorption capacity in multisolute mixtures is common in dye–carbon systems, although the extent of reduction varies with the type of dyes investigated [10,12,15]. In this study, for reactive yellow: a reduction of 16% in adsorption capacity was found in the presence of reactive black; a 17% reduction was found in the presence of reactive red; and a 17% reduction was found in the ternary system. However, a 42% reduction in adsorption capacity of reactive black in the presence of reactive yellow was found, and a 17% reduction in reactive black in the presence of reactive red. High competition

Table 2
Parameters of Langmuir, Redlich–Peterson and Freundlich equilibrium isotherm models

System	C_e[a] range (mg dm^3)	Q^1 (mg g^{-1})	K_L (dm^3 g^{-1})	r^2	K_R (dm^3 g^{-1})	a_r	b	r^2	K_F (dm^3 g^{-1})	n	r^2
Yellow single	0–225	714	196.08	0.995	196.08	0.28	0.99	0.998	303.46	0.17	0.932
Y with B	0–170	600	72.46	0.958	72.46	0.29	0.80	0.940	–	–	–
Y with R	1–55	590	204.10	0.952	–	–	–	–	–	–	–
Y with B & R	4–425	590	28.05	0.998	28.65	0.06	0.96	0.995	112.02	0.29	0.900
Black single	1–600	278	16.75	0.994	16.75	0.10	0.91	0.998	55.20	0.29	0.937
B with Y	1–800	160	24.04	0.997	24.04	0.02	1.33	0.988	–	–	–
B with R	1–750	230	46.73	0.991	46.73	0.18	1.02	0.991	–	–	–
B with Y & R	1–850	140	5.75	0.984	5.75	0.01	1.30	0.991	–	–	–
Red single	20–450	213	3.60	0.987	3.60	0.02	0.93	0.979	11.36	0.53	0.860
R with Y	1–800	185	42.55	0.993	42.55	0.41	0.91	0.984	–	–	–
R with B	1–470	80	4.22	0.955	4.22	0.57	1.40	0.965	–	–	–
R with Y & B	15–750	65	1.81	0.950	–	–	–	–	–	–	–

[1] Maximum adsorption (mg g^{-1}).

[a] Correlation analyses were made on the entire equilibrium concentration range (concentration range for all isotherms is: 0–1000 mg dm^{-3}. See Table 1 for experimental conditions).

for adsorption was observed when reactive black was adsorbed in the presence of the two other dyes; a reduction in capacity of 50% was found when compared to adsorption from single solute solution.

The data indicate that reactive black has a higher affinity for FS400 than reactive red, as the reduction in reactive red adsorption capacity was 62% in the presence of reactive black. A 70% reduction was obtained in adsorption capacity of reactive red simultaneously adsorbed with reactive yellow and black. The data indicate a low degree of competition between reactive yellow and reactive red; a 13% reduction in reactive red adsorption capacity was observed in the presence of reactive yellow. However, the data indicate that adsorption of reactive dyes from multisolute systems onto activated carbon utilizes more the active adsorption sites on the activated carbon. The mass of adsorbed reactive yellow, reactive black, and reactive red were 714, 278, and 213 mg g^{-1}, respectively in the single solute systems. The combined adsorbed mass of the three dyes in the ternary system was 795 mg g^{-1} (590 + 140 + 65 respectively), which is higher than the individual single solute systems. These phenomena, of increased total solid phase adsorbate concentration in multicomponent systems, were also found by previous investigators in an acid dye–activated carbon system [16].

The preferential adsorption of reactive yellow in binary and ternary systems may be due to intraparticle diffusion not being impeded to the same extent by the presence of other dyes. Generally, the adsorption capacities of each individual dye are proportionally less with another solute. This can be attributed in the main to the interaction between the dyes on the solid surface, with non-equal competition attributed to the heterogeneity of the carbon surface. Other factors may include the electrical repulsion of a dye from the carbon surface by other adsorbed dyes of similar charge, and the attraction of dyes to each other on the surface. In addition the dye with the higher saturation value (i.e., reactive yellow in this study) may effectively occupy most of the active sites hindering further adsorption of other dyes with possessing a lower affinity [7]. Allen et al. [12] considered the competitive adsorption of three basic (cationic) dyes. Their results showed that the adsorption capacity of an individual dye decreased in the presence of a second or a third dye. They reported that reduced capacities could be attributed to a combination of a number of factors. These include: (i) interaction between dyes in solution; (ii) change of the adsorbent surface charge due to adsorption; (iii) competitive adsorption between dyes for active sites on the carbon surface where displacement effects replace the other dyes from the adsorption sites.

