Section 2: Process Optimisation

This page intentionally left blank

COLOUR REMOVAL FROM EFFLUENT AND WATER REUSE IN COURTAULDS TEXTILES

Peter Cooper

INTRODUCTION

The removal of residual colour from dyehouse wastewaters is currently a major environmental issue in the Textile Sector. Progress on resolution of the problem has been made. This paper describes how the work carried out by Courtaulds Textiles has resulted in an acceptable environmental solution but also how that solution allowed improvements in waste minimisation (and hence sustainable development) and cost benefit.

Coloration is a key factor in the commercial success of textile products, particularly those with a high fashion content, especially garments, furnishings and upholstery. However, the consumer requires, in fact demands, easy-care properties such as acceptable performance characteristics and fashion colours with high fastness to light, washing and perspiration. To ensure these colours and properties are available initially and after prolonged wear and wash, the substances that confer the properties on the substrate have to be robust to most treatments and conditions. The reactions necessary to introduce the substances onto the substrate do not always run to total exhaustion, or completion. Therefore residual dyes and chemicals are left in the process water and are discharged in the wastewater leaving the site.

In the dye-making industry there is considerable debate on what level of environmental hazard is produced by coloured effluent. Beckmann and Sewekow[1], stated in 1991 that there are 'no tenable arguments for the classification of dyestuffs as dangerous substances' in effluent. They go even further to say that 'dyestuffs should not be regarded as water pollutants' since 'the harmful effect is negligible'. Nonetheless, even though the colour problem could be argued to be only aesthetic, we have to accept that the general public does not like coloured amenity water, and the problem therefore has to be rectified.

Not all dyes give the same level of problem. Factors such as extent of fixation on different substrates and residual amounts in wastewater affect physical and chemical behaviour in the sewage treatment works. Primary settling removes relatively high proportions of insoluble disperse and vat dyes, while activated sludge removes medium to high proportions of soluble basic and direct dyes, principally by adsorption. However, this system only removes low levels of reactive and certain acid dyes and also fails to deal with some dyes when they are in combination with others. Some dyes are bio-degradable, under anaerobic conditions, after activated sludge treatment, but again not reactives and acids. Therefore without tertiary treatment these residual dyestuffs tend to colour receiving waters, particularly those with low dilution factors. It has been estimated that certain colours show at 1 -2 ppm levels in the receiving water.

The point is often made that effective environmental solutions are often not those that are end-of-pipe but those that attack the problem at source (i.e. cause rather than effect). This view has certainly been applied to the colour problem on three main levels: fixation, dye molecule selection and performance. The dye molecules need to be robust to meet the performance standards required and have been developed accordingly. The chemical structures that give the presently available wide variety of colours have also

been finely tuned over a long period. To change these structures to give more biodegradable alternatives would lead to less colour choice and poorer performance. The dye supply industry indicates a further major structural change of the dye molecules is unlikely in the medium term.

The possibilities for improving dye fixation is perhaps the one area of hope. An improvement in the ability of the molecule to stay on the fibre would reduce the quantity of dye required, and hence the cost, and would improve the quality of the effluent. A range of high-fixation dye over a limited colour range is now available. This should help to alleviate the problem of colour in effluent but will not completely solve it.

REGULATORY APPROACH

A few UK midlands, major textile processors who discharge directly to river and have their own sewage treatment works and a couple of Water Company Sewage Treatment Works have been required to remove colour from effluent for some time. This has generally been achieved by a tertiary treatment with coagulation and flocculation techniques using polyelectrolytes and/or inorganic flocculants (such as ferric and aluminium salts). This process is carried out after settlement and biological treatment so that a significant proportion of the pollution load of the effluent such as COD and those process chemicals that are adsorbed onto the sludge has already been removed. However the combination of poor removal efficiency at some sewage treatment works - to which over 90% of textile processors discharge - and low dilution in receiving waters has led to public complaints and, consequently, in the early nineties the National Rivers Authority (NRA) began to progressively apply specific levels of colour control on discharges to rivers. This regulation is being applied primarily to the water companies that run the ineffective sewage treatment works. If they cannot meet these control parameters, because they have no effective treatment or because dilution factors make the colour treatment non-viable, they in turn are applying those same control parameters - in many cases excluding dilution factors - to the discharger, who must exercise the appropriate control.

Table 1: Measurement of colour in a typical textile industry untreated effluent against 'constant' standard

ABSORBANCE		
Wavelength (nm)	Consent Level	Actual Level (prior to treatment)
500	0.103	0.753
550	0.108	0.564
600	0.062	0.560
650	0.062	0.408

The effectiveness of colour removal is judged by an absorbance technique carried out against a consent standard at a number of wavelengths, shown in Table 1.

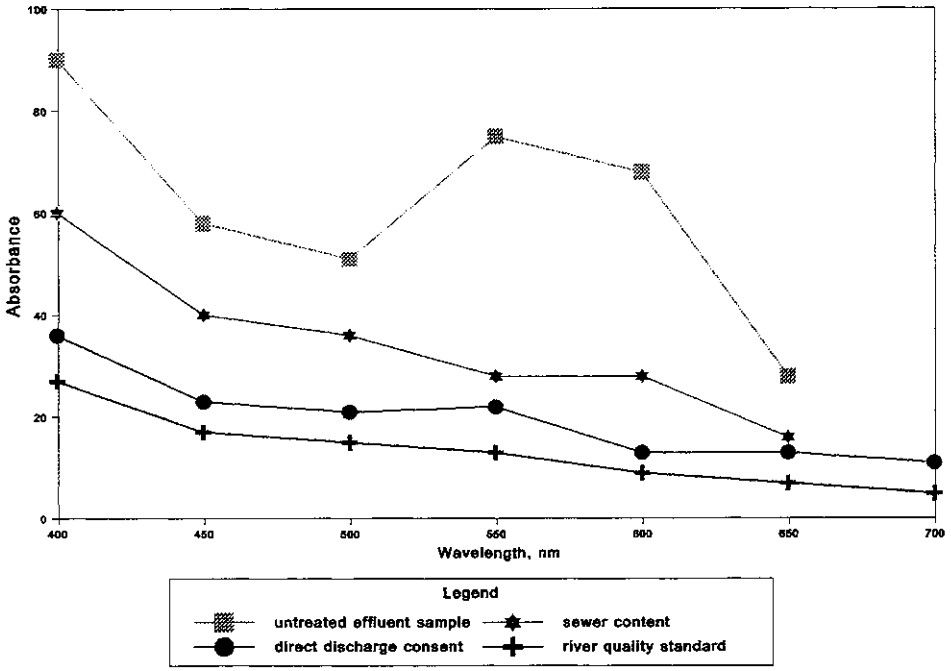


Figure 1: Absorbance techniques can show how untreated samples compare with various agreed standards

Figure 1 shows graphically how an untreated effluent sample compares with a sewer consent, direct discharger's consent and a proposed river quality standard on colour in rivers.

The numbers shown on Table 1 and Figure 1 are slightly different because they are from two different geographical areas.

One sewage treatment plant - the Leek works of the Severn-Trent River Authority, did make the decision to invest in tertiary treatment. The decision was made because the Leek works benefits from a particularly high textile processing load in the industrial effluent it receives, which in turn is high compared with the domestic effluent load. This situation is rare, and therefore dilution is less of a problem, making treatment of the coloured effluent viable for the water company. The treatment technology - ozonisation - has both high capital and running costs. Under the polluter pays principle the costs of this investment are recovered from the polluter - i.e. the textile industry/processor in Leek - and this essentially doubled the cost of effluent discharge for all dyes and finishers in the district. As Courtaulds Textiles (CT) have two dyers in the area the additional cost was some £250k. Additionally the tertiary ozone treatment is practical in very few cases as in most areas dilution from other sources is so significant that the sewage treatment works cannot viably treat the combined effluent to remove colour successfully. The combination of these two factors - high cost and the unlikelihood of a service from the Water Company(ies) elsewhere - was an incentive for CT to investigate ways of colour removal as an on-site, "end of pipe" solution prior to discharge to the sewer.

SEARCH FOR SOLUTIONS

In the three and a half years, from late 1989/early 1990 - when we were first advised of the problem - to mid 1993, Courtaulds Textiles worked with some 12 suppliers of removal technology in all the recognised technical areas, namely:

- Coagulation/flocculation;
- Destructive techniques (oxidation, chlorine dioxide);
- Membrane technology;
- Adsorption techniques (carbon, organic and inorganic); and
- Newer technologies (electrolysis with various electrodes/brine cell, combinations)

It may be interesting to quickly review the reasons why some of the more widely recognised successful removal techniques were not appropriate to Textile effluents.

Activated charcoal

Activated charcoal is a widely used adsorption technique. It is most effective with volatile organic compounds (VOC), which can be readily and effectively adsorbed onto the surface from a waste steam. A VOC is also capable of rapid and efficient desorption and so the activated charcoal, which itself has a high unit cost, can be reused a number of times. However, although molecules of coloured materials are reasonably well adsorbed onto the charcoal, desorption of these large and inert molecules is extremely difficult. Regeneration costs therefore soar, either because the incineration required for desorption is significant or because disposal costs are high.

