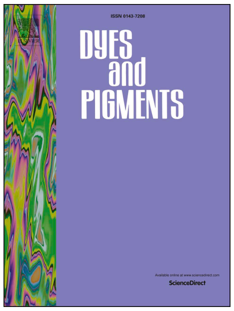
Article:

Burkinshaw, SM orcid.org/0000-0001-9940-1354 and Salihu, G (2019) The role of auxiliaries in the immersion dyeing of textile fibres: Part 6 analysis of conventional models that describe the manner by which inorganic electrolytes promote reactive dye uptake on cellulosic fibres. Dyes and Pigments, 161. pp. 595-604. ISSN 0143-7208

https://doi.org/10.1016/j.dyepig.2017.09.028



The role of auxiliaries in the immersion dyeing of textile fibres: Part 6 analysis of conventional models that describe the manner by which inorganic electrolytes promote reactive dye uptake on cellulosic fibres

Stephen M. Burkinshaw, George Salihu

PII: S0143-7208(17)31913-7

DOI: 10.1016/j.dyepig.2017.09.028

Reference: DYPI 6253

To appear in: *Dyes and Pigments*

Received Date: 10 August 2017

Revised Date: 8 September 2017

Accepted Date: 13 September 2017

Please cite this article as: Burkinshaw SM, Salihu G, The role of auxiliaries in the immersion dyeing of textile fibres: Part 6 analysis of conventional models that describe the manner by which inorganic electrolytes promote reactive dye uptake on cellulosic fibres, *Dyes and Pigments* (2017), doi: 10.1016/j.dyepig.2017.09.028.

The role of auxiliaries in the immersion dyeing of textile fibres: Part 6 analysis of conventional models that describe the manner by which inorganic electrolytes promote reactive dye uptake on cellulosic fibres

***Stephen M Burkinshaw and George Salihu**

s.m.burkinshaw@leeds.ac.uk; g.salihu@leeds.ac.uk

University of Leeds, Leeds, LS2 9JT, UK

*corresponding author

Abstract

An analysis is provided of the various models that have been proposed to account for the manner by which added NaCl or Na_2SO_4 promotes the uptake of reactive on cellulosic fibres. Although conventionally, mathematical interpretations of isothermal equilibrium dye adsorption data are employed to describe the mechanism by which reactive dye adsorption occurs, such an approach does not satisfactorily explain why reactive dyes display inherently low uptake on cellulosic fibres in the absence of added inorganic electrolyte, nor does it explain why added inorganic electrolyte is so effective in promoting dye uptake.

Highlights

- the role of inorganic electrolyte in reactive dye application is modelled
- interstitial water is used to show that added electrolyte reduces dye solubility
- added electrolyte promotes dye aggregation

keywords: dyeing cotton; dyeing auxiliaries; electrolyte; reactive dyes; salt-free dyeing

1 Introduction

This paper concerns the role of some of the auxiliaries that are used in the application of dyes to textile fibres from aqueous dyebaths using immersion processes. Although various types of auxiliary are available that offer different kinds of assistance to immersion dyeing processes, the manner by which many auxiliaries function is unclear (1). In view of the enduring popularity of cotton and other cellulosic fibres a critical analysis was undertaken (2) of published work relating to the role of the most important auxiliary utilised in the exhaust dyeing of cellulosic fibres with direct dyes, namely inorganic electrolyte (either NaCl or Na_2SO_4). This resulted in a theoretical model being devised to explain the role of added NaCl or Na_2SO_4 in the application of direct dyes (3). According to this model, which invoked the concept of interstitial water, the addition of inorganic electrolyte to the dyebath promotes dye aggregation which reduces the solubility of the dye in the dyebath, so that the inherent preference of the highly soluble dye to favour the aqueous phase shifts towards the fibre phase and, therefore, dye uptake is promoted; two equations were derived to interpret this theoretical model of direct dye adsorption (3). Subsequently, it was shown that the same theoretical model could also be used to explain the promotional effect which reducing the liquor ratio used for dyeing has on the uptake of direct dyes on cellulosic fibres (4). The two theoretical models were utilised to interpret the results obtained when three commercial grade direct dyes were applied to cotton using different liquor ratios in both the absence and presence of added NaCl (5). This latter study (5) demonstrated that because reducing the liquor ratio used for dyeing and adding inorganic electrolyte to a direct dye dyebath achieve the same outcome, namely promotion of direct dye uptake, it is possible to dye cotton to realistic depths of shade using direct dyes in the absence of added inorganic electrolyte through the use of very low liquor ratios.

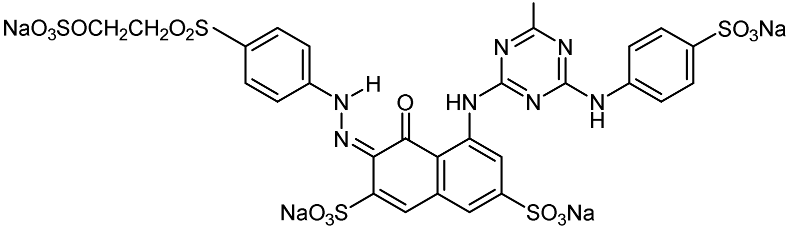
The objectives of the work described in this part of the paper were to clarify the manner by which added inorganic electrolyte influences reactive dye uptake on cellulosic substrates.

2 reactive dyes for cellulosic fibres

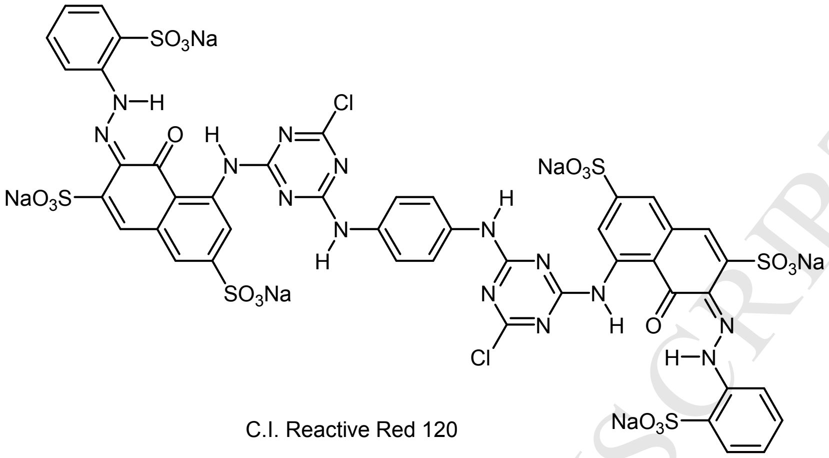
By way of introduction, reactive dyes are one of five classes of dye (direct dyes, sulphur dyes, vat dyes, azoic colorants and reactive dyes) that can be applied to cotton and other cellulosic fibres using immersion dyeing processes. Different conditions (pH, temperature, etc.) are employed to apply the five types of colorant to cellulosic fibres and the characteristic attributes of the resulting dyeings (eg fastness, brightness, etc.) vary for the five classes of dye. However, for each of the five types of dye, inorganic electrolyte, in the guise of either NaCl or Na_2SO_4, must be added to the aqueous dyebath in order to achieve satisfactory levels of dye uptake; in the case of reactive dyes, the added electrolyte also promotes the extent of dye-fibre fixation (ie covalent fixation of the dye to the substrate).

The use of reactive dyes for cellulosic fibres has enjoyed virtually continuous growth since their commercial introduction ~60 years ago, which stemmed from the ground-breaking research of Stephen and Rattee (6-8). Consequently, global consumption of the other four dye classes has declined and reactive dyes nowadays account for ~ 55-60% of global dye consumption for cellulosic fibres (2).

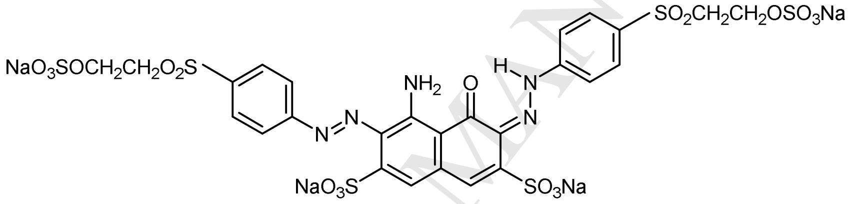
The development of reactive dyes, as well as their chemistry and application to cellulosic fibres, have received considerable attention [see for example (6-25)]. In essence, the vast majority of reactive dyes are non-metallised azo structures, although metallised azo dyes as well several non-azo dye classes are represented, as exemplified by C.I. Reactive Red 198, C.I. Reactive Red 120 and C.I. Reactive Blue 2.



