Colour in textile effluents – the origins of the problem

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The potential restrictions of the discharge of coloured effluent has generated a great deal of work on decolorisation technology, but the problem has not been fully defined, let alone measured. Here, Jeff Pierce gives theoretical models, worst case scenarios and actual measurements of colour in effluent.

In the UK and much of Northern Europe, the textile industry discharges its aqueous effluent to municipal treatment plants which are biological in nature and designed for the treatment of domestic rather than industrial effluents. Thus, in general, substances that are biodegradable or insoluble are removed; non-biodegradable substances pass through unchanged and are discharged to the receiving river.

A very simplified description of an activated sludge sewage treatment works (STW) is:

- Coarse screens
- Fine screens
- Primary settling
- Aerobic biological treatment
- Tertiary settling
- Discharge to river.

After the tertiary settling, a proportion of the sludge is recycled to maintain the biomass concentration while the excess goes either to anaerobic digestion or incineration.

Of the various dyestuff types that enter an STW, those that are insoluble in water (disperse, vat, sulphur, azoic dyes and so on) will be removed at the primary settling stage. Water-soluble dyestuffs will pass to biological treatment.

Dyestuff manufacturers have expended a great deal of research on the development of dyestuff that are as stable (fast) as possible, so it is not surprising that their aerobic biodegradability is low. These dyestuffs may be removed by a biomass, though not by biodegradation but by adsorption. This mechanism is termed bioelimination, adsorbed dyestuff being destroyed during sludge disposal.

Of the water-soluble dyestuff classes, basic and direct dyes are almost completely removed by bioelimination, as are most (but not all) acid dyes. For reasons that are not understood, reactive dyes are not adsorbed onto conventional biomasses to any great degree, with a maximum of 30%, and only 10% on average. Thus, 90% of the reactive dye entering an STW will pass through unchanged and be discharged to river. The problem is exacerbated by the low fixation of reactive dyes relative to other classes, 70% on average, while direct, basic and acid dyes exhaust to over 90%.

Reactive dye colour in rivers is mainly a problem where the dilution factor, that is the volumetric flow of the receiving river relative to the outfall from the STW, is low. This is particularly the case in the East Midlands area of the UK, where dilution factors can fall to below 2:1.

The National Rivers Authority (NRA) has been very successful in reducing pollution in rivers in the UK, but this in turn has made water soluble colour more visible. This is sometimes called the 'swimming pool effect' in that while the colour of the water is constant, it appears more intense at the deep end. Thus, the cleaner the river, the further light can penetrate, and the more obvious colour pollution becomes. The human eye can detect concentrations of reactive dye as low as 0.005 ppm in a clear river, particularly in the red and reddish-purple areas.

The less polluted a river becomes, the more likely it is that the general public will use it for recreational activities. This, together with heightened environmental awareness, has led to an increase in complaints to the NRA about pollution incidents. Colour, being very visible, was the subject of over 500 complaints in 1992, the majority of these in the Severn Trent area.

After much investigation, the NRA has set river quality objectives (RQOs) for colour. These are absorbance values (optical densities) at a series of wavelengths, normally at 50 nm intervals. A simplified RQO is shown in Table 1.

Table 1

Wavelength (nm)	Optical density (1 cm cell)
400	0.025
500	0.015
600	0.008
700	0.003

As a general guide, 1 ppm of pure reactive dye (or 2 ppm of commercial grade) will give an optical density of 0.05 in a 1 cm cell at the wavelength of maximum absorption (λ_{max}). These figures therefore equate to concentrations of 1 ppm to 0.1 ppm.

A model dyehouse dyeing only cotton and using only reactive dyes will discharge on average 60 ppm of dyestuff (see 'theoretical models' section) and most of this will pass through the receiving STW to the river. Thus, a combined dilution factor, that is non-colour:coloured effluent received and river flow:STW outfall of at least 60, and 600 at critical wavelengths, would be necessary to achieve the RQOs. Clearly, areas with a large number of dyehouses and/or small rivers have a major problem.

It has been suggested that problem of colour in river water would be solved by the development of reactive dyes with fixation approaching 100%. The dyestuff manufacturers, via the Chemical Industries Association, have categorically stated that this will not happen this century, if at all. It has also been suggested that alternative dyestuff classes should be used for the dyeing of cotton rather than reactive dyes. In fact, consumers, including those that complain about colour in rivers, demand fastness levels, brightness and a shade gamut that can only be achieved by the use of reactive dyes.

Control of colour in rivers

The NRA has identified 13 areas where there is an ongoing problem of colour in rivers, the origin being low dilution factors for one or both of the reasons mentioned previously.