The technique is most effective with relatively small volumes on short time-scales so that interchange can take place. With the high volumes of water involved with dyeing, the size and cost of the plant required becomes disproportionate to the problem, and payback is poor. The technical problems of desorption/regeneration and cost considerations mean that this technique is not always viable. Lower-cost, high-surface-area carbons may improve the position in the medium term.

Membrane technology

Membrane technology can be further subdivided into three categories; ultrafiltration, nanofiltration and reverse osmosis. Ultrafiltration is of no use in colour removal as the membrane hole size is too large to prevent dye molecules passing through. On the other hand, both nanofiltration and reverse osmosis membranes are effective in separating large dye molecules from the effluent.

The technique is capable of treating large volumes fairly quickly but capital cost is high. Cleaning of the membrane can cause problems and the abrasive nature of textile effluent reduces membrane life.

The major drawback to the system is that a coloured residue still remains for disposal. More colour is consolidated into less volume, but that aqueous concentrate is still an effluent so membrane technology is not a preferred option, but improvement in disposal techniques for concentrates may make it more acceptable.

Destructive treatments

Destruction techniques, remove colour from effluent by cleaving bonds in the dye molecule to produce colourless species. Such techniques can be used on large volumes

of effluent and reaction is reasonably quick, although the capital cost is high. A drawback to the system seems to be the possible toxicity of the breakdown products. Dyes often contain nitrogen, chlorine and/or sulphur, and oxidation of such complex molecules could result in metabolites that could be more toxic to the receiving environment than the parent molecule itself. Although a number of systems are now being marketed there is no information available, either from suppliers or in the literature, on the relative pollution load and toxicity of the treated effluent.

In my view this needs to be fully clarified before the technique is totally acceptable. If this were to be done the technique would have one additional benefit: it would reduce the COD of the treated effluent. Any reduction in COD would necessarily reduce costs and offer an advantage to the textile processor.

Coagulation/flocculation

Coagulation/flocculation techniques, particularly using the newer generation of polyelectrolytes, are used, with varying degrees of success, as a tertiary treatment to remove colour from textile effluent. Research and development programmes at Courtaulds Textiles have established that coagulation/flocculation of raw balanced effluent, prior to discharge to sewer, can effectively remove colour to a level that meets the consent standard. Balanced effluent varies in terms of dye molecule type, composition and concentration, dependent on production requirements and flow. Hence the polyelectrolyte has to be overdosed both to improve the efficiency of reaction and to enable the dark and least reactive molecules to be completely removed. This leads to residual concentrations of the polyelectrolyte in the effluent, which has a detrimental effect on the nitrification process.

As ammonia levels in discharge to watercourses are a key control parameter also, probably the most critical to aquatic life, the water companies need to satisfy themselves that the selected polyelectrolyte has no effect. The technique also has the advantage of COD reduction but sludge production is high.

It is estimated that the cost of pilot plants, chemicals, time (own and partners) and overhead recovery for this corporate research and development project was in excess of £200,000. Recent research published in the Journal of the Society of Dyers and Colourists [2] in March 1993 provided the concluding paragraph:

"Colour removal after biological treatment is operationally feasible. The requirement to remove colour from textile coloration effluents on site prior to discharge to sewer currently represents a 'technology void' and/or a 'viability vacuum'. Therefore development work on new colour removal techniques needs to be significantly accelerated. Otherwise operators of treatment works and the discharger face the possibility of prosecution by the independent regulator, and heavy fines if found guilty."

Later that same year the SDC were so concerned about the development of appropriate technologies that they commissioned a book, entitled "Colour in Dyehouse Effluent", to draw together, as a single reference point, currently available developments which were likely to lead to a technical solution.[3]

COURTAULDS TEXTILES' RESOLUTION OF THE PROBLEM

In the interim the continuation of research at CT lead to the investment at Courtaulds Socks, a CT plant in Leicester (which was the area after Leek affected by the new regulatory approach), in the "Macrosorb" system.

Macrosorb is the trade name of a range of particulate absorbent developed jointly by Crosfield and Unilever Research. It is classed as a "synthetic inorganic clay", having the layered structure typical of such materials. Macrosorb has a fixed positive character but includes balancing inter-layer negative units that are readily exchangeable. It is this negative exchange characteristic that gives the Macrosorb range its unique properties including the ability to remove dyes, chemicals and other contamination from aqueous streams very rapidly and down to very low levels.

The decision to invest in the system was based on initial bench work on site, followed by a pilot plant treating 10 per cent of the flow and finally bulk trials treating 50 per cent of flow. The trials were very encouraging allowing colour consent requirements to be achieved.

A full size plant was then designed, built and installed by Bergmann Technology (part of the Linatex Group), the engineering partner of Crosfield. The plant was commissioned in July 1995 and has been in operation since then.

The system, shown schematically, comprises of Tank 1 - reaction tank; Tanks 2 and 3 - flocculation and coagulation and Tank 4 - crossflow clarifier. In Tank 1 the effluent is treated, if necessary, to correct pH for effective Macrosorb treatment. Macrosorb is then added together with inorganic salts.

The residence time in Tank 1 is adjusted to allow for absorption of contamination (chemicals - referred to as chemical oxygen demand - and colour) onto the Macrosorb particles, with sufficient agitation to ensure adequate contact between Macrosorb and the material which is to be absorbed.

During the passage between Tanks 1 and 2, caustic soda is added to rapidly increase pH. This alkali shock fulfils several functions - it produces a primary floc from dissolved organic contaminants and also converts metallic acid salts into their hydroxides. Both effects reduce the concentration of dissolved contaminants and these additional flocs aid gravity settlement by weighting the Macrosorb suspension.

Settlement is further aided by the addition of a high molecular weight coagulant. Passage onwards through the system is driven by hydrostatic head. Separation is accelerated in the Crossflow Clarifier by passage of the effluent stream, through an array of closely spaced inclined plates, which present a very large effective surface area for solid/liquid separation. The contamination particles have only to settle a short distance before contacting the plates, effectively removing them from the effluent stream. Treated effluent continues to either waste or is redirected for re-use.

The contamination particles slide down the plates and collect as sludge in the bottom of the tank. The sludge can then be concentrated in a conventional thickener. It can be further concentrated to a 30 per cent - 40 per cent dry solids content filter cake using a plate-and-frame filter press. This is part of the full system described below. However the flocculated solids from the system at C.Socks are currently being discharged direct to sewer, with the approval of Severn Trent, and the increase in suspended solids attracts an additional charge through the Mogden formula.

The capital cost of the C.Socks installation, including new dyehouse drains, a new collection sump, collection tanks and balancing tanks, was some £400k but the process equipment cost is somewhat less than this.

The effectiveness of the colour removal capability of the plant is monitored by optical density, at each individual wavelength contained in the consent against the consent limit. The figures underline the need for adequate balancing of the effluent in order to achieve optimum mixing and consequent removal. The plant was originally designed to balance the equivalent of four hours' flow but this will be increased in line with higher production levels.