C.I. Reactive Red 198



C.I. Reactive Red 120



C.I. Reactive Black 5

In essence, reactive dyes comprise a chromogen (eg azo, AQ, etc.) that contains one or more substituted aromatic rings which carry sulfonate/sulfonic acid groups, to which is attached a reactive system that contains one or more electrophilic groups that enable the dyes to form a covalent bond with nucleophilic hydroxyl groups in the cellulosic substrate. A wide range of different types of reactive dye are commercially available for cotton and other cellulosic fibres, including monofunctional types that contain either a single reactive group or two, equivalent reactive groups, bifunctional dyes that contain two reactive systems per dye molecule and include both homobifunctional types which carry identical reactive systems and heterobifunctional reactive dyes that comprise different types of reactive system, as well as (commercially-rare) polyfunctional reactive dyes. Owing to differences in the dyeing behaviour of different types of reactive dye on cellulosic substrates, dye makers commonly specify optimal application conditions (temperature, electrolyte concentration, pH, etc.) for their particular range(s) of reactive dyes.

From a structural perspective, reactive dyes are essentially long, planar, anionic molecules solubilised by one or more ionised sulfonate groups. As such, reactive dyes bear a close structural resemblance to direct dyes and, therefore, it is not surprising that in the absence of dye-fibre reaction (ie prior to the dye forming a covalent reaction with the cellulosic fibre), the adsorption of reactive dyes on cellulosic fibres is assumed to occur in a manner analogous to that of direct dyes (25). The mechanism by which added inorganic electrolyte promotes reactive dye uptake prior to dye-fibre fixation is also assumed to be analogous to that described for direct dye uptake (25).

2.1 dye-fibre reaction

The dyes are applied under aqueous alkaline (eg NaOH, Na_2CO_3) conditions so as to deprotonate the cellulosic hydroxyl groups (Cell-OH) and generate the far more strongly nucleophilic, ionised hydroxyl groups (Cell-O^-; aka *cellulosate anions*) within the substrate. The two most commercially exploited types of covalent reaction between reactive dyes and cellulosic substrates are nucleophilic addition to an alkene and aromatic nucleophilic substitution. Because, at the end of the immersion dyeing process, the chromogen is covalently bound to the fibre then dyeings on cotton and other cellulosic fibres obtained using reactive dyes characteristically display excellent fastness to wet treatments (eg washing, perspiration, etc.).

2.2 dye fixation

From the viewpoint of dye-fibre systems in general, the term *fixation* can be defined as *the proportion of dye that was originally applied to a substrate which remains on the substrate after dyeing and associated processes, such as wash-off* (25). However, in the case of reactive dyes, the term *fixation* is generally acknowledged as referring explicitly to the proportion of (reactive) dye applied to a substrate (eg cotton) that is covalently bound to the substrate at the end of dyeing (25).

The related term *fixed dye* describes reactive dye that has become covalently attached (ie fixed) to the fibre during the course of dyeing.

2.3 dye hydrolysis

As mentioned, reactive dyes are applied to cellulosic fibres under aqueous, alkaline conditions, so as to optimise dye-fibre reaction via the generation of the strongly nucleophilic, ionised hydroxyl groups within the substrate. Unfortunately, these conditions result not only in dye fixation (ie covalent bond formation with the substrate) but also unwanted alkali-induced hydrolysis of the reactive dye. This confers inherently low levels of dye-fibre fixation efficiency upon all types of commercial reactive dyes. Indeed, as dye-fibre fixation and dye hydrolysis take place concurrently during all immersion reactive dyeing processes, the extent of dye fixation achieved using reactive dyes is characteristically quite a distance from 100%. For example, dye-fibre covalent bonding efficiencies of 57-76% and 50-68% for medium depth (3% omf) and full depth (6% omf) dyeing, respectively, were recorded for six types of reactive system (26). In the context of such alkali-induced dye hydrolysis, the term *unfixed dye* is the antonym of *fixed dye* and, unsurprisingly, describes reactive dye that is not covalently attached to the substrate during dyeing. However, in terms of reactive dyeing, there are two types of unfixed dye, namely hydrolysed dye that is no longer capable of covalently attaching to the fibre as well as reactive dye which for some reason or other was not covalently bound to the fibre during application, and which often is referred to as *unreacted dye*.

Alkali-induced dye hydrolysis has far-reaching economic and environmental consequences. Since dye hydrolysis always accompanies dye-fibre fixation then hydrolysed dye, as well as any unreacted dye, will be present in both the residual dyebath and in the final dyed material. The amount of such undesirable hydrolysed (ie non-reactive) dye and non-covalently bound reactive dye present in the dyeing at the end of dye application can be of the order of ~30-50% of the dye applied. The fixation efficiency of a given commercial range of reactive dyes is an important consideration from the viewpoint of the dyer, since high dye-fibre fixation is obviously preferable in terms of the economics of exhaust dyeing. High fixation efficiency will also lead to lower amounts of residual, unfixed dye in dyehouse wastewater, which will serve to reduce environmental loads and lower wastewater treatment costs. Several methods can be used to determine the extent of dye fixation [eg (27-30)].

2.4 wash-off

Owing to the intrinsic inefficiency of dye-fibre fixation imparted by dye hydrolysis, the immersion application of reactive dyes to cellulosic fibres comprises a two-stage process, namely, the *dyeing stage* in which the reactive dye is applied to the substrate under aqueous alkaline conditions to promote dye-fibre fixation, which is followed by the *wash-off stage* in which the ensuing dyed material is subjected to a rigorous, aqueous treatment to remove unfixed dye from the dyeing that arises primarily from the concurrent dye hydrolysis that takes place during dyeing. It is important that all un-reacted and non-reactive dye is removed from the dyed material to avoid the loss of vagrant dye molecules from the dyeing during subsequent wet treatments, such as domestic laundering, which otherwise, will result in the ensuing dyeings displaying low fastness to wet treatments.

2.5 wastewater

In the dyeing of cellulosic fibres using reactive dyes, the wash-off stage is as vitally important as the dyeing stage in terms of the quality of the dyeing achieved (hue, levelness, fastness, etc.). Wash-off also contributes significantly to the overall effluent load generated during dyeing because of the presence of residual unfixed dye in the wastewater, the high level of residual electrolyte that is present in the dyed fibre at the end of the dyeing stage and also because of proprietary wash-off agents that are used in the wash-off process to expedite unfixed dye removal. Thus, both the dyeing stage and the subsequent wash-off stage characteristically generate very large amounts of wastewater that contains residual hydrolysed dye, unreacted dye, as well as very high levels of inorganic electrolyte and other dyeing auxiliaries. As such, reactive dyeing wastewater typically presents considerable environmental and economic challenges, as it is remarkably resilient to biodegradation. Whilst many effluent treatment strategies have been considered [eg (31-35)], the treatment of reactive dyeing wastewater is especially complex and routinely consumes large amounts of both energy and chemicals owing to the presence of high levels of NaCl or Na_2SO_4 [eg (36-40)]. The pronounced salinity of reactive dye wastewater has prompted the adoption of treatments that remove electrolyte for reclamation/disposal and enable recycling of some process water [eg (41-46)].

3 added electrolyte in the dyeing of cellulosic fibres with reactive dyes

The use of added electrolyte to promote the uptake of reactive dyes onto cotton (and other cellulosic fibres) dates from the introduction of the first range of commercial reactive dyes (the dichlorotriazinyl *Procion M;* ICI) in 1956. Although numerous ranges of reactive dye for cellulosic fibres have been marketed by many dye makers, and a variety of different types of reactive system utilised, the immersion application of all commercial ranges of reactive dye to cellulosic fibres routinely entails the use of significant levels of added inorganic electrolyte in the form of sodium sulfate or sodium chloride.

Despite the quite remarkable levels of research interest that both the chemistry and application of this dye class have attracted over several decades, the primary focus of the very large body of patents and papers that relate to reactive dyes and their application, has been the development of reactive systems from the viewpoint of increasing dye-fibre fixation efficiency. Indeed, neutral observers could be forgiven for assuming that the very rationale for utilising astonishingly large amounts of added electrolyte in exhaust dyeing figured very little, if at all, in the dye maker’s development aspirations for reactive dyes.