Figs. 2–4 illustrate adsorption isotherms for each single dye, and adsorption isotherms for each dye in the multisolute systems (nine isotherms). The competitive isotherm data (having less regular shape than normal L-type isotherm) show clearly the interactive effect of the dyes on each other. In single component systems the adsorption isotherm curve rises steeply at low liquid phase concentration indicating complete adsorption with a plateau formed when the maximum adsorption capacity is achieved. However, in multicomponent adsorption (particularly multisolute adsorption systems: Figs. 3 and 4), a less regular isotherm shape is found, possibly indicating that the concentration of the dye being adsorbed increased and then decreased, i.e., a displacement effect. This may be due to reactive yellow having a displacement effect, effectively displacing and replacing the other dyes of lower carbon affinity from the adsorption sites [5,14,9]. This effect is evident in the adsorption capacity values reported for these reactive dyes in single and multicomponent systems (Table 2). It is noted, that a more regular isotherm shape (i.e., type L) was obtained for reactive yellow in comparison to reactive black and reactive red dye. This may indicate that reactive yellow displaces both dyes especially at low equilibrium concentration (Figs. 3 and 4).

3.2. Fitting adsorption data to adsorption models

Adsorption data of the three dyes in single and multisolute solutions were fitted to Langmuir, Freundlich, and Redlich–Peterson models (Eqs. (1)–(3)). Analysis of these models for describing adsorption behaviour of dyes in single and multisolute solutions was made by comparing correlation coefficients (r^2) generated by the linear regression of each model. Previous researchers have indicated that the modelling of multisolute (binary and ternary) adsorption systems can be successfully described by the Langmuir isotherm model where apparent dye displacement occurs [17]. The data in Table 2 agree with this previous research as high correlation coefficients were obtained for Langmuir analysis of the multicomponent reactive dye systems ($r^2 > 0.95$). Furthermore, it was found that the Redlich–Peterson isotherm model was also able to describe multisolute adsorption to a large extent ($r^2 > 0.94$, see Table 2).

Freundlich equation fitted adsorption data of single solute system to an moderate degree of accuracy (see Table 2). However, it has a limited application for describing multisolute adsorption systems. The correlation coefficients obtained for describing multisolute systems by Freundlich equation were very low ($r^2 < 0.50$). It is noted that the fitting of adsorption data using the three equilibrium isotherm models was made over the entire concentration range, which extends from few of ppm ($\mathrm{mg\,dm^{-3}}$) to hundreds of ppm in most isotherms. A higher correlation coefficient, r^2, could be obtained if the fitting analyses were made on certain concentration ranges within the complete concentration range. Allen et al. [12], divided the equilibrium concentration range into lower and higher ranges and applied Langmuir, Freundlich, and Redlich–Peterson on each concentration range. Bairthi [17] has shown that Langmuir model is more applicable to the adsorption of multisolute systems than Freundlich model. Allen and Brown [13], in contrast, successfully applied Freundlich equation to describe adsorption in multisolute systems. In this study the correlation coefficient, r^2, for the Langmuir isotherm model are higher compared to those obtained on applying the Freundlich and Redlich–Peterson models. This would support the assumption (within the Langmuir model) that the number of adsorption sites on activated carbon are limited and that the dye mixtures form a monomolecular layer on the adsorbent at saturation. It is noted that the r^2 values of the tertiary mixtures are higher for Langmuir than Freundlich, which lends further support to the theory that different dyes may not be adsorbing onto mutually common adsorption sites but that each dye may have selective adsorption sites [7].

4. Conclusions

FS400 activated carbon showed a high adsorption capacity for three reactive dyes from single and multicomponent solutions. It was found that equilibrium adsorption capacities decreased in multicomponent systems (as compared to single dye systems). Experimental data indicated that competitive adsorption for active sites on the carbon surface results in a reduction in the overall uptake capacity of the reactive dyes investigated. Experimental adsorption data from single, binary, and ternary systems were successfully described by the Langmuir and Redlich–Peterson equilibrium isotherm models, which may indicate that the number of adsorption sites available for dyes on activated carbon is limited, and that an adsorbate monolayer was established at saturation. The Freundlich equilibrium isotherm model had a limited success in describing adsorption of reactive dyes from multisolute systems onto activated carbon.

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