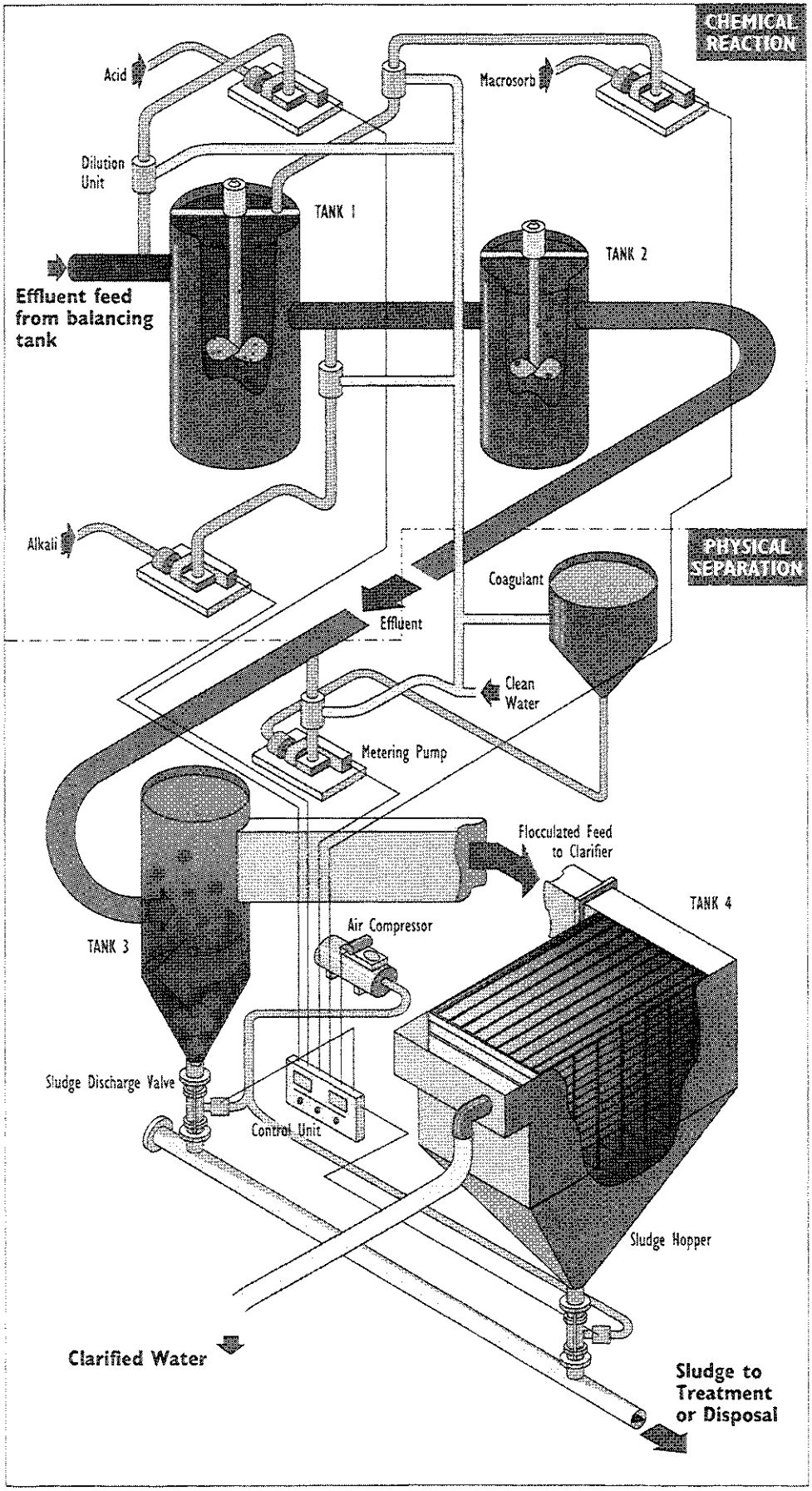


Figure 2: The Macrosorb treatment system

The major investment benefit, however, will be derived from the capability to re-use some 50 per cent of the process water treated via the plant. The re-use level is achieved consistently and the business's only customer, Marks and Spencer, to whom C.Socks supply men's, ladies and children's socks, is receiving goods processed with recycled water which maintains the required standards of quality and performance.

Current development work suggests that higher water re-use levels can be obtained. There are also other operational benefits. The recycled water has already been softened and it retains some of the heat applied during previous use and as a consequence energy and chemical savings can be made. The final benefit is that the business does not have to pay an additional 25p/m^3 now levied on the rest of the Leicester based dyers and finishers for a removal service now possible at Wanlip S.T. plant. These benefits make the investment at Courtaulds Socks viable, i.e. a no cost situation.

We have also utilised the absorption/precipitation concept - together with micro-biological polishing and the filter press mentioned earlier - in the design of a complete effluent treatment plant, for discharge of treated water into watercourse, in a joint venture investment in China and in a new dyehouse in the Philippines.

The benefits of water reuse and energy recovery are built into the systems, which meet all the discharge standards placed on us - BOD_5, COD, suspended solids, chromium VI, colour, aniline residues - and these standards are very close to the standards applied in the UK and the authorities are paying a lot of attention to how they actually perform. But the other major benefits we have obtained, compared with conventional combined biological/chemical treatment systems, are low capital cost, and a space requirement at least a quarter that of conventional systems. The key reason is that the chemical treatment gives a significant reduction of COD, which then means that the biological polishing unit can be small and compact and also be efficient to the 20 mg/l of BOD_5 required - plus achieving all other parameters.

CHALLENGE FOR THE FUTURE

Despite the benefits of the removal system described, the solution is still "end of pipe". Additionally, the Crosfields system and three or four other systems that are now technically operational and reasonably effective, at capital costs of £200 - 400k per installation and £50 - 100k per annum running costs - based on 30m^3/hr - put the viability of significant numbers of SMEs - which are the majority of the industry - at risk. There is a real belief that the textile colouration sector can survive in the UK, because of the dual benefits of being near to the market and quick response, but the operational expenses identified need to be significantly reduced to ensure the belief remains a reality. As the colour problem, inevitably, becomes more of an international problem, there is a major prize for the supplier who minimises the problem at source or reduces significantly the costs of end of pipe solutions.

REFERENCES

1. W.Beckmann and U.Sewekow, Textil Praxis, (April 1991) 346.
2. P.Cooper, JSDC, (March 1993) **109** 97.
3. P.Cooper (ed), *Colour in Dyehouse Effluent*, published by Society of Dyers and Colourists, Bradford, 1995, ISBN 0901956694.

BIOCHEMICAL TREATMENT OF RECALCITRANT DYESTUFF EFFLUENT

J. Binkley, T. M. Evans, J. Hargreaves and G. Smart

INTRODUCTION

Chemical constituents in organic molecules can transform them from biodegradable to persistent compounds. Such substituents include amino-, methoxy-, sulphonyl-, nitro- and chloro- groups, a range of meta-substituents on the benzene ring, ether linkages and carbon chain branching. The presence of such substituents is frequently found in dye molecules [1].

Chlorinated compounds are of particular interest partly because some are extremely toxic or persistent, eg. DDT, and partly because organochlorines are rare in nature and are usually xenobiotic. The biodegradation of many of these compounds is dependent on initial reductive dechlorination, which occurs anaerobically. This is particularly important in the case of chlorinated aliphatic compounds. In contrast, chlorinated benzene derivatives and polychlorinated biphenyl's (PCBs) appear to be degraded only aerobically.

Although aerobic processes are still much preferred for industrial waste treatment, anaerobic conditions appear to be more favourable for reactions involving nitrosamine degradation, epoxide and nitro reduction and degradation of certain aromatic compounds. Since much of the information available on structure-degradability relationships is based on generalities, it is usual when considering potential treatment options to conduct biodegradability tests on the waste stream in question.

Biodegradability testing can be sub-divided into three categories:

(i) tests on compounds which readily and rapidly degrade in the environment, referred to as "ready biodegradability";

(ii) tests on compounds which degrade under favourable test conditions, that is "inherently biodegradable", and

(iii) simulation testing - this involves the use of a bench scale activated sludge plant with artificial effluent, which is kept fed with controlled amounts of the required nutrients. The pollutant under test is then added and periodic monitoring carried out. The setting up of the plant is usually done in duplicate and the sludge in each interchanged, to ensure as close to identical conditions are maintained.

It is essential that colour from textile effluent is minimised to an acceptable level by the best practicable means not exceeding excessive cost. The aims of this work are as follows:

(i) to set up and maintain the running of a pilot plant activated sludge system;

(ii) to acclimatise strains of micro-organisms to gradually increasing concentrations of recalcitrant dye molecules;

(iii) to study the effect of a variety of similar dye molecules with only slight differences in structure, eg. functional groups, position and degree of substitution;

(iv) to attempt to remove a variety of different reactive dyes utilising activated sludge by either adsorption or biodegradation.

Decoloration of wet processing effluent by activated sludge is known predominantly to take place by an adsorption process, the mechanism of which is not fully understood [2]. Some of the major factors which affect the efficiency with which colour is removed from wet processing effluent may be considered to be: (a) the type of activated sludge; (b) the size and shape of the dye molecule and (c) the chemical structure of the dye.

The purpose of the initial investigation was to assess the relative efficiencies of three different activated sludges in the removal of colour from textile dye effluent. The reactive

dyes were hydrolysed to simulate their state in a dye-bath liquor, as colour from these dyes can be very difficult to remove.

EXPERIMENTAL

The dyes chosen were Procion Blue H-EGN 125, Procion Blue H-EXL, Procion Crimson CXB and Procion Navy H-EXL. Dye solutions were made up as 1% w/v stock solutions. Hydrolysed dye solutions were produced by adding 2% Na_2CO_3 ($10cm^3$) to $500cm^3$ of dye stock solution.

Absorbance measurements were carried out on a Perkin Elmer Lambda 2 spectrophotometer. Absorbance readings were taken on the supernatant dye solutions after centrifuging for 8 minutes at 2000rpm, in order to remove any turbidity which might have otherwise caused absorbance reading errors. All absorbance readings were taken at the wavelength of maximum absorbance, λ max, for each dye against either a distilled water or sludge supernatant blank.

COD measurements were carried out using a Hack DR/700 Colorimeter and EPA approved Reactor Digestion method. The Olympus Optical Microscope was used for micro-organism and floc studies. The electron microscope was an SX25 scanning electron microscope, made by International Scientific Instruments.