Whilst the amount of electrolyte that is used in the immersion application of reactive dyes to cellulosic fibres varies according to the type of dye and amount of dye applied, an estimation can be made of the amount of inorganic electrolyte that is likely to be consumed globally. The exhaust application of this dye type to cellulosic fibres is carried out typically in the presence of between 10-

30 gl^{-1} NaCl, with upto 50 gl^{-1} for lower substantivity dyes, upto 80 gl^{-1} for low substantivity vinylsulfone dyes (47) and 100 gl^{-1} of NaCl or Na_2SO_4 in the case of dark shades (48). If it is assumed that an average liquor ratio of 1:8 is utilised in exhaust dyeing processes and that all of the ~50-55% of global cellulosic fibre production in 2015 was dyed using reactive dyes (2) employing an immersion process, then the dyeing of the ~15 x 10^6 T of cellulosic fibre that was produced using reactive dyes in the presence of 50 gl^{-1} added NaCl or Na_2SO_4 would have consumed 6 x 10^6 T of added inorganic electrolyte. Despite the somewhat overly simplistic approach adopted in this estimate and its inherent imprecision, it nevertheless provides an indication of the sizeable amounts of added inorganic electrolyte that are likely to be consumed globally in the immersion dyeing of cellulosic fibres using reactive dyes. In this context, the level of electrolyte usage described above corresponds to the consumption of ~0.4 T of NaCl or Na_2SO_4 per tonne of cellulosic fibre dyed, which is roughly 1/3rd of the 1.2 T of electrolyte per tonne of dyed cotton reportedly consumed in industry (2). As mentioned, because all of the inorganic electrolyte that is used during dyeing with reactive dyes must be removed from the dyed material, so as to achieve desired fastness levels, the habitual use of such high levels of inorganic electrolyte poses severe wastewater treatment problems.

As recounted, despite the plethora of patents, research papers and reports that have been published on reactive dyes and their application to cellulosic fibres over the past six or so decades, very little of this voluminous output has focussed on the fundamental nature of the role of added inorganic electrolyte in the immersion application of reactive dyes to cotton and other cellulosic fibres. However, one aspect of this abundant research activity has resulted in the introduction of so-called ‘low salt’ reactive dyes for cellulosic fibres.

For example, the high substantivity, bis(aminofluorotriazine) *Cibacron LS* (Ciba-Geigy) range [eg (23, 49, 50)] [now the *Novacron LS* range of Huntsman], which was launched in the mid 1990’s and require 1/3 of the electrolyte required by standard reactive dyes (51), were first introduced in areas with arid climatic conditions and negative water balance (52). A more contemporary example of a ‘low salt’ reactive dye range is the trifunctional *Avitera SE* (Huntsman) (53, 54) dyes which offer electrolyte savings of 20%. The use of such types of reactive dye offers potential savings in terms of not only the amount of electrolyte consumed in dyeing but also the direct cost of the added NaCl or Na_2SO_4, as exemplified by the data shown in Table 1 (51).

Table 1 comparison of electrolyte usage for conventional reactive dye and *Novacron LS* dye; 10,000 kg cotton; 1:15 liquor ratio (51)

	conventional	*Novacron LS*
amount of liquor/ l	150,000	150,000
amount of electrolyte/ gl^{-1}	80	20
total amount of electrolyte per day/ kg	12,000	3,000
total amount of electrolyte per year/ kg	3,000,000	750,000
NaCl cost/ US$ (US$ 0.1 kg)	300,000	75,000
Na_2SO_4 cost/ US$ (US$ 0.2 kg)	600,000	150,000

Despite such developments in dye chemistry that utilise increased dye-fibre reaction efficiency to achieve what, in effect, are only moderate reductions in the amount of added electrolyte employed in the immersion application of reactive dyes to cellulosic fibres, the vast majority of commercial exhaust dyeing processes utilise ‘conventional’ reactive dyes that require the use of typically very high amounts of inorganic electrolyte. As Table 1 shows, such widespread usage of conventional reactive dyes in the immersion dyeing of cotton and other cellulosic fibres represents a major direct cost, insofar as each of the 1.2 T of added NaCl or Na_2SO_4 that is consumed per T of cotton dyed, costs either US$ 12 or US$ 24, depending on whether NaCl or Na_2SO_4, respectively, is used in dyeing, amounting to an annual electrolyte cost of US$ 300,000 or US$ 600,000. If such chemical costs were applied to the estimated 6 x 10^6 T of added inorganic electrolyte that may have been consumed in reactive dyeing in 2015, it is obvious that very large amounts of money (ie US$

72,000,000 to US$ 144,000,000) would have been expended on buying electrolyte. To this already high level of direct electrolyte expense must be added the substantial energy, water and chemical costs that must be incurred in treating the significant amounts of reactive dyeing wastewater that is contaminated by high levels of NaCl or Na_2SO_4.

The replacement of inorganic electrolyte with alternative compounds that promote reactive dye uptake has been investigated, as exemplified by the use of cationic surfactants, various chlorides and carboxylic acid salts (55), betaine (56), sodium edate (57, 58), trisodium citrate (59) and trisodium nitrilo triacetate (60); however, such an approach has not as yet enjoyed widespread commercial application.

In relatively recent times, the possibility of enhancing the uptake of reactive dyes on cotton (and other cellulosic fibres) by treating the substrate prior to dyeing with a quaternary amine (*cationisation*) or with aliphatic amino groups (*amination*) has received research attention [see (25) for a summary of such approaches]. In essence, the introduction of *N*-containing species via pre-treatment of the cellulosic substrate increases the basicity of the cellulosic material which enhances the substantivity of the treated substrate towards the anionic reactive dye; as such, immersion dyeing should therefore be achievable using reduced levels of added electrolyte. However, despite the often marked enhancement in dye substantivity that such pretreatments can impart, the approach does not enjoy broad commercial success, as treatments can, for example, promote ring dyeing and, also, dyeings can display alteration of hue, as well as reduced fastness to light and rubbing.

4 why is inorganic electrolyte used in the dyeing of cellulosic fibres with direct dyes?

In essence, adding either NaCl or Na_2SO_4 to a reactive dye dyebath increases the inherent low substantivity displayed by the dyes towards cellulosic fibres and, as a result, dye uptake is promoted. Both the characteristically low levels of dye-fibre substantivity displayed by reactive dyes in the absence of added electrolyte and the remarkable effectiveness of added inorganic electrolyte in promoting dye uptake, can be attributed to the combined effects of their long, linear structure and the presence of one (or most usually) more sulfonate groups which impart both anionicity and water solubility. In the latter context, reactive dyes display characteristically high levels of water solubility, as exemplified by values of 70-100 gl^{-1} @ 20^{o}C (61), 60-120 gl^{-1} at 25^{o}C (62), 70 gl^{-1} @ 20^{o}C (63) and 50-100 gl^{-1} @ 50^{o}C (64) having been recorded for various types of commercial grade reactive dye. Although such high aqueous solubility contributes to the renowned simplicity of the immersion reactive dyeing process, it also means that the liquor ratio used for dyeing, which determines the amount of water available in the dyebath, not only has a pronounced effect on both the rate and extent of reactive dye uptake, but also influences the effectiveness with which added electrolyte promotes dye uptake.

This is reflected in commercial immersion dyeing processes that are used to apply reactive dyes to cellulosic fibres. The dyer manipulates the level of substantivity displayed by the dye towards the substrate so as to ensure that uniform dyeings of the desired depth of shade are obtained within a given dyeing time. To achieve this, a particular amount of added inorganic electrolyte is used in combination with a particular liquor ratio (and at a given dyeing temperature). In this way, the relative contributions that the added electrolyte and liquor ratio make to the overall level of dye-fibre substantivity are regulated. Thus, a change in the liquor ratio selected for dyeing demands a corresponding change in the amount of added electrolyte employed (and visa versa), so that a particular degree of dye-fibre substantivity is achieved that is consistent with securing uniform dyeings of the desired colour strength, within the required time frame.