They have imposed, or intend to impose, colour consent limits on the STWs in these areas in order to achieve the RQOs, taking into account river dilution factors. These consent limits are shown in Table 2, at 100 nm intervals only.

Table 2

Location	Consent limit (absorbance) at nm 400	500	600	700
Pinxton	0.047	0.023	0.016	0.004
Wanlip	0.035	0.050	0.014	0.008
Loughborough	0.0031	0.013	0.013	0.003

These limits equate to concentrations from 2 ppm to 0.1 ppm.

Pinxton receives approximately 43% of its inflow from dyehouses and, while Wanlip receives of the order of 14%, it is a 130 Ml/day works that discharges to the relatively small river Soar; the situation at Loughborough is similar.

All the STWs that the NRA currently intend to consent are in the Severn Trent plc area, whose reaction is currently unknown. Given that it has probably the best record of the ten water companies on terms of meeting the other NRA consent limits, it must be assumed that it would not wish to compromise its reputation. There is, however, currently no economically viable technology available for the removal of low concentrations of dyestuff from high volume flows.

Without presuming to read the collective mind of Severn Trent plc, it appears that if the NRA imposes and strictly monitors the proposed colour consent limits, Severn Trent will have little option in the short or medium term other than to impose colour consent limits on its customers, the dyehouses.

Whether or not it allows for dilution from non-coloured effluent, or passes on the NRA limits directly to allow for shock loadings, the limits are likely to be of the order of 1 ppm. This figure is purely hypothetical and a gross oversimplification. Nevertheless, it should be borne in mind when reading the following sections.

Theoretical models

These calculations are based on the following reactive dyeing sequence.

Baths 1, 2, 3	Preparation
Bath 4	Dyeing
Baths 5, 6	Rinsing
Bath 7	'Soaping'
Baths 8, 9	Rinsing
Bath 10	Finishing

The average depth of shade dyed on cotton with reactive dyes in 2%; this may vary with season and fashion, but is a well documented figure. The average level of fixation of a reactive dye applied by exhaust methods at a liquor ratio of 10:1 is 70%, again widely accepted.

Jet dyeing model

Fabric	100% cotton
Batch size	250 kg
Dye class	Reactive
Depth of shade	2%
Dye fixation	70%
Liquor ratio	10:1
Number of baths	10

Weight of dye applied	$250 \times 0.02 = 5$ kg
Weight of unfixed dye	$5 \times 0.03 = 1.5$ kg
Total water usage	$250 \times 10 \times 10 = 25\,000$ l

Concentration of fully balanced effluent is 1.5/25 000 = 60 ppm.

Again, this figure is found to be typical, when annual dye and water usage statistics from a number of dyehouses are examined.

Thus, in order to achieve a 'potential' colour consent level of 1 ppm, complete balancing would have to be achieved followed by an 'end-of-pipe' decolorisation technique which would reduce the colour concentration by 98%.

Two other points can also be made. Even if the 'potential' consent level of 1 ppm is low by a magnitude, a colour removal efficiency of almost 90% would be required. With reference to high-fixation reactive dyes, if a fixation level of 99% is substituted for the 70% figure, the dyestuff in a fully balanced, average effluent would be 2 ppm, above the 'potential' colour consent limit.

In order to achieve perfect balancing, extremely large tanks would be required and many dyehouses do not have the space, let alone the money, for such a civil engineering project. Few dyehouses have other than rudimentary balancing which is normally associated with pH and temperature consent limits rather than colour. Thus any end-of-pipe decolorisation technique prior to discharge must be capable of dealing with shock loadings.

Full black shade

Black shades are currently very popular, and the deeper the better. CI Reactive Black 5 and shaded variants are used almost exclusively and while this dyestuff has excellent exhaustion and fixation levels, the build-up graph is plateauing at this depth which is 6% grains, though a 40 or 50% liquid brand would more likely be used.

Fabric	100% cotton
Batch size	250 kg
Dye class	CI Reactive Black 5 (shaded variant)
Depth of shade	6% (grains)
Dye fixation	80%
Dye exhaustion	90%
Liquor ratio	10:1

Weight of dye applied	$250 \times 0.06 = 15$ kg
Weight of unfixed dye	$15 \times 0.2 = 3$ kg
Total water usage	$250 \times 10 \times 10 = 25\,000$ kg

Concentration of fully balanced effluent is 3/25 000 = 120 ppm.

Again, this assumes full balancing, but the shock loading from the exhausted dyebath would be:

Weight of non-exhausted dye	$15 \times 0.1 = 1.5$ kg
Water usage, single bath	$250 \times 10 = 2500$ kg
Shock loading	$1.5/2500 = 600$ ppm

Using the approximate relationship given earlier, this equates to an optical density of 15 at λ_{max}.