Samples of activated sludge were obtained from Strines Textiles, Bolton Sewage Treatment Works and Bridgwater Paper Mill and typified sludges available from UK water treatment plants,

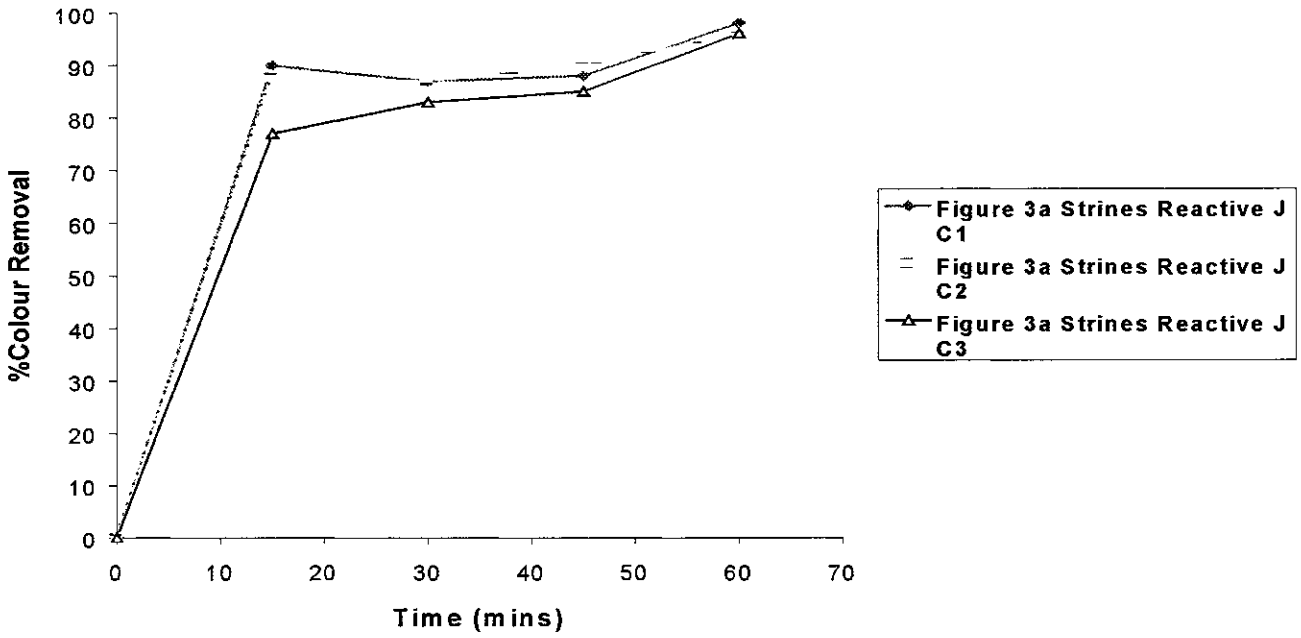
Sludge maintenance was carried out on a daily basis with pH kept in the range 6.5 - 8.5 with regular additions of sulphuric acid 5mol dm^{-3}. Sodium ethanoate solution 1.0 mol dm^{-3} was fed to the sludge on alternate days at a feed rate of $20cm^3$ per litre of sludge. Nitrogen and phosphor containing salts were added initially in order to supply the necessary nutrients for microbial growth. The solids content was checked at regular intervals and recorded as $5gdm^{-3}$ (+/-$0.1gdm^{-3}$).

RESULTS AND DISCUSSION

A pilot plant was set up and maintained for four weeks in order to stabilise such conditions as solids content, pH and COD. Micro-organism identification was carried out with each of the sludges using an optical microscope. The main population of the Bridgwater paper mill and Bolton STW sludges were protozoa, rotifers and nematodes. The major constituent of the slide samples were the flocs themselves. The composition of the Strines activated sludge seemed to be mostly the bacterial flocs, which would suggest that the sludge could be acting as a huge adsorbent biomass. It may be that this very different biological makeup was responsible for the differences manifest in the initial part of this work. The appearance of the Strines sludge under the microscope was virtually just the flocs themselves, and appeared to be in greater abundance than the other two sludges, despite the solids concentration being the same. It may therefore be assumed that the adsorption taking place is directly related to the floc density.

It has been stressed that activated sludge is not known to be particularly effective at removing reactive dyes from textile effluent [2]. The intention of this work was to test the validity of such a hypothesis. The reactive dye chosen here was Procion Reactive Blue H-EGN 125. As expected the Bridgwater and the Bolton STW sludges show little or no reactive dye removal as shown by Figures 1b and c. However, the Strines sludge, Figure 1a, is found to be very effective in the removal of the reactive dye from solution. Its efficiency

Figure 1a: %Colour removal versus time. Strines sludge and Procion blue H-EGN 125 hydrolysed reactive dye



was found to be most effective regardless of the concentration of any of the dye. The weaker solutions were more efficiently decolourised, with upwards of 90% change in the measured absorbance after 45 minutes from the 0.005, 0.01 and 0.02% solution concentrations. It would appear from this that even the Strines sludge was nearing its saturation point in terms of its capacity to deal with the reactive dye over these time-scales.

Figure 1b: %Colour removal versus time. Bolton STW and Procion blue H-EGN 125 hydrolised reactive dye

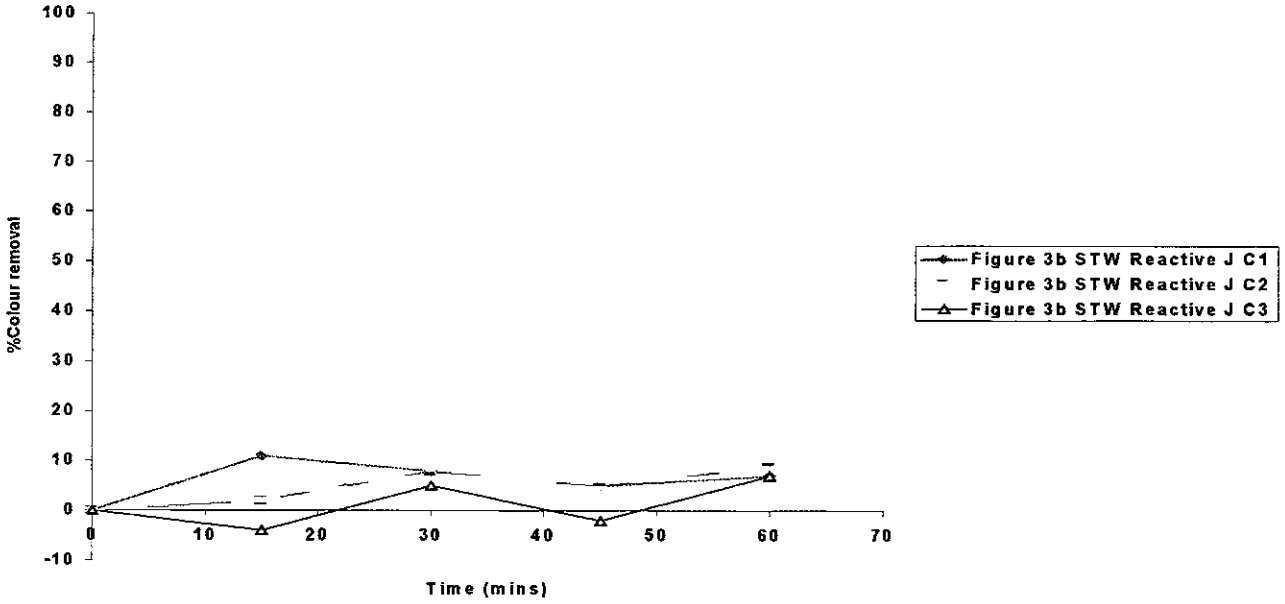
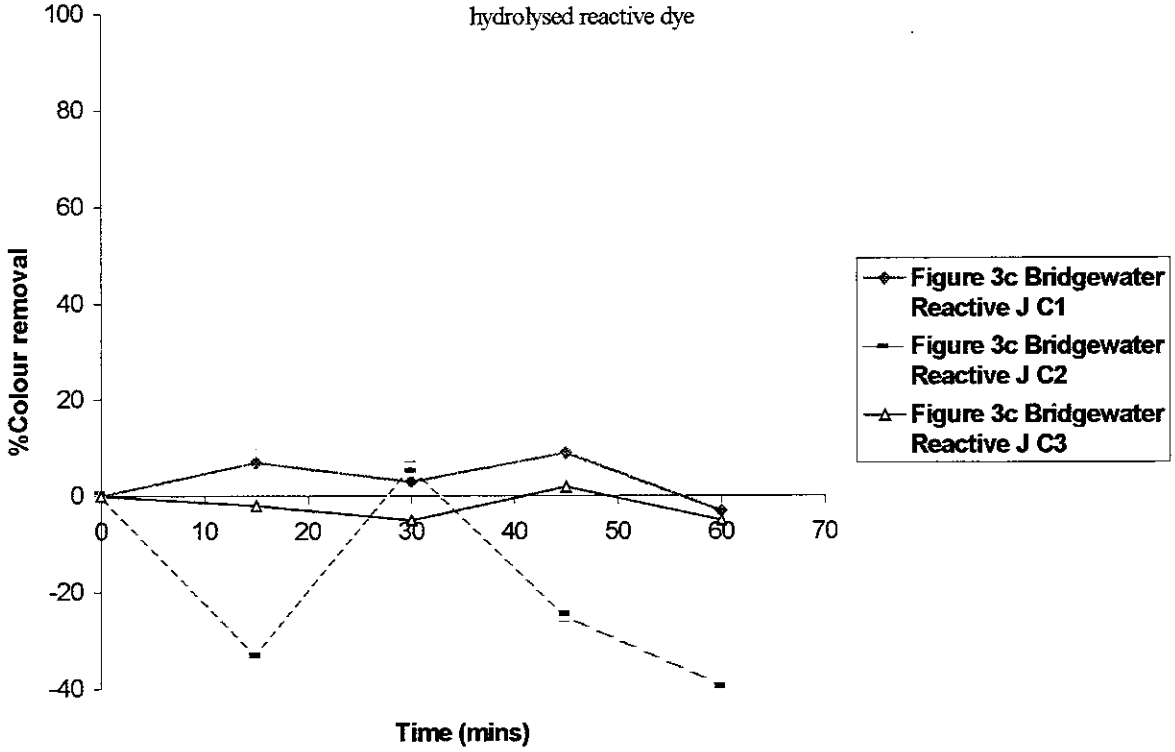


Figure 1c: % Colour removal versus time. Bridgewater sludge and Procion blue H-EGN 125 hydrolysed reactive dye



During the course of this work a distinctive colour change was noticed in the solution containing the Strines sludge and the reactive dye. In all previous treatments with the different combinations of dye and sludge, the solutions were seen to become visibly decolourised with time. There was, however, no change in the actual colour, only its perceived strength.