Table 2 amounts of added electrolyte and alklai required for immersion dyeing using *Novacron FN* dyes (65)

liquor ratio	electrolyte & alkali	dye/% omf						
		< 0.5	0.5	1	2	3	4	≥5
< 1:6	NaCl/ gl^{-1}	20	30	40	50	60	70	80

	NaHCO$_3$/ gl^{-1}	14	16	18	20	20	20	20
< 1:8	NaCl/ gl^{-1}	20	30	40	50	60	70	80
	NaHCO$_3$/ gl^{-1}	10	12	14	16	18	20	20
> 1:8	NaCl/ gl^{-1}	30	40	50	60	80	90	100
	NaHCO$_3$/ gl^{-1}	8	10	12	14	16	18	18
< 1:6	NaCl/ gl^{-1}	20	30	40	50	60	70	80
	NaHCO$_3$/ gl^{-1}	10	10	5	50	5	5	5
	NaOH 36^{o}Bé/ cm^3 l^{-1}	0.5	1	2	2.5	3	3.5	4
< 1:8	NaCl/ gl^{-1}	20	30	40	50	60	70	80
	NaHCO$_3$/ gl^{-1}	10	5	5	5	5	5	5
	NaOH 36^{o}Bé/ cm^3 l^{-1}	-	0.75	1.25	1.5	2	2.5	3
> 1:8	NaCl/ gl^{-1}	30	40	50	60	80	90	100
	NaHCO$_3$/ gl^{-1}	8	5	5	5	5	5	5
	NaOH 36^{o}Bé/ cm^3 l^{-1}	-	0.5	1	1.25	1.5	2	2.5

Dye manufacturers therefore commonly recommend the amount of inorganic electrolyte to be used in dyeing as a function of the particular ratio selected for dyeing, as illustrated in the data shown in Table 2 (65).

Hence, the two seemingly disparate variables of a reactive dye dyebath, namely the presence of added electrolyte and the volume of the dyebath (ie liquor ratio used for dyeing), influence dye-fibre substantivity and, thus, dye uptake. It therefore seems reasonable to suggest that the most likely physical attribute of reactive dyes that might be affected by both added inorganic electrolyte and liquor ratio is aqueous solubility.

Whilst the effect of liquor ratio on dye uptake in immersion dyeing processes in general has received much attention and the role of liquor ratio in reactive dyeing has been widely studied, our understanding of the manner by which liquor ratio influences dye uptake remains unclear (3). More significantly (3), the combined effects of liquor ratio and added inorganic electrolyte on the uptake of dye anions (eg reactive dyes, direct dyes, etc.) on cellulosic fibres has not been addressed. In the latter context, as mentioned, it has been shown in the case of the dyeing of cotton using commercial direct dyes, that the addition of inorganic electrolyte (3) and reduction of liquor ratio (4) impart the same promotional effect on dye uptake, as the two, apparently incongruent actions of adding electrolyte to the dyebath and reducing the liquor ratio used in dyeing, have the same result, namely that of encouraging dye aggregation in the dyebath, which reduces the solubility of the direct dye in the dyebath, which, in turn, increases the concentration gradient in the dyebath, resulting in increased dye uptake.

In view of these findings (3, 4) and the previously discussed assumption that prior to the reactive dye forming a covalent reaction with the cellulosic fibre, the adsorption of reactive dyes on cellulosic fibres is assumed to occur in a manner analogous to that of direct dyes, it seems reasonable to propose that in order to understand the manner by which added inorganic electrolyte promotes the uptake of reactive dyes on cellulosic fibres, the mechanism by which liquor ratio influences dye uptake must also be clarified.

5 current mechanistic views of the role of added electrolyte in the dyeing of cellulosic fibres using reactive dyes

Despite the widespread use of added electrolyte in the dyeing of cellulosic fibres, not only in the case of reactive dyes but also other types of both anionic dye (direct dyes) and dye precursors (azoic coupling components, leuco vat anions and sulphur anions), coupled with the fact that the mechanism by which added electrolyte promotes both the rate and extent of uptake of anionic dyes on cellulosic fibres has received considerable attention over many years, the precise nature of the promotional effect imparted by added inorganic electrolyte on reactive dye uptake has not been elucidated (2).

It may appear initially surprising, given the current dominance of reactive dyes in cellulosic fibre dyeing and the remarkable level of commercial development which this type of dye has enjoyed, that very little research interest has attended the mechanism by which added electrolyte promotes dye uptake. This situation becomes perhaps more understandable when it is recalled that our knowledge of the mechanism by which added inorganic electrolyte promotes reactive dyeing is based on the findings of studies that were carried out into the mechanism by which added NaCl or Na_2SO_4 promotes direct dye uptake on cellulosic fibres. Indeed, as mentioned, from the perspective of the thermodynamic treatment of the equilibrium adsorption of reactive dyes on cellulosic fibres, it is assumed that in the absence of dye-fibre reaction (ie prior to dye-fibre fixation), reactive dye adsorption occurs in a manner analogous to that of direct dyes (25). Unfortunately, contemporary views of the thermodynamics and kinetics of direct dyeing are founded mostly on detailed, elegant studies undertaken in the 1930’s and 1940’s (decades prior to the introduction of reactive dyes), that employed relatively few purified direct dyes (which nowadays enjoy limited current commercial usage) as well as very high liquor ratios. Furthermore, the precise nature of the mechanism by which direct dyes are adsorbed onto cellulosic fibres has not been satisfactorily resolved. Indeed, the observed inconsistencies between theoretically derived equations that attempt to describe experimentally derived observations can be attributed to the inherently complicated nature of direct dye-inorganic electrolyte interactions and a somewhat diffuse appreciation of the mechanism by which added inorganic electrolyte influences dye-fibre substantivity (2). It is therefore not surprising that our current understanding of the precise manner by which added electrolyte promotes reactive dye uptake on cellulosic fibres leave much to be desired.

In this context, several theories have been proposed to describe the promotional effect of added electrolyte on the uptake of direct dyes on cellulosic fibres, which, in turn, have been adopted by workers seeking to explain the role of added inorganic electrolyte in the immersion dyeing of cellulosic fibres with reactive dyes. Of these theories, the three that have gained most attention will be briefly discussed in the context of reactive dyes for cellulosic fibres.

5.1 electrical repulsion effects

Many researchers consider that the negative charge that is developed at the surface of cotton and other cellulosic fibres in water is lowered in the presence of inorganic electrolytes, which enables long-range repulsive forces operating between the negatively charged cellulosic substrate surface and the negatively charged dye anions in the dyebath to be reduced, thereby leading to enhanced dye uptake. For instance, Hildebrand (12), favoured the idea that reduced electrical repulsion expedites reactive dye uptake and also suggested that because polar media facilitates the formation of a transition state of the Meisenheimer complex type, added electrolyte may exert a positive effect on the rate of dye-fibre reaction. Lidyard *et al* observed that a reduction in electrolyte concentration led to greater repulsion between the anionic dye and the negatively charged cellulosic substrate, resulting in reduced substantivity (66). However, whilst the notion that added electrolyte promotes anionic dye uptake by lowering the electrical repulsion between the negatively charged cellulosic fibre and the dye anions, this particular explanation does not appear especially convincing in its own right, bearing in mind the poor relationship between the amount of electrolyte that is theoretically required to overcome the surface charge of cellulosic substrates and the amount of added NaCl of Na_2SO_4 typically utilised in the exhaust dyeing of cellulosic fibres with anionic dyes (25). This is of especial significance with regards reactive dyes, for which upto 100 gl^{-1} of added inorganic electrolyte can be employed in dyeing. For example, in a study of the effect of different electrolytes on the sorption of hydrolysed reactive dyes on cotton (67), it was concluded that whilst the observed increase in dye uptake that accompanied an increase in electrolyte concentration may be attributed to partial screening of the cellulosic fibre surface charge by the crowding of electrolyte cations at the cellulose-water interface, this theory did not explain the relative effectiveness of different electrolytes (eg NaCl, $(NH_4)_2SO_4$, LiCl) in modifying dye sorption at a given, equivalent, electrolyte concentration.

5.2 dye aggregation/reduced dye solubility

In the second part of this paper (2), which sought to establish the mechanism by which added electrolyte enhances the uptake of direct dyes on cotton, it was concluded that electrical repulsion effects contribute little and that adding NaCl or Na_2SO_4 to the dyebath encourages dye aggregation in the dyebath which reduces the aqueous solubility of the dye, so that the inherent predilection of the previously highly soluble dye to favour the aqueous phase shifts towards the fibre phase and the distribution of the dye between the dyebath and the fibre therefore favours the latter. Since it is assumed that the mechanism by which added electrolyte promotes reactive dye uptake prior to dye-fibre fixation is analogous to that described for direct dye uptake, then the effects of the added inorganic electrolyte on reactive dye uptake might also arise from the effects which increased dye aggregation and reduced solubility of the anionic reactive dyes in the dyebath have upon the distribution of the dye between the dyebath and the substrate.