To decolorise this shock loading to the potential colour consent limit of 1 ppm would require an end-of-pipe decolorisation technique with an efficiency of 99.9%.

Doomsday scenario

Even CI Reactive Black 5 has its limitations. With the demand from retailers for deeper and deeper black shades, fixation and exhaustion levels fall. If the dyebath exhaustion of a 7% (grains) shade were to fall to 80%, the potential shock loading of the dyebath would be:

Weight of dye applied	$250 \times 0.07 = 17.5$ kg
Weight of dye in exhausted dyebath	$17.5 \times 0.2 = 3.5$ kg
Water usage, single bath	2 500 l
Shock loading	$3.5/2500 = 1400$ ppm

This equates to an optical density of 3.5 at λ_{max}.

Actual measurements
These were carried out at a jet dyehouse in the Severn Trent area that dyes mainly 100% cotton knitwear (dyehouse A) and funded by a company active in decolorisation technology (see acknowledgements).

A sampling device was inserted in the outflow to sewer, this being triggered by a float. Each sample represents a discharge of approximately 2500 l. The time for this discharge was 5 min, the final 2 min being gravity draining rather than pumped discharge. The sampling device activated after approximately 1 min.

Other parameters essential to the design of a decolorisation system, temperature and pH, were also monitored.

The optical density of the samples was measured at 550 nm, the critical reddish-purple area, and on the very first run an optical density of 16.5, 21 at λ_{max}, was recorded. Thus the Doomsday scenario is not as outrageous as it might first appear.

Three sets of 24 sequential discharges were monitored, as shown in Figures 1–3.

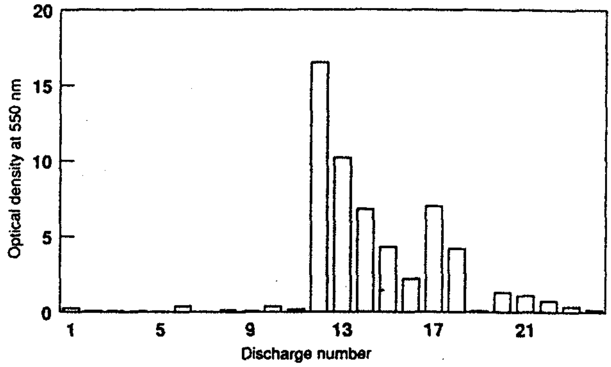

Figure 1

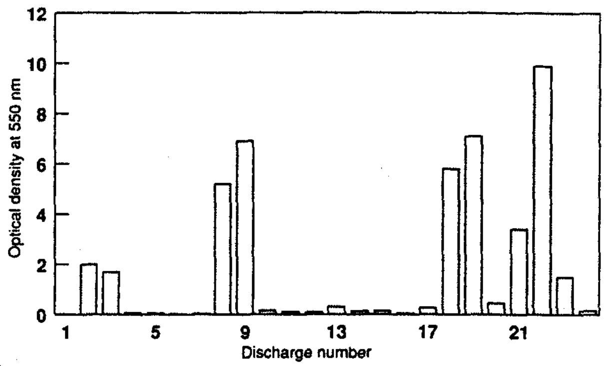

Figure 2

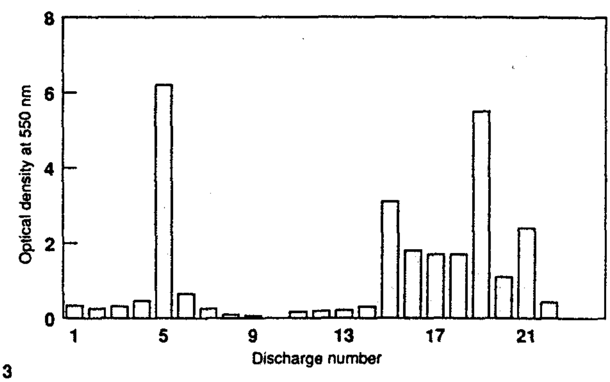

Figure 3

Conclusions

- The theoretical models are valid, at least at dyehouse A.
- Effluent balancing is essential to reduce shock loading, whether or not colour removal equipment is installed.
- Segregating highly coloured streams is theoretically advantageous, but impractical at most dyehouses given the existing drainage systems and the cost involved.
- Collective decolorisation at an STW could be practical but only if there were a high percentage of dyehouse effluent received. Balancing would occur in the sewers, but so would dilution, making decolorisation less efficient and more expensive.
- Could an STW segregate, and treat, highly coloured streams using optical density monitoring?
- The use of reactive dyes is not going to diminish, and neither are the associated problem of colour in rivers and public pressure to do something about it.

As a philosopher once said, 'I don't know the solution, but you have a wonderful problem.'

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