Figure 2: Absorption spectra for hydrolysed Procion blue H-EGN 125 reactive dye before and after treatment with Strines sludge

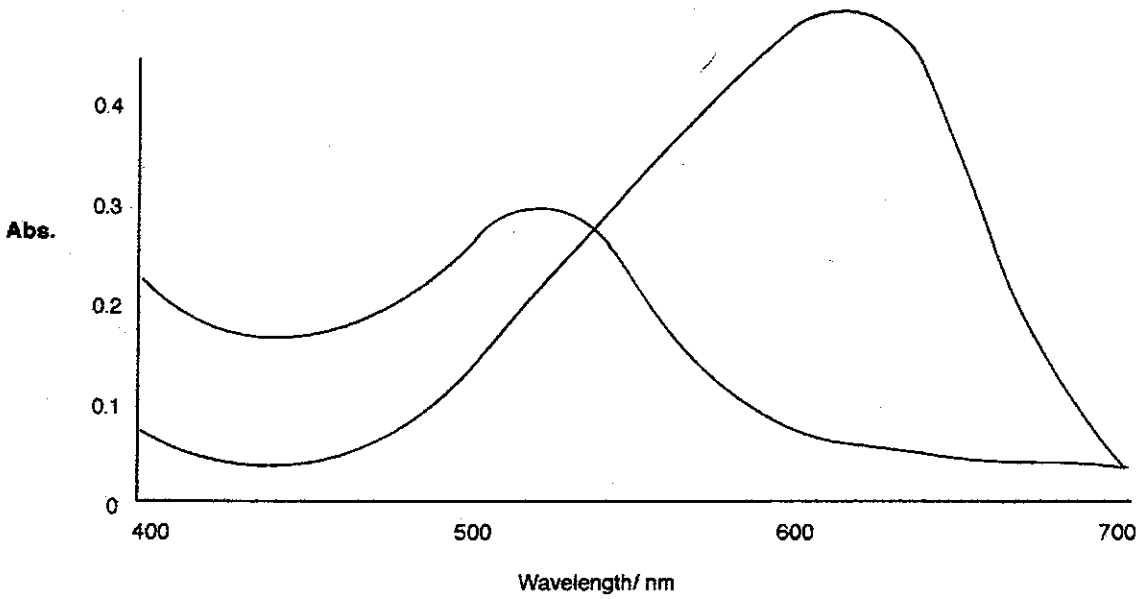


Figure 2 shows the absorption spectrum of the supernatant liquor from the Strines sludge/reactive dye solution before and after treatment. During the hour in which the 0.005% solution was under investigation the initially blue solution became a weak red colour. It was also noticed that the solutions of increasing concentration exhibited hues of lilac, purple and blue respectively.

It is widely known that some commercial reactive dyes are bicomponent mixtures with other dyestuffs. However, in this case, the Procion dye is definitely known to be a single structure. The detailed structure cannot, as yet, be disclosed. However, once the dye has had sufficient contact with the Strines sludge, as little as 15 minutes, the appearance of the spectrum has significantly changed with the new shape and position being more consistent with that of a red dye. The product of this process could be the oxidised red product of biochemical degradation. The oxidation product(s) of this particular dye, according to the manufacturers, exhibit a red colour. It might appear, therefore, that reactive dyes might be biologically degraded, as the results might seem to imply. However, the chances of biodegradation taking place in such a short time period are fairly slim. It is probably more likely that the rapid appearance of the red colour is due to dye already adsorbed in a previous treatment process with this particular sludge, and desorption following under this set of conditions. Further speculation as to the actual mechanisms of colour removal would require additional information about the nature of the sludge and particularly the three dimensional structure of the dye molecules. Unfortunately this information is not commonly disclosed by the dye manufacturers, but will have to be made available if the results here are to be exploited to there full potential. From the work carried out it is apparent that adsorption takes place within the first few minutes of contact with the flocs.
Other reactive dyes selected for similar treatment and study are shown in Table 1.

Table 1: % Dye removal after 32 minutes using plant 2

Procion Blue H-EGN 125	97%
Procion Blue H-EXL	91%
Procion Crimson CXB	87%
Procion Navy H-EXL	92%

All four reactive dyes were successfully removed presumably by adsorption onto activated sludge floc. This is depicted in Figures 3 and 4.

Plant 2 has only a very slightly higher solids content, so the difference in dye uptake with the two sludges is not because of their different solids content. After examination of the sludges with the aid of a scanning electron microscope it was noticed that the physical appearance of the two sludges was distinctly different as shown by the micrographs in Figure 5. The dried sludge from plant 2 being more porous/fibrous and as a result probably having a higher surface area to mass ratio than sludge 1. The latter sludge appeared to have a greater degree of crystal structures present, which would indicate that as the sludge dried out, dissolved salts in solution would be forced to recrystallise forming the structures observed. The presence of such crystals could be the salts from the dyes' original formulation, or from a variety of dyeing and finishing processes. The least effective sludge could then be considered to be more saturated with dissolved salts, the flocs themselves acting as points of nucleation for recrystallisation to occur, this would result in the adsorption sites within the flocs becoming clogged up and therefore preventing dye adsorption from taking place as readily as with the other plant sludge.

Figure 3: % Colour removal versus time of procion reactive dyes after treatment in pilot plant 1

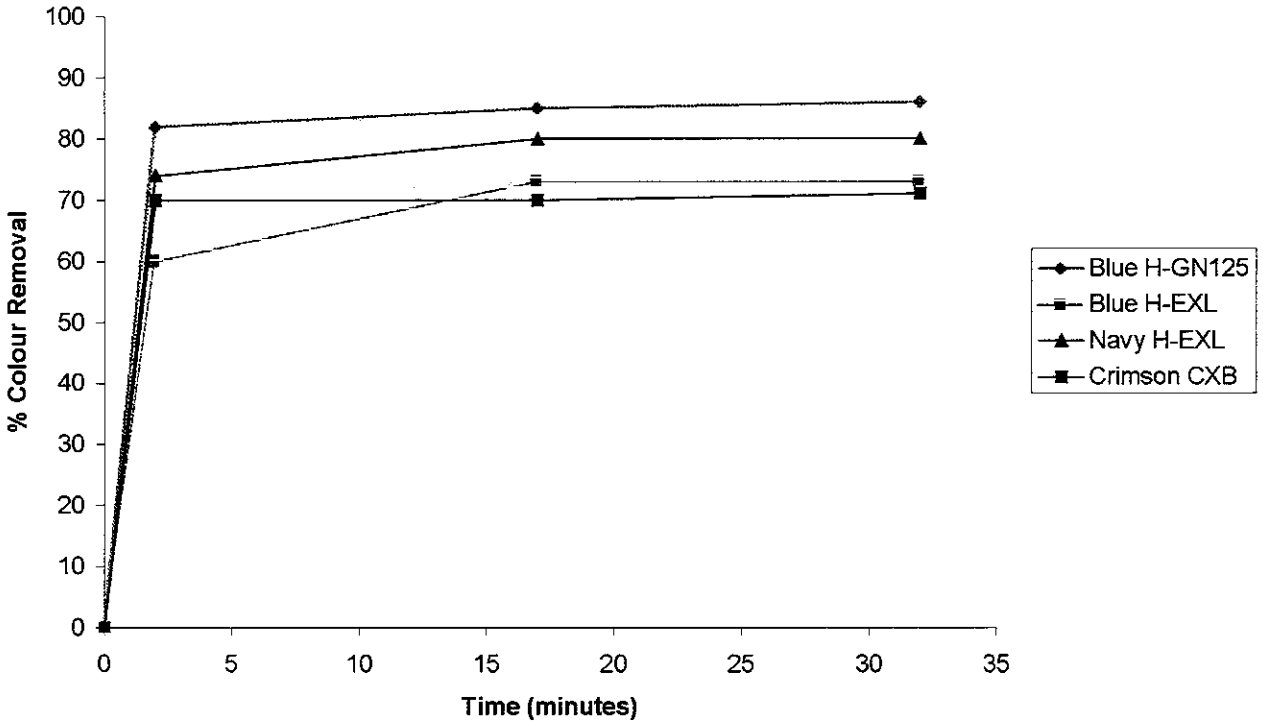


Figure 4: % Colour removal versus time of Procion reactive dyes after treatment in pilot plant 2