In this context, the typically, long, planar structure of reactive dyes not only favours dye-fibre substantivity (47) but also explains the dye's remarkable proclivity to aggregate in aqueous solution via coplanar association, as is well-documented in the case of direct dyes [eg see (2, 25)]. As also observed for direct dyes (2), self-association of this kind is favoured by high dye concentrations and low temperatures, as well as the addition of inorganic electrolyte. By way of example, NaCl was found to increase the extent of aggregation of C.I. Reactive Blue 4 (68) and both C.I. Reactive Red 180 and

C.I. Reactive Red 2 in aqueous solution (69). The aggregation tendency, in water, of triphenodioxazine dyes carrying vinylsulfone reactive centres was promoted by the addition of NaCl (70), whilst LiCl was found to be more effective than NaCl in terms of the dimerization of C.I. Reactive Blue 2 (71). Furthermore, the finding (62) that the adsorption capacity of several reactive dyes from aqueous solution onto activated carbon increased with increasing ionic strength was attributed to dye aggregation in solution, whilst the marked effect of NaCl upon the removal of C.I. Reactive Black 5 from solution using nanofiltration membrane was attributed to aggregation (72); similarly, the adsorptive capacity of C.I. Reactive Black 5 on various adsorbents were promoted by both NaCl and Na_2PO_4 (73). Bredereck and Schumacher (74) observed that the aggregation, in solution, of twelve monoazo H-acid based reactive dyes containing both a monochlorotriazine and a vinylsulphone reactive system, was enhanced by the addition of electrolyte (Na_2SO_4) and also by increasing dye concentration, the latter finding being also reported in the case of other reactive dyes (70), such as C.I. Reactive Blue 4 (68). Other types of electrolyte have been shown to promote reactive dye aggregation in solution, including $MgCl_2$ and $MnCl_2$ (75) whilst various electrolytes were found to promote the uptake of the hydrolysed form of four different reactive dyes on cotton (76).

As discussed in the case of direct dyes (2), the remarkable ability of both NaCl and Na_2SO_4 to encourage reactive dye self-association in solution can be attributed to the added inorganic electrolyte counterions (ie Na^+) screening the anionic charge derived from $-SO_3^-$ groups on the dye anions, which reduces electrostatic repulsion between neighbouring charged dye anions and, thereby, promotes hydrophobic interaction between planar aromatic rings in adjacent reactive dye molecules. As π-π interactions between aromatic regions in the dye molecules will be expedited by the screening of the anionic charge on the dye anions by the electrolyte counterions. dye-dye interactions that favour dye self-association. Such hydrophobic interaction, of which dye aggregation is a corollary, will be driven by the need for the surrounding water molecules to minimise their interaction with the reactive dye solutes and so diminish the extent to which water structure is disrupted by the dye molecules.

As ionisation of the reactive dye molecules will be supressed as a consequence of both the strong π-π interactions operating between aromatic regions in neighbouring dye molecules and the screening of the $-SO_3^-$ groups by the Na^+ counterions, the dye molecules that are present within the dye aggregates (ie dye dimers, trimers, *n*-mers, etc.) will likely possess lower aqueous solubility than their monomolecularly dissolved reactive dye counterparts in the aqueous dyebath. Also, because hydrophobic interaction will result in less water being available to the dye aggregates in the dyebath, the aggregates will tend to coalesce and form particles (ie clusters of dye aggregates) that will constitute a dye dispersion within the aqueous dyebath. As a consequence of electrolyte-induced dye self-association, the concentration of reactive dye in solution in the dyebath will therefore be reduced, from which it follows that the addition of NaCl or Na_2SO_4 to a reactive dye in solution will reduce the solubility of the dye, as indeed has been observed. For example, the solubility of C.I. Reactive Black 8 and C.I. Reactive Blue 49 decreased as a function of KCl concentration (77) and the aqueous solubility of *Novacron FN* (Huntsman) reactive dyes is reported to be lowered from 100 gl^{-1} in water at both 30^{o}C and 60^{o}C to 30 gl^{-1} at 60^{o}C in 60 gl^{-1} aqueous electrolyte solution (65).

Thus, as proposed in the case of direct dyes (2), applying reactive dyes to cotton and other cellulosic fibres in the presence of added NaCl or Na_2SO_4 can be considered as a process of controlled dye precipitation onto the substrate, in that the amount of added inorganic electrolyte used is such as to induce the formation of a dispersion of dye particles in the aqueous dyebath whilst avoiding flocculation of the dye.

However, as discussed below, despite the fact that electrolyte-induced reactive dye self-association may offer a realistic explanation as to the manner by which added inorganic electrolyte promotes reactive dye adsorption, the physical process of dye aggregation in solution and, more importantly, its encouragement by added inorganic electrolyte, cannot be accounted for satisfactorily using the physico-chemical models that have been proposed to describe reactive dye adsorption on cellulosic fibres.

5.3 thermodynamics of dyeing

For general accounts the reader is directed to (7, 15, 18, 22, 25, 78-80) and the references therein.

As the adsorption of reactive dyes onto cellulosic fibres prior to dye-fibre reaction is assumed to parallel that of direct dyes, the mechanism by which the dyes are adsorbed is also presumed to resemble that of direct dyes (2), being interpreted from equilibrium adsorption data using either Freundlich or Langmuir equations that assume a Donnan distribution of ions and invoke usage of the concept of fibre internal volume, *V* (25). However, as previously discussed in the case of direct dye adsorption (2), Freundlich-type and Langmuir-type interpretations of experimentally obtained equilibrium dye adsorption data differ fundamentally not only from the viewpoint of the nature of the interactions that can occur between the adsorbing dye molecules and the substrate but also, importantly, in terms of the possible contribution that dye aggregation makes towards dye-fibre interaction and, therefore, the role of added inorganic electrolyte in dye adsorption. The generally poor correlation obtained between such theoretical interpretations of experimentally observed equilibrium dye adsorption data reflect the highly complex nature of dye-electrolyte-fibre interactions and a less than complete understanding of these fundamentally important aspects of dye adsorption. Furthermore, currently accepted physico-chemical models of reactive dye adsorption are unable to account for either the low uptake observed when the dyes are applied in the absence of added inorganic electrolyte or the marked promotional effect of added NaCl or Na_2SO_4 on dye uptake; in part, such a situation can be attributed to a somewhat unclear understanding of the role of added electrolyte in dyeing.

In the latter context, as previously recounted (2), owing to the complicating effect of added NaCl or Na_2SO_4 on dye adsorption, several thermodynamic models of direct dye adsorption on cellulosic fibres and, therefore, by extrapolation, that of reactive dyes, have been developed of which the *diffuse adsorption* model (81) is most widely accepted (25).

$$K = \frac{[D]_f}{[D]_s} \qquad 1$$

In essence (25, 80), such models seek to describe the partition of the dye between the fibre phase and the solution phase (ie dyebath) achieved under equilibrium conditions in terms of the thermodynamic standard affinity of the dye, $-\Delta\mu^{\theta}$, employing mathematical interpretations of Eq 1, where $[D]_f$ is the amount of dye present in the fibre phase (ie the substrate) relative to the amount of fibre and $[D]_s$ is the amount of dye in solution (ie the dyebath) relative to the amount of solution and K is the equilibrium partition coefficient which describes the distribution of the dye between the dyebath, s and fibre, f, phases; the higher the value of K then the greater is the partition of the dye in favour of the fibre phase (ie $[D]_f > [D]_s$) and the greater is the extent of dye uptake onto the substrate. The second part of the paper (2) considers the consequences of using the same or different units for measuring values of $[D]_f$ and $[D]_s$.

Whilst such mathematical treatments seek to account for the effects of temperature and inorganic electrolyte on dye equilibrium, the latter aspect of both direct dye and reactive dye adsorption has a marked complicating impact on the models. In the case of reactive dyes, an additional obfuscating issue arises because of the alkaline conditions that are required to apply the dyes, and the need for a mathematical treatment that takes into account the influence of alkali-induced ionisation of the hydroxyl groups in the substrate on dye adsorption (80, 82). Furthermore, as dye hydrolysis always accompanies dye-fibre reaction, the mechanism of dye hydrolysis has received considerable attention, in which context, attempts have been made to quantify the efficiency of dye-fibre reaction in terms of various dyebath parameters.

The thermodynamic analysis of the adsorption of reactive dyes onto various types of substrate, including cellulosic materials, has attracted much attention, various adsorption models having been proposed [eg (83-89)].

From the foregoing, it is clear that the thermodynamic treatment of the reactive dye/inorganic electrolyte/cellulosic fibre dyeing system is complicated because of the need to add NaCl or Na_2SO_4 to reactive dye dyebaths in order to promote dye uptake. From this it follows that if it were possible to dye cellulosic fibres using reactive dyes in the absence of added inorganic electrolyte then a much simpler thermodynamic treatment of the resulting, more straightforward, reactive dye/cellulosic fibre dyeing system could be advanced that may offer improved agreement between theoretical mathematical interpretations and experimentally determined dye adsorption data. This is the subject of a subsequent part of this paper.

