Journal of Cleaner Production 87 (2015) 50–57

Contents lists available at ScienceDirect

Journal of Cleaner Production

journal homepage: www.elsevier.com/locate/jclepro

Review

A review on developments in dyeing cotton fabrics with reactive dyes for reducing effluent pollution

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ARTICLE INFO

Article history:
Received 23 July 2013
Received in revised form
29 August 2014
Accepted 5 September 2014
Available online 16 September 2014

Keywords:
Cotton
Reactive dyes
Environmentally sustainable dyeing
Effluent pollution and treatment

ABSTRACT

Most cotton fabrics are dyed with reactive dyes because they produce a full range of bright fashion colours with a high degree of wash fastness. Application of these dyes, however, causes high and undesirable levels of dissolved solids and oxygen demand in the effluent. This is due to the use of considerable quantities of inorganic salt and alkali to ensure efficient utilisation and fixation of the reactive dyes. Dye that is unfixed on cotton also contributes to effluent pollution. There are two approaches to deal with the effluent problem: 1. alternative dyeing techniques and technology, 2. effluent treatment after dyeing. The effluent treatment requires additional capital investment and high treatment and maintenance costs. Therefore, the first approach is always preferable. There have been a number of options developed to overcome the polluted effluent problem of dyeing cotton fabric with reactive dyes. This paper reviews the options to improve sustainability of the dyeing process through development of reactive dyes, modification of dyeing machinery and processes, chemical modification of cotton fibre prior to dyeing, use of biodegradable organic compounds in dyebath formulation, and effluent treatment processes. The paper highlights the significance and limitations of these ways of improving sustainability in reactive dyeing, and proposes the areas for further improvements.

1. Introduction

Globally, the textile dyeing industry is known to be one of the major contributors to environmental pollution (Christie, 2007). This is mainly due to heavy discharges of inorganic salts, alkalis, other processing aids such as surfactants and organic matter such as dyes to effluent. Particularly, effluents from dyeing cotton with reactive dyes are highly polluted and have high oxygen demand, colour, and salt load. The industry also consumes large volumes of clean water. Effluent treatment and water-recycling can play a significant role in reducing discharge pollution and providing reusable processing water. A brief account of such treatments is presented at the end of the paper due to their wide practice. However, these treatments are expensive. The better approach would obviously be to modifying the textile processing technologies and chemistry to reduce the effluent pollution. Such preventive approach to environment protection has become more significant worldwide during 1990s (Schramm and Jantschgi, 1999). As a result, the practice of determining 'best available techniques/technologies (BAT)' and maintaining BAT documents started.

Per capita demand for apparel textiles is projected to grow continuously. Therefore, it becomes important to find solutions for reducing water use and the discharge of polluting chemicals. For apparel textiles, the predominant dye-fibre combination is that of reactive dyes and cotton (King, 2007). However, of all the dye-fibre combinations, cotton dyed with reactive dyes consumes the highest volume of water per kg of the fibre. Moreover, this combination causes the highest discharge of salts, alkalis and organic matter per unit fibre mass (Smith, 2003). Brief explanation to its reason is given in following paragraphs.

Since 1950s, when ICI introduced the first commercial reactive dyes for cotton, this dyeclass has become increasingly popular (Holme, 2004). That is mainly due to high levels of washing fastness, a wide gamut of bright colours, and versatility for different application methods. The high fastness to washing of reactive dyes is due to their unique reactive group(s), which form(s) covalent bonds with the hydroxyl groups of the cotton cellulose under alkaline pH conditions.

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http://dx.doi.org/10.1016/j.jclepro.2014.09.017

The dyes also react with hydroxide ions present in the aqueous dyebath under alkaline pH conditions. This produces nonreactive hydrolysed dye which remains in the dyebath as well as in the fibre. In order to obtain the required levels of washing fastness, it is necessary to remove all unreacted and hydrolysed (unfixed) dye from the cotton fibre. It is achieved by 'washing-off'; a series of thorough rinsing and 'soaping' steps. Around 50% of the dyeing cost is related to the washing-off and effluent treatment (Mohsin et al., 2013). The dye remained on the fibre after washing-off is considered as dye fixed on the fibre. The dye fixation efficiency is typically in the range of 50–80% (Smith, 2003); i.e. 20–50% of the dye necessary to achieve the desired depth of colour is discharged to the environment.

Reactive dyes are soluble anionic dyes which, in solution, are repelled by the negatively charged surface of the cotton fibre. A salt such as sodium chloride or sodium sulphate is added as an electrolyte to promote the dye transfer (exhaustion) to the fibre (Gordon and Hsieh, 2007). It also supports dye penetration into the fibre interior (diffusion) which leads to better dye fixation (Khatri et al., 2014a,b). The amount of the salt can vary up to 2 kg per kg of the fibre depending on the dye structure, depth of shade and dyeing method. Once sufficient dye is on the fibre, either by exhaustion (exhaust dyeing methods) or padding (pad dyeing methods), alkali such as sodium carbonate, sodium bicarbonate or sodium hydroxide is added to the dyebath to initiate the dye-fibre reaction. The quantities and composition of the alkali depend on the pH required for the particular type of reactive group of the dye and the dyeing method.