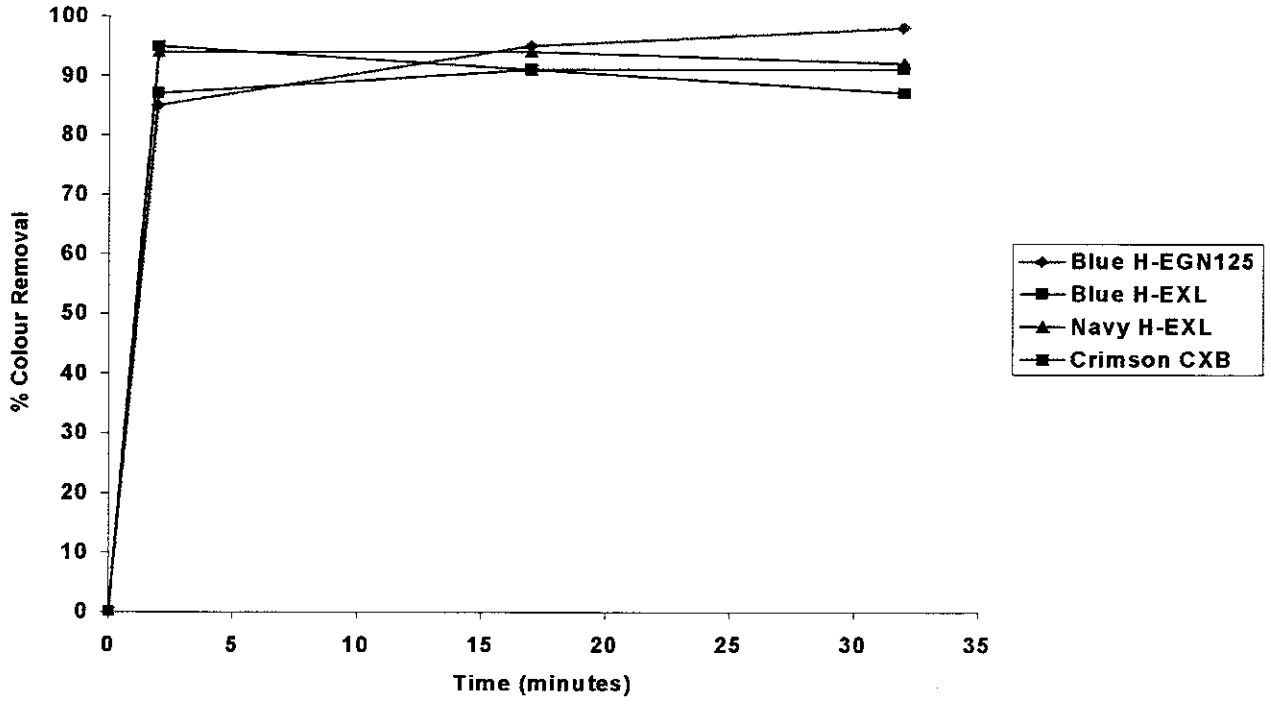
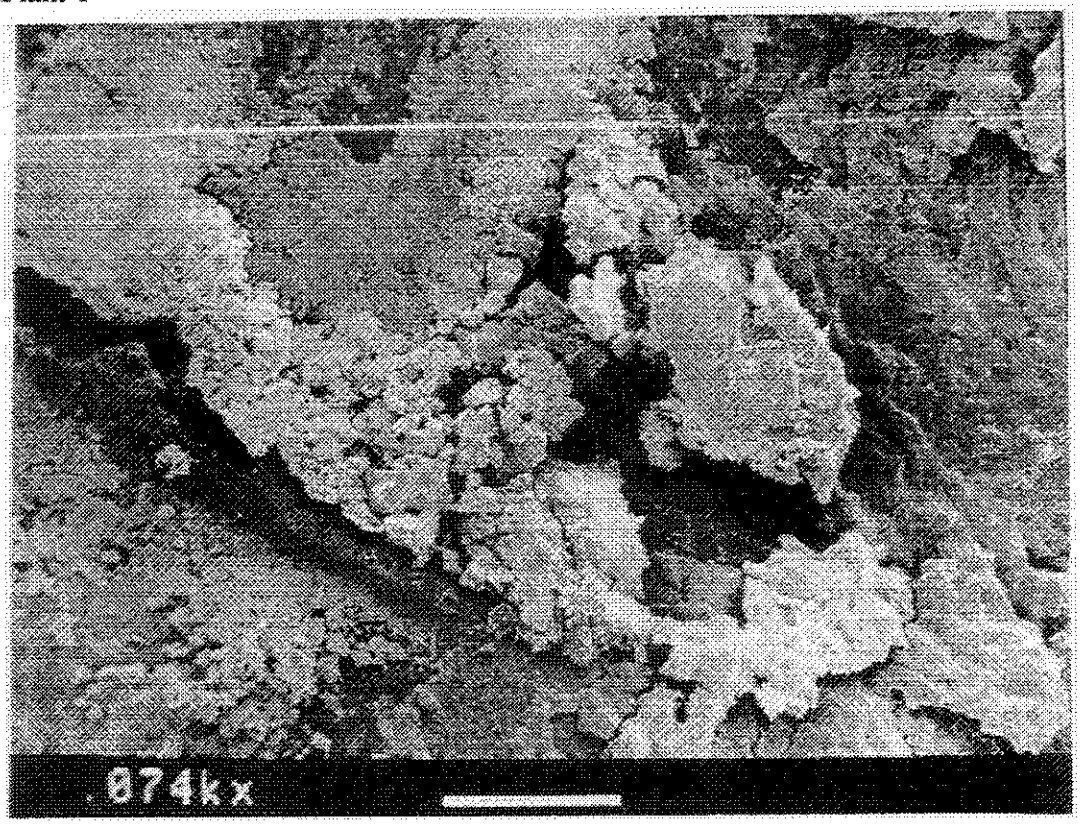
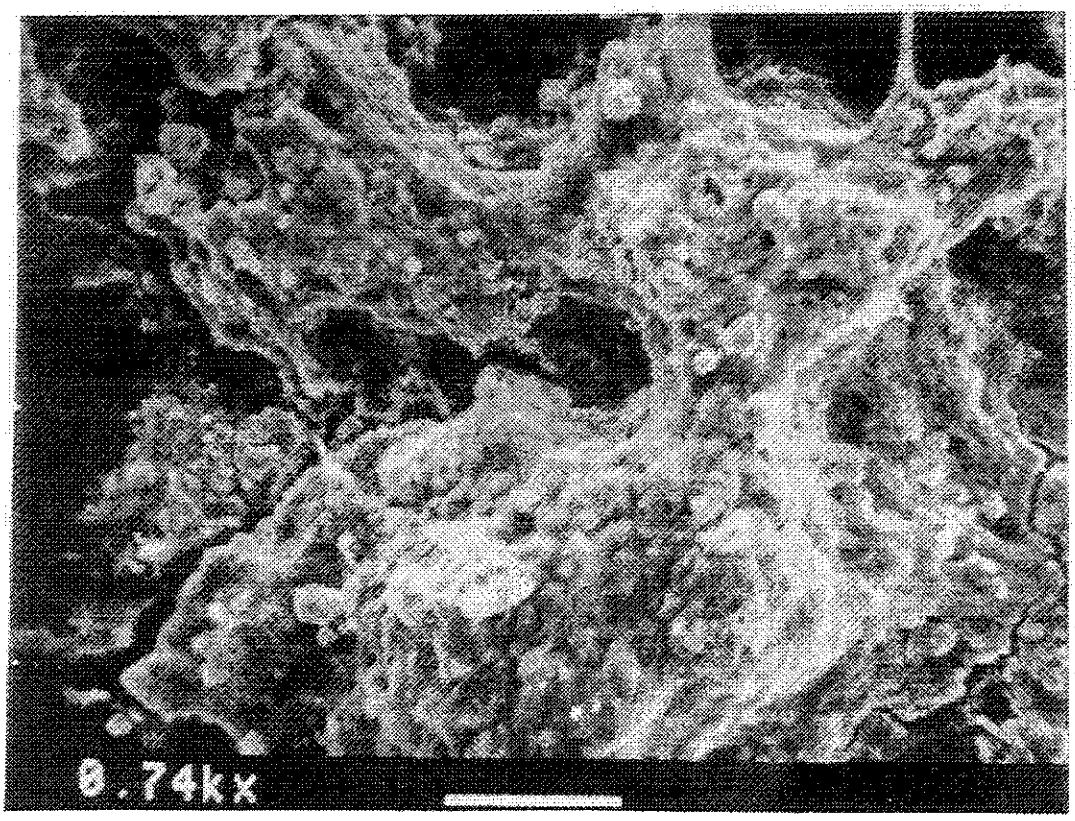


Figure 5 Electron micrographs for plant 1, the original, and plant 2 was set up 8 weeks after the first and from the same source.

Plant 1



Plant2



The only other noticeable fact from this data is the speed with which adsorption takes place. The time taken for the major part of the adsorption process could theoretically be any time up to when the centrifuging is complete, which in turn could be anywhere up to about 10 minutes. However, it is considered quite likely that adsorption takes place more or less immediately after the dye solution is introduced to the sludge and before centrifuging. This assumption is based on the fact that subsequent readings at 17 and 32 minutes after addition of dye to sludge, no significant further adsorption takes place.