5.4 kinetics of dyeing

The mechanism by which reactive dyes diffuse within cellulosic fibres prior to dye-fibre reaction can initially be considered (25) to be comparable to that of direct dyes (2), being described in terms of the, essentially mechanical, pore model of dye diffusion (90-92); generally, dye diffusion is markedly influenced by added added inorganic electrolyte. However, in the case of reactive dyes, owing to the alkaline conditions that are used to expedite dye-fibre covalent reaction, physical adsorption onto pore walls via intermolecular forces of interaction can also be accompanied by dye fixation, namely, chemisorption onto ionised hydroxyl groups on the walls. Under such conditions, it seems likely that in addition to dye diffusion occurring in accordance with the pore model of diffusion, namely, that diffusion of the dye molecules within water-filled pores is accompanied by simultaneous physical adsorption onto the pore walls, the diffusing dye molecules can also undergo simultaneous chemical reaction with ionised hydroxyl groups on the pore walls. As such, the kinetics of dyeing cellulosic fibres with reactive dyes is very complicated because of the marked heterogeneous nature of the diffusional process. Consequently, mathematical interpretations of the kinetics of reactive dyeing are necessarily complex as they must account for both physical diffusion and simultaneous dye-fibre reaction [eg (22, 93-100)].

In relatively recent times, the analysis of the kinetics of reactive dye removal from wastewater by adsorption onto various types of substrate, including cellulosic materials, has attracted attention [eg (61, 86, 101-104)].

The foregoing account reveals that the highly complex, multi-faceted diffusional process of reactive dyes within cellulosic substrates is complicated not simply because of the influence of added inorganic electrolyte but also due to the fact that dye diffusion involves simultaneous physical adsorption and chemisorption. Thus, if it were possible to dye cellulosic fibres using reactive dyes in the absence of added electrolyte perhaps a simpler interpretation of the ensuing reactive dye-cellulosic fibre diffusion process may result; this will be addressed in a subsequent part of this paper.

6 conclusions

As the adsorption of reactive dyes onto cellulosic fibres in the absence of dye-fibre reaction is assumed to parallel that of direct dyes, the mechanism by which the dyes are adsorbed is also presumed to resemble that of direct dyes. As such, the same theories which have been proposed to explain the promotional effect imparted by added inorganic electrolyte on the uptake of direct dyes are assumed to apply in the case of reactive dyes. Unfortunately, none of these theories satisfactorily explains the promotional effect of added electrolyte in terms of the currently accepted method of describing the mechanism by which reactive dyes are adsorbed on cellulosic fibres, namely, mathematical interpretations of isothermal equilibrium dye adsorption data that seek to calculate the thermodynamic standard affinity of reactive dyes on cellulosic substrates, $-\Delta\mu^{\theta}$.

Furthermore, such interpretations do not describe how dyeing proceeds prior to equilibrium being achieved, a situation that is relevant to commercial exhaust dyeing processes which do not achieve equilibrium dye uptake, nor do they adequately account for either the inherently low substantivity displayed by reactive dyes towards cellulosic fibres in the absence of added inorganic electrolyte nor the marked ability of added NaCl or Na_2SO_4 to promote dye uptake.

In the latter context, it seems probable that the addition of either NaCl or Na_2SO_4 to a reactive dye dyebath utilises the inherent propensity of the dyes to aggregate in solution via coplanar association, and that such electrolyte-induced dye aggregation reduces the solubility of the dye in the dyebath. However, accepted physico-chemical models of the mechanism by which reactive dyes are adsorbed on cellulosic fibres are unable to adequately account for the effects of electrolyte-induced dye self-association in solution and, more significantly, cannot explain the effects of reduced dye solubility on the dye adsorption process. Thus, an alternative model is required which can explain the effects of both electrolyte-induced dye self-association and consequent reduced dye solubility on reactive dye uptake. This is the subject of the next part of this paper.

References

1. Burkinshaw SM, Salihu G. The role of auxiliaries in the immersion dyeing of textile fibres: Part 1 ???? 2017;?

2. Burkinshaw SM, Salihu G. The role of auxiliaries in the immersion dyeing of textile fibres: Part 2 analysis of conventional models that describe the manner by which inorganic electrolytes promote direct dye uptake on cellulosic fibres. ???? 2017;?

3. Burkinshaw SM, Salihu G. The role of auxiliaries in the immersion dyeing of textile fibres: Part 3 theoretical model to describe the role of inorganic electrolytes used in dyeing cellulosic fibres with direct dyes. ???? 2017;?

4. Burkinshaw SM, Salihu G. The role of auxiliaries in the immersion dyeing of textile fibres: Part 4 theoretical model to describe the role of liquor ratio in dyeing cellulosic fibres with direct dyes in the presence of inorganic electrolytes. ???? 2017;?

5. Burkinshaw SM, Salihu G. The role of auxiliaries in the immersion dyeing of textile fibres: Part 5 practical aspects of the role of inorganic electrolytes in dyeing cellulosic fibres with direct dyes. ???? 2017;?

6. Stephen WE. Early work on reactive dyes for cellulose. Chimia. 1965;19(5):261-73.

7. Rattee ID. Reactive Dyes in the Coloration of Cellulosic Materials. Journal of the Society of Dyers and Colourists. 1969;85(1):23-31.

8. Rattee ID. Reactive Dyes for Cellulose 1953–1983. Review of Progress in Coloration and Related Topics. 1984;14(1):50-7.

9. Stamm OA. Mechanisms of Reaction of Reactive Dyes with Cellulosic and other Fibres. Journal of the Society of Dyers and Colourists. 1964;80(8):416-22.

10. Beech WF. Fibre-reactive dyes. London: Logos Press; 1970.

11. Allen RLM. Reactive dyes. Colour Chemistry. New York: Springer US; 1971. p. 201-25.

12. Hildebrand D. Reative dyes: application and properties. In: Venkataraman K, editor. The Chemistry of Synthetic Dyes, Volume VI. New York: Academic Press; 1972. p. 327-449.

13. Siegel E. Reactive dyes: reactive groups. In: Venkataraman K, editor. The Chemistry of Synthetic Dyes, Volume VI. New York: Academic Press; 1972. p. 1-209.

14. Schündehütte K-H. Reactive dyes: chromophore systems. In: Venkataraman K, editor. The Chemistry of Synthetic Dyes, Volume VI. New York: Academic Press; 1972. p. 211-325.

15. Rattee ID, Breuer MM. The Physical Chemistry of Dye Adsorption. London: Academic Press; 1974.

16. Peters RH. Textile Chemistry, Volume 3. Amsterdam: Elsevier; 1975.

17. Rosenthal P. The Chemistry and Application of Reactive Dyes — A Literature Review, Sept 1971–July 1975. Review of Progress in Coloration and Related Topics. 1976;7(1):23-34.

18. Rattee ID. Reactive dyes: physicochemical aspects of dye fixation and dye-fiber bond hydrolysis. In: Venkataraman K, editor. The Chemistry of Synthetic Dyes Volume VIII. New York: Academic Press; 1978. p. 1-36.

19. Renfrew AHM, Taylor JA. Cellulose reactive dyes: recent developments and trends. Review of Progress in Coloration and Related Topics. 1990;20(1):1-9.

20. Renfrew AHM. Reactive dyes for textile fibres. Bradford: Society of Dyers and Coloursits; 1999.

21. Venkataraman K. Introduction. In: Venkataraman K, editor. The Chemistry of Synthetic Dyes Volume III. New York: Academic Press; 1970. p. 1-60.

22. Fox MR, Sumner HH. Dyeing with reactive dyes. In: Preston C, editor. The dyeing of cellulosic fibres. Bradford: The Dyers Company Publications Trust; 1986. p. 142-95.

23. Shore J. Chemistry of reactive dyes. In: Shore J, editor. Colorants and Auxiliaries, Volume 2: Auxiliaries, 2nd Ed. Bradford: Society of Dyers and Colourists; 2002. p. 356-443.

24. Lewis DM. Developments in the chemistry of reactive dyes and their application processes. Coloration Technology. 2014;130(6):382-412.