Irrespective of the dyeing method and the type of reactive group(s), almost all of the potentially toxic nonbiodegradable inorganic salt (Ahmed, 2005), inorganic alkali and unfixed dye are discharged to dyeing effluent. This leads to the environmental problem of a highly-coloured effluent with high levels of dissolved solids (Khatri et al., 2013) and oxygen demand (Ali et al., 2014).

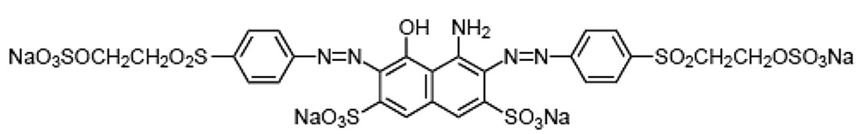
2. Development of reactive dyes

A number of improved dye structures and mixtures have been developed, since the reactive dye was invented. Most of the major advances for reducing effluent pollution are discussed below.

2.1. Bifunctional reactive dyes

The first commercial reactive dyes for cotton were based on the dichloro-*s*-triazine reactive group. Since then many other reactive groups have been developed (Ahmed, 1995). The most widely used reactive groups, in the order of increasing level of reactivity, are trichloropyrimidine, aminochloro-*s*-triazine, sulphatoethylsulphone, dichloroquinoxaline, aminofluoro-*s*-triazine, difluorochloropyrimide and dichlorotriazin. The extent of dye-fibre reaction and the ultimate discharge of unfixed dye vary widely with the type of reactive group and the dyeing technology used.

The use of two reactive groups in a dye molecule results in higher fixation efficiencies (Shore, 2002). For exhaust dyeing methods, fixation efficiency typically improves from the range of 50–60% to that of 70–80% (Smith, 2003). Many of the reactive dyes available today contain two reactive groups. Such dyes are known as bifunctional reactive dyes and are further classified as homo-bifunctional, containing two identical reactive groups (e.g. the ICI Procion HE dyes with two aminochloro-*s*-triazine groups), and hetero-bifunctional, containing two different reactive groups (e.g. the Sumitomo Sumifix Supra dyes with aminochloro-*s*-triazine and sulphatoethylsuphone groups) (Taylor, 2000). Technically, the bifunctional dyes have increased probability of reaction with the fibre. Thus, they give higher fixation yields and thus leave less colour in the dye-house effluent. For example, the CI Reactive Black 5 (Structure I) is a dye containing two sulphatoethylsulphone precursor groups. This dye has long been successful and known to produce a high degree of fixation.



(Structure I, CI Reactive Black 5 containing *bis*(sulphatoethylsulphone) reactive group)

Urea, which is often used in pad dyeing methods (Kissa, 1969) and in reactive printing (Koch, 1992) to increase dye solubility and yield of the dye-fibre reaction, is another environmentally undesirable chemical (Hyde et al., 1996). Urea, when used in the pad-dry-bake dyeing process, decomposes and increases the nitrogen content of the effluent (Chavan, 2001).

There have been a number of developments for improving the quality of effluent for cotton dyeing systems with reactive dyes. This paper presents a review of such developments under following five principal areas. The discussion focuses primarily on how researchers and industry are addressing the issues of how to reduce the discharge amounts of inorganic chemicals (salt, alkali and urea) and unfixed dye, and followed by effluent treatment processes.

- Development of reactive dyes
- Developments in dyeing machinery and processes
- Chemical modification of cotton fibre prior to dyeing
- Use of biodegradable organic compounds in dyebath formulation
- Effluent treatment processes

The hetero-bifunctional dyes provide better fixation with more flexibility for the colouration method and the process parameters. Some bifunctional dyes are claimed to provide a fixation efficiency of up to 95% when applied on cotton by the pad-batch dyeing method (Luttringer, 1993). Such improvements in dye fixation efficiency result in significant reductions in the amount of unfixed dye in dyeing effluent. The use of commercially available bi- or poly-functional reactive dyes have been recommended as the best available technique for increasing the dye fixation efficiency (European Commission, 2003).

2.2. Polyfunctional reactive dyes

Incorporating more than two reactive groups into the dye molecule should theoretically increase the fixation efficiency. However, these additional reactive groups can have an impact on important dyeing properties such as substantivity and migration because they change the molecular size and alter the extent and mode of reactivity. Therefore, the idea of additional reactive

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