Solids content

Figure 6 shows how the extent of dye removal varies with solids content. Naturally, we can see that as we increase the solids content we improve the degree of removal of dye. In this case the dye used was Procion H-EGN 125. At the lower end of the solids concentration range it can be seen that an increase in solids content of $1gdm^{-3}$ exhibits a vast increase in

Figure 6: % Colour removal versus time with variable solids content
Procion H-EGN 125

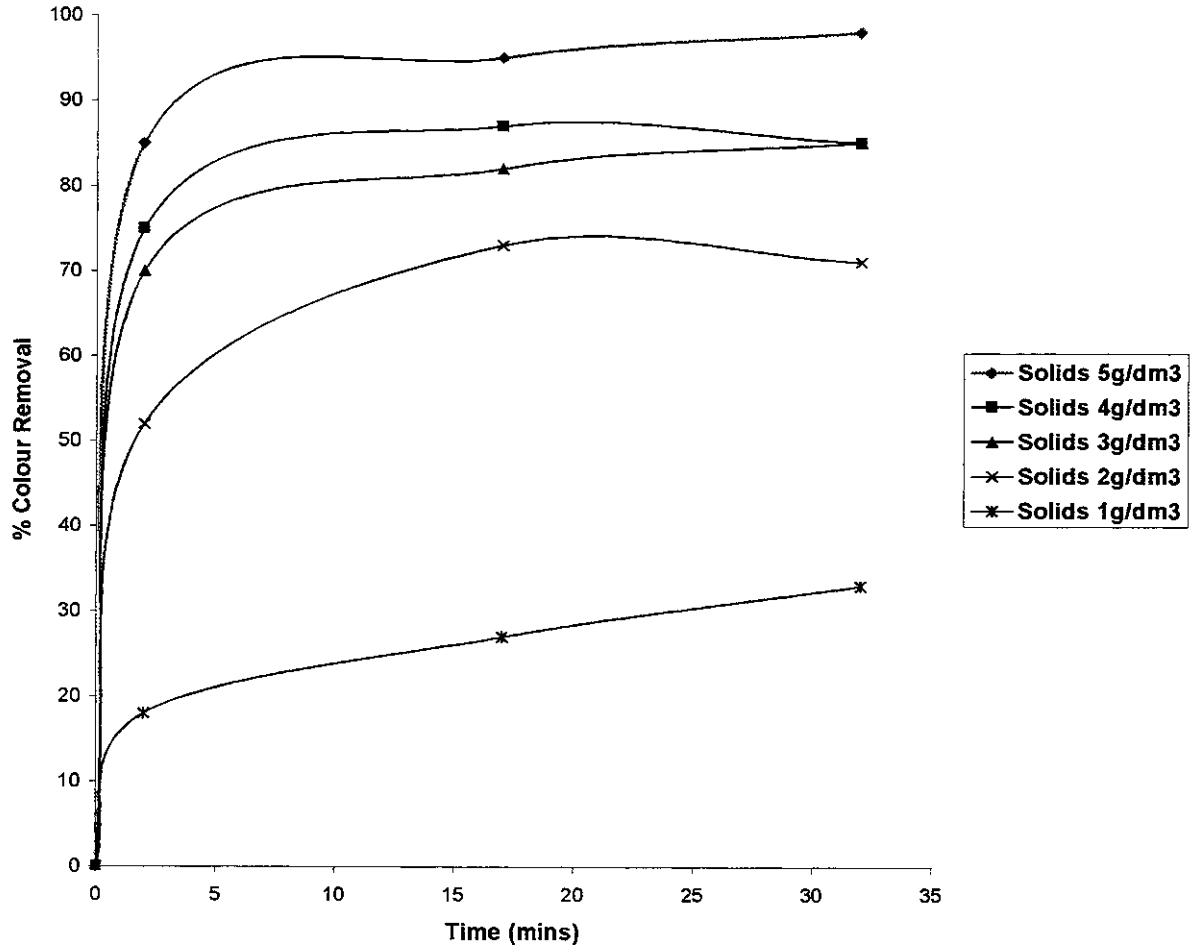
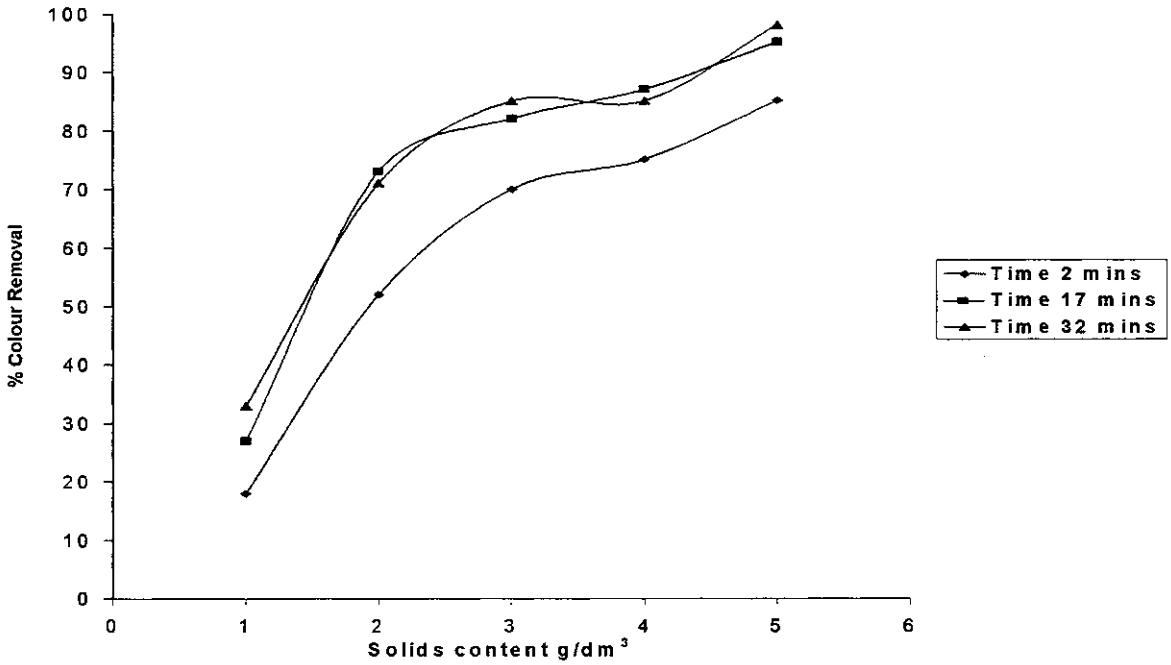


Figure 7: % Colour removal Versus variable solids content with time
Procion H-EGN 125



the amount of dye removed. In fact considering the data at 17 minutes, for the initial increase in solids content, the colour removal increases by 45%. This is a much greater increase than for subsequent increases in solids content. For the sludge, which had the 5 gdm^{-3} solids, after 32 minutes there is nearly 100% colour removal. In order to see the effect of solids content on colour removal we note from Figure 7, a plot of % Colour Removal versus Solids content, that there is a critical solids concentration where the effectiveness at colour removal markedly changes. At a solids concentration of about 2.4 gdm^{-3} the slope of the plot decreases from 31 to 7 dm^3g^{-1}. This indicates that there is a critical solids concentration at which the rate of colour removal decreases with increasing solids. This behaviour is more than likely associated with the fact that the initial adsorption takes place rapidly and as the number of adsorption sites are consumed the chance encounter of dye with further sites becomes less, resulting in a slower adsorption rate.

CONCLUSIONS

The Strines-conditioned sludge is capable of removing the following dyes, probably by an adsorption process, from solution, namely, Procion Blue H-EGN 125, Procion Blue H-EXL, Procion Crimson CXB and Procion Navy H-EXL (hydrolysed reactives). The degree to which these dyes were removed varied from 80 to 97% using the Strines sludge. Removal of all the reactive dyes was very successful using this sludge. Adsorption takes place very quickly, within the first few minutes of dye solution being in contact with the sludge. Biodegradation usually occurs over a much more extended period of time.

REFERENCES

1. Dart R. K. and Stretton R. J., *Microbiological Aspects of Pollution Control.* Elsevier Scientific Publishing Company, Amsterdam - Oxford - New York, 1980.

2. Hitz H. R., Huber W. and Reed R. H., The Adsorption of Dyes on Activated Sludge., *JSDC*, 1978, 94 (2), 71 - 78.

DECOLOURISATION OF TEXTILE WASTE WATER BY PHOTOOXIDATION AND ITS RE-USE

Ayse Uygur

INTRODUCTION

Textile waste waters are coloured by the dyes used, but it has been suggested that dyes should not be regarded as water pollutants since their biological effects are negligible[1].Textile waste water, including dyes, do not have high biological oxygen demand (BOD) content levels. However, it is also true that some azo dyes, for example benzidine -based direct dyes, are easily reduced in waste water to colourless primary organic amines which are more toxic than the original dyes[2]. Reactive dyes give much more washed-off dyes to the waste waters than the other dye groups. Because strong colour may cause considerable disturbance to the receiving waters, the waste waters must be treated before being discharged into the environment[3].

Conventional biological treatments, however , are not efficient for decolourising some textile waste waters, so more useful chemical treatment techniques have been investigated, such as activated charcoal, osmotic membrane, coagulation- flocculation , biological absorbers and reductive and oxidative technologies. There is no single colour removal technique which is optimum in terms of cost, technological, environmental and practical considerations[4]. Ignoring cost, the most promising technique in terms of these considerations is the use of photooxidative techniques.

Oxidative processes such as biological oxidation, oxidation with UV irradiation, oxidation with sodium hypochloride (NaClO), hydrogen peroxide (H_2O_2), ozone (O_3) and nitric acid (HNO_3), incineration and wet oxidations (low pressure/high pressure) are previously applied types of photooxidative processes. The oxidative decolourisation reaction occurs in the smaller molecules of the organic dyes such as aldehydes, acids, sulphates, carbon dioxide, water, nitrogen, etc., depending both on the dye molecular structure and on the strength of the oxidative technique[5].