25. Burkinshaw SM. Physico-chemical aspects of textile coloration. Chichester: Wiley; 2016.

26. Douthwaite FJ, Harrada N, Washimi T. Proceedings IFATCC Conference (Vienna). 1996:447-51.

27. Renfrew AHM, Taylor JA. Reactive dyes for cellulose. Concurrent methoxide-hydroxide reactions of triazinyl reactive systems: a model system for assessment of potential fixation efficiency. Journal of the Society of Dyers and Colourists. 1989;105(12):441-5.

28. Burkinshaw SM, Gandhi K. The dyeing of conventional decitex and microfibre nylon 6,6 with reactive dyes - I. Chlorodifluoropyrimidinyl dyes. Dyes and Pigments. 1996;32(2):101-27.

29. Burkinshaw SM, Wills AE. The dyeing of conventional and microfibre nylon 6,6 with reactive dyes - 3. Vinyl sulphone and chlorotriazine dyes. Dyes and Pigments. 1997;34(3):243-53.

30. Murtagh V, Taylor JA. A simple titrimetric method for the estimation of reactive dye fixation on cellulosic fabrics. Dyes and Pigments. 2004;63(1):17-22.

31. Robinson T, McMullan G, Marchant R, Nigam P. Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative. Bioresource Technology. 2001;77(3):247-55.

32. Anjaneyulu Y, Sreedhara Chary N, Samuel Suman Raj D. Decolourization of Industrial Effluents – Available Methods and Emerging Technologies – A Review. Reviews in Environmental Science and Biotechnology. 2005;4(4):245-73.

33. Hai FI, Yamamoto K, Fukushi K. Hybrid Treatment Systems for Dye Wastewater. Critical Reviews in Environmental Science and Technology. 2007;37(4):315 - 77.

34. Zahrim AY, Tizaoui C, Hilal N. Coagulation with polymers for nanofiltration pre-treatment of highly concentrated dyes: A review. Desalination. 2011;266(1–3):1-16.

35. Jegatheesan V, Pramanik BK, Chen J, Navaratna D, Chang C-Y, Shu L. Treatment of textile wastewater with membrane bioreactor: A critical review. Bioresource Technology. 2016;204:202-12.

36. Carliell CM, Barclay SJ, Shaw C, Wheatley AD, Buckley CA. The Effect of Salts Used in Textile Dyeing on Microbial Decolourisation of a Reactive Azo Dye. Environmental Technology. 1998 1998/11/01;19(11):1133-7.

37. Koyuncu I. Influence of dyes, salts and auxiliary chemicals on the nanofiltration of reactive dye baths: experimental observations and model verification. Desalination. 2003 2003/03/01;154(1):79-88.

38. Koyuncu I, Topacik D. Effects of operating conditions on the salt rejection of nanofiltration membranes in reactive dye/salt mixtures. Separation and Purification Technology. 2003;33(3):283-94.

39. Muthukumar M, Selvakumar N. Studies on the effect of inorganic salts on decolouration of acid dye effluents by ozonation. Dyes and Pigments. 2004;62(3):221-8.

40. Dong Y, Chen J, Li C, Zhu H. Decoloration of three azo dyes in water by photocatalysis of Fe (III)–oxalate complexes/H2O2 in the presence of inorganic salts. Dyes and Pigments. 2007;73(2):261-8.

41. Arslan I, Balcioglu IA. Effect of common reactive dye auxiliaries on the ozonation of dyehouse effluents containing vinylsulphone and aminochlorotriazine dyes. Desalination. 2000;130(1):61-71.

42. Vishnu G, Palanisamy S, Joseph K. Assessment of fieldscale zero liquid discharge treatment systems for recovery of water and salt from textile effluents. Journal of Cleaner Production. 2008;16(10):1081-9.

43. Kabdaşlı I, Vardar B, Arslan-Alaton I, Tünay O. Effect of dye auxiliaries on color and COD removal from simulated reactive dyebath effluent by electrocoagulation. Chemical Engineering Journal. 2009;148(1):89-96.

44. Dasgupta J, Sikder J, Chakraborty S, Curcio S, Drioli E. Remediation of textile effluents by membrane based treatment techniques: A state of the art review. Journal of Environmental Management. 2015;147:55-72.

45. Lin J, Ye W, Huang J, Ricard B, Baltaru M-C, Greydanus B, et al. Toward Resource Recovery from Textile Wastewater: Dye Extraction, Water and Base/Acid Regeneration Using a Hybrid NF-BMED Process. ACS Sustainable Chemistry & Engineering. 2015 2015/09/08;3(9):1993-2001.

46. Thamaraiselvan C, Noel M. Membrane Processes for Dye Wastewater Treatment: Recent Progress in Fouling Control. Critical Reviews in Environmental Science and Technology. 2015 2015/05/19;45(10):1007-40.

47. Leube H, Rüttiger W, Kühnel G, Wolff J, Ruppert G, Schmitt M, et al. Textile Dyeing. Ullmann's Encyclopedia of Industrial Chemistry. New York: Wiley; 2000.

48. Philips DAS. Environmentally friendly, productive and reliable: priorities for cotton dyes and dyeing processes. Journal of the Society of Dyers and Colourists. 1996;112(7-8):183-6.

49. Lewis DM. The chemistry of reactive dyes and their application processes. In: Clark M, editor. Handbook of Textile and Industrial Dyeing: Volume 1 Principles, Processes and Types of dyes. Cambridge: Woodhead; 2011. p. 303-64.

50. Taylor J. Recent developments in reactive dyes. Review of Progress in Coloration. 2000;30:93-107.

51. Anon. Textile Effects: Novacron LS reactive dyes; exhaust dyeing with low salt addition. Huntsman Textile Effects 118003e: July 2007: Huntsman 2007.

52. Chavan RB. 16 - Environmentally friendly dyes. In: Clark M, editor. Handbook of Textile and Industrial Dyeing: Woodhead Publishing; 2011. p. 515-61.

53. Revolutionary Avitera SE dyes: http://www.huntsman.com/corporate/a/Innovation/AVITERA_R%20SE (accessed 17/5/2016. Huntsman; 2016.

54. Textile Effects: A revolution in reactive dyeing; Avitera SE for exhaust application. Huntsman; 2014.

55. Rucker JW, Guthrie DM. Reduction of salt requirements in dyeing cotton with fiber reactive dyes. Book of Papers, international conf And exhibition AATCC, Atlanta, 1997. [Article]. 1997:329-36.

56. Liu LJ, Yao JB. Application of betaine in low-salt dyeing of cotton fabric with reactive dyes. Journal of Tianjin Polytechnic University. [Article]. 2009;28(4):53-7.

57. Ahmed NSE. The use of sodium edate in the dyeing of cotton with reactive dyes. Dyes and Pigments. [Article]. 2005;65(3):221-5.

58. El-Shishtawy RM, Youssef YA, Ahmed NSE, Mousa AA. The use of sodium edate in dyeing: II. Union dyeing of cotton/wool blend with hetero bi-functional reactive dyes. Dyes and Pigments. 2007;72(1):57-65.

59. Prabu HG, Sundrarajan M. Effect of the bio-salt trisodium citrate in the dyeing of cotton. Coloration Technology. [Article]. 2002;118(3):131-4.

60. Memon H, Khatri A, Ali N, Memon S. Dyeing Recipe Optimization for Eco-Friendly Dyeing and Mechanical Property Analysis of Eco-Friendly Dyed Cotton Fabric: Better Fixation, Strength, and Color Yield by Biodegradable Salts. Journal of Natural Fibers. [Article]. 2016;13(6):749-58.

61. Dizge N, Aydiner C, Demirbas E, Kobya M, Kara S. Adsorption of reactive dyes from aqueous solutions by fly ash: Kinetic and equilibrium studies. Journal of Hazardous Materials. 2008;150(3):737-46.

62. Al-Degs YS, El-Barghouthi MI, El-Sheikh AH, Walker GM. Effect of solution pH, ionic strength, and temperature on adsorption behavior of reactive dyes on activated carbon. Dyes and Pigments. 2008;77(1):16-23.

63. Şayan E. Optimization and modeling of decolorization and COD reduction of reactive dye solutions by ultrasound-assisted adsorption. Chemical Engineering Journal. 2006;119(2–3):175-81.

64. Netpradit S, Thiravetyan P, Towprayoon S. Adsorption of three azo reactive dyes by metal hydroxide sludge: effect of temperature, pH, and electrolytes. Journal of Colloid and Interface Science. 2004;270(2):255-61.

65. Anon. Textile Effects: Novacron FN reactive dyes; warm exhaust dyeing. Huntsman Textile Effects 122007e: July 2007: Huntsman 2008.

66. Lidyard AM, Woodcock A, Noone P. Economic considerations from the exhaust application of reactive dyes under ultra-low liquor ratio conditions*. Journal of the Society of Dyers and Colourists. 1992;108(11):501-4.

67. Madan GL, Patel MM, Srivastava HC. Studies on the Structure of Never-dried Cotton, Part I: Physical Characteristics of Cotton Dried under Controlled Conditions. Indian J Text Res. 1976;1(null):1-8.

68. Epolito WJ, Lee YH, Bottomley LA, Pavlostathis SG. Characterization of the textile anthraquinone dye Reactive Blue 4. Dyes and Pigments. 2005;67(1):35-46.

69. Hamlin JD, Phillips DAS, Whiting A. UV/Visible spectroscopic studies of the effects of common salt and urea upon reactive dye solutions. Dyes and Pigments. 1999;41(1–2):137-42.

70. Hihara T, Okada Y, Morita Z. The aggregation of triphenodioxazine reactive dyes in aqueous solution and on cellulosic and nylon substrates. Dyes and Pigments. 2000;45(2):131-43.

71. Alberghina G, Bianchini R, Fichera M, Fisichella S. Dimerization of Cibacron Blue F3GA and other dyes: influence of salts and temperature. Dyes and Pigments. 2000;46(3):129-37.

72. Koyuncu I. Reactive dye removal in dye/salt mixtures by nanofiltration membranes containing vinylsulphone dyes: effects of feed concentration and cross flow velocity. Desalination. 2002 2002/06/10;143(3):243-53.

73. Ip AWM, Barford JP, McKay G. Reactive Black dye adsorption/desorption onto different adsorbents: Effect of salt, surface chemistry, pore size and surface area. Journal of Colloid and Interface Science. 2009;337(1):32-8.

74. Bredereck K, Schumacher C. Structure Reactivity Correlations of Azo Reactive Dyes Based on H-acid: I. NMR Chemical Shift Values, pKa Values, Dyestuff Aggregation and Dyeing Behaviour. Dyes and Pigments. 1993;21(1):23-43.

75. Bouyakoub AZ, Lartiges BS, Ouhib R, Kacha S, El Samrani AG, Ghanbaja J, et al. MnCl2 and MgCl2 for the removal of reactive dye Levafix Brilliant Blue EBRA from synthetic textile wastewaters: An adsorption/aggregation mechanism. Journal of Hazardous Materials. 2011;187(1–3):264-73.

76. Madan GL, Shrivastava SK. Physical Chemistry of Dyeing of Cellulosic Fibers with Reactive Dyes: Part I : The Role of Electrolytes in the Sorption of Hydrolyzed Reactive Dyes. Textile Research Journal. 1979 June 1, 1979;49(6):322-5.

77. Han HK, Jung H-K. Solubility and growth rate of reactive blue49 and black8 dyes in salting-out system. Korean Journal of Chemical Engineering. 2009 2009//;26(1):246-9.

78. Rys P, Zollinger H. Reactive dye-fibre systems. In: Bird CL, Boston WS, editors. Theory of Coloration of Textiles Bradford: Society of Dyers and Coloursits; 1975. p. 326-58.

79. Rhys P, Zollinger H. Reactive dye-fibre systems. In: Johnson A, editor. Theory of Coloration of Textiles, Second Edition. Bradford: Society of Dyers and Coloursits; 1989. p. 428-76.

80. Sumner HH. Thermodynamics of dye sorption. In: Johnson A, editor. Theory of Coloration of Textiles, 2nd edition. Bradford: Society of Dyers and Coloursits; 1989. p. 255-372.

81. Marshall WJ, Peters RH. The heats of reaction and affinities of direct cotton dyes for cuprammonium rayon, viscose rayon and cotton. Journal of the Society of Dyers and Colourists. 1947;63(12):446-61.

82. Sumner HH. The Mechanism of Dyeing with Procion Dyes I—The Mechanism of Alkali Adsorption by Cellulose. Journal of the Society of Dyers and Colourists. 1960;76(12):672-8.

83. Al-Degs Y, Khraisheh MAM, Allen SJ, Ahmad MN. Effect of carbon surface chemistry on the removal of reactive dyes from textile effluent. Water Research. 2000;34(3):927-35.

84. Santhy K, Selvapathy P. Removal of reactive dyes from wastewater by adsorption on coir pith activated carbon. Bioresource Technology. 2006;97(11):1329-36.

85. Lee J-W, Choi S-P, Thiruvenkatachari R, Shim W-G, Moon H. Evaluation of the performance of adsorption and coagulation processes for the maximum removal of reactive dyes. Dyes and Pigments. 2006;69(3):196-203.

86. Xue Y, Hou H, Zhu S. Adsorption removal of reactive dyes from aqueous solution by modified basic oxygen furnace slag: Isotherm and kinetic study. Chemical Engineering Journal. 2009;147(2–3):272-9.

87. Asgher M. Biosorption of Reactive Dyes: A Review. Water, Air, & Soil Pollution. 2012 2012//;223(5):2417-35.

88. Ziane S, Marouf-Khelifa K, Benmekki H, Schott J, Khelifa A. Removal of a reactive textile azo dye by dolomitic solids: kinetic, equilibrium, thermodynamic, and FTIR studies. Desalination and Water Treatment. 2015 2015/10/16;56(3):695-708.

89. Sellaoui L, Lima EC, Dotto GL, Dias SLP, Lamine BL. Physicochemical modeling of reactive violet 5 dye adsorption on home-made cocoa shell and commercial activated carbons using the statistical physics theory. Results in Physics. 2017;7:233-7.

90. Morton TH. The dyeing of cellulose with direct dyestuffs; the importance of the colloidal constitution of the dye solution and of the fine structure of the fibre. Transactions of the Faraday Society. 1935;31(0):262-76.

91. Neale SM. General discussion. Transactions of the Faraday Society. 1935;31(0):282-3.

92. Valko E. General discussion. Transactions of the Faraday Society. 1935;31(0):278-9.

93. Beckmann W, Hildebrand D. Kinetics of the Reaction between Reactive Dyes and Cotton in Dyeing from Long Liquors. Journal of the Society of Dyers and Colourists. 1965;81(1):11-6.

94. Gerber H, UlshÒFer U. Colour Yield and Appearance of Cellulosic Fibres Dyed with Reactive Dyes. Journal of the Society of Dyers and Colourists. 1974;90(2):60-7.

95. Rusznak I, Levai G, Zobor-Frankl J. Investigation of cellulose-reactive dye heterogeneous systems. Chemical Engineering. 1975;19(3):177-93.

96. Rusznák I, Zobor J, Lévai G. Kinetic investigation of reactive dyeing. Dyes and Pigments. 1981;2(4):285-303.

97. Brennan C, Bullock J. The heterogeneous kinetics of reactive and disperse dyeing. In: Peters AT, Freeman H, editors. Physico-chemical principles of colour chemistry. London: Blackie; 1996. p. 44-82.

98. Sumner HH, Weston CD. Pad-Dyeing Methods for Reactive Dyes on Cotton: The Practical Implications of a Theoretical Study. American Dyestuff Reporter. 1963;52:442-50.

99. Motomura H, Morita Z. Diffusion with simultaneous reaction of reactive dyes in cellulose. II. Effect of hydrolysis. Journal of Applied Polymer Science. 1979;24(7):1747-57.

100. Motomura H, Morita Z. Diffusion with simultaneous reaction of reactive dyes in cellulose. Journal of Applied Polymer Science. 1977;21(2):487-99.

101. Yang X, Al-Duri B. Kinetic modeling of liquid-phase adsorption of reactive dyes on activated carbon. Journal of Colloid and Interface Science. 2005;287(1):25-34.

102. Walker GM, Hansen L, Hanna JA, Allen SJ. Kinetics of a reactive dye adsorption onto dolomitic sorbents. Water Research. 2003;37(9):2081-9.

103. Nourouzi MM, Chuah TG, Choong TSY. Adsorption of Reactive Dyes by Palm Kernel Shell Activated Carbon: Application of Film Surface and Film Pore Diffusion Models. E-Journal of Chemistry. 2009;6(4):949-54.

104. Yang X-Y, Al-Duri B. Application of branched pore diffusion model in the adsorption of reactive dyes on activated carbon. Chemical Engineering Journal. 2001;83(1):15-23.

Highlights

- the role of inorganic electrolyte in reactive dye application is modelled
- interstitial water is used to show that added electrolyte reduces dye solubility
- added electrolyte promotes dye aggregation