Photooxidative decolourisation processes are the combination of UV irradiation and ozone or hydrogen peroxide. If ozone or hydrogen peroxide is introduced simultaneously with UV irradiation, there is an increase in the destruction rate and strength of dyes when compared with the destruction rates achieved through the use of only one agency[6]. Oxidation potential of some oxidants are given in Scheme 1 where it can be seen that hydroxyl radicals produced after the catalytic action of heavy metal ions or UV irradiation in the presence of hydrogen peroxide or ozone have higher oxidation potentials than either that of ozone and hydrogen peroxide alone[5].

Scheme 1 : Oxidation potential of some chemicals

$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	Eo = 1.23 V
$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	Eo =1.78 V
$O_3 + 2H^+ + 2e^- \rightarrow H_2O_2 + \frac{1}{2} O_2$	Eo= 2.07 V
$.OH + H^+ + e^- \rightarrow H_2O$	Eo=2.28 V

Ultraviolet irradiation catalyses the chemical oxidation of organic compounds in water. First, the organic compounds absorb the energy of the UV irradiation and thus undergo a

change in chemical composition or bond type which makes them more reactive towards the chemical oxidising agents. Secondly, UV irradiation generates hydroxyl radicals from hydrogen peroxide or ozone. These hydroxyl radicals have the highest oxidation potential and so more easily oxidise any substances in the waste water into final products[7].

As a result, oxidative and photooxidative decolourisation of textile waste waters are both promising as real methods, but both need further improvements. Photooxidative decolourisation is relatively recent and most research on this technique has been carried out during the five past five years. In this study, some chemical parameters will be determined in textile waste water decolourised by photooxidation and the reuse potential and suitability of this waste water for dyeing processes will be investigated. It is hoped that these results will help to answer some questions about photooxidative decolourisation.

EXPERIMENTAL

Materials

Dye : Procion Yellow MX 8G (CI Reactive Yellow 8G) (Zeneca)
Fabric :153 g/m^2 cotton, knitted fabric
Dyeing Machine : Termal, closed system
UV lamp :Phillips, HPM 17, 320-450 nm , 550-1000-1500 watt adjustable
UV-Visible Spectrophotometer : Shimadzu-UV 240
COD Reactor : Hach, DR 2000, Direct reading spectrophotometer
TOC : Shimadzu, TOC analyzer 500 , Automatic sample, injector ASI 502
Oxygenmeter : YSI Model , 54 A
Ion Chromatography: Dionex Conductivity Detector, Series 4000 i
Color Matching :Wincolor V:2-Database, CM, Macbeth-Color Eye 300

Method

The reactive dye Procion Yellow MX 8G for cotton was chosen for the experimental studies and the dyeing and washing-off procedures were applied according to the directions of the dyestuff manufacturer.

The waste water of initial dyeing was decolourised in quartz cuvettes by UV irradiation at 1000 watt in the presence of 1 ml/l H_2O_2. Quartz cuvettes were set 10 cm away from the UV lamp and exposed to UV irradiation for 20 minutes.

Chemical oxygen demand (COD), biological oxygen demand (BOD), total organic carbon (TOC) tests were applied according to the literature[8].

In the first reuse of decolorised waste water in dyeing , 10% amount waste water of the initial dyeing was used. The waste water from the initial dyeing consisted of dyeing waste water and washing-off waste water which was collected and diluted to 1 litre by deionised water. In the second reuse of decolorised waste water in dyeing , 10% amount waste water of the dyeing with first reuse of waste water was used. Since 10% (w/v) of sodium sulphate was available in decolourised waste water, the dyeing with first reuse of decolourised waste water was carried out by adding 90% (w/v) of sodium sulphate and the dyeing with second reuse of decolourised waste water was carried out by adding 80% (w/v) of sodium sulfate.

RESULTS AND DISCUSSION

Chemical Analyses Of Waste Water

COD, BOD and TOC Determinations were carried out. It was observed that 40% of H_2O_2 which was released after the decolourisation treatment was harmful for and influenced COD, BOD test results. Therefore these tests were repeated after removal of H_2O_2. The results are given in Table 1.

Table 1: COD,BOD,TOC Values of decolourised waste water of dyeing with Procion Yellow MX 8G dye (mg/l)

Waste Water	COD	COD decrease %	BOD	BOD increase %	TOC	TOC decrease %
Initial dyeing	145.2	0.0	20	0.0	98.1	0.0
Decolourised	189.4	-	-	-	70.1	28.6
Decolourised and H_2O_2 removed	104.1	28.4	56	280	-	-

As can be seen in Table 1, the COD value of initial dyeing waste water was lower than those of decolourised waste water containing H_2O_2 , but it is higher after the removal of H_2O_2. There is not enough knowledge about the COD test procedure of waste water containing H_2O_2, however. The COD decrease is 28.4% and this suggests that the decomposition of organic dye is occurring after photooxidation .

The BOD test could not be applied because of the harmful effect of H_2O_2 to bacteria, therefore the test was repeated after the removal of H_2O_2. Decolourised and H_2O_2-removed waste water had higher BOD values than that of the waste water from the initial dyeing. This result suggested that more biodegradable products occurred after photooxidation. This knowledge is in accordance with the literature[9].

The decrease in TOC was 28.6% under the experimental conditions suggesting that the decomposition of dye molecule was occurring to CO_2 and H_2O was at this ratio. The more oxidisable part of dye molecule could be possibly turned into the smaller colourless molecules. Photooxidative decolourisation was also carried out at various time periods of UV irradiation and the TOC values of these applications are given in Table 2 below. These results show that TOC decreased as the exposure or decolourisation time increased and this decrease reached 52.8% of the value for waste water from the initial dyeing at the end of an hour's exposure to UV irradiation . This suggests that the decomposition ratio of dye molecule to CO_2 and H_2O increased while the photooxidation time increased. This result is important for the potential reuse of waste water, since the total removal of organic compound in waste water may be possible after photooxidation for a long time.

Table 2: TOC Values of decolourised waste water of dyeing with Procion Yellow MX 8G in various time periods (mg/l)

Time(minute)	0	20	40	60	80
TOC	98.1	70.1	61.8	46.3	44.2
TOC Decrease %	0.0	28.6	37.0	52.8	55.0

Sulphate ions were also determined by ion chromatography method and the results are given in Table 3.

Table 3: Sulphate ion values in decolourised waste water of Procion MX 8G(mg/l)

Waste water of initial dyeing	**Decolourised waste water**	**% Difference**
2537.0	2511.6	1.1

If ± 4% experimental error is accepted for sulphate ion determination , it can be concluded that sulphate ions have not changed after photooxidative decolourisation treatments. This suggests the probability of reuse of sodium sulfate besides reuse of water.

Reuse of Decolourised Waste Water

Some dyeings were carried out following the reuse of decolourised waste water, these results are given in Table 4. As can be seen in Table 4, decolourised waste water was not of the reusable quality directly for dyeing treatments, because colour strength of this dyeing was only 3.4% of standard dyeing. The released H_2O_2 (40% amount of total H_2O_2) and decomposition products of organic dye in decolourised waste water probably prevented effective dyeing during this reuse of waste-water treatment. Therefore, subsequent dyeings were carried out after the removal of H_2O_2 in decolourised waste water by different methods (a) and (b); colour strengths of these dyeings were 98.40% and 99.38% of standard dyeing successively. If the acceptance limits were 4±% difference from standard dyeing , dyeings with waste waters which were decolourised and with H_2O_2 removed by either the (a) or (b) method gave rise to colour strengths within the desired limits. Thus these dyeings gave similar colour strengths to standard dyeing. ΔE values of these dyeings were 0.12 and 0.6 repectively under the D65 light. If the acceptance limit was ΔE=0.9, colour differences of these dyeings from standard dyeing were also within the limits. Since colour differences and colour strengths of dyeings carried out on waste waters which were decolourised and with H_2O_2 removed either by the (a) or (b) method were within the limits, it may be concluded that these waste waters are of reusable quality. These results show that there is the prossibility of recycling the waste waters which have been decolourised by photooxidation and with H_2O_2 removed by either of the different methods.

Table 4 : Color differences and colour strengths of dyed fabrics by reusing various types of decolourised waste water comparing to dyed fabric by standard dyeing method with Procion MX 8G

Waste water types used in dyeings	Colour Strength %	Colour differences						
		Light	ΔL*	Δa*	Δb *	ΔC*	ΔH*	ΔE*
Decolourised	3.42	D 65	3.609	3.908	-65.578	-65.210	7.959	65.793
		F 11/10	1.853	2.977	-70.273	-70.206	4.264	70.361
		C/10	1.709	-2.058	-62.253	-62.254	2.026	62.310
Decolourised and H_2O_2 removed (a) (first reuse)	98.40	D65	0.123	0.004	-0.040	-0.040	0.000	0.129
		F11/10	0.126	-0.043	-0.037	-0.034	0.046	0.138
		C/10	0.125	-0.022	-0.020	-0.021	0.022	0.129
Decolourised and H_2O_2 removed (b) (first reuse)	99.38	D 65	-0.107	0.076	-0.553	-0.558	-0.010	0.568
		F 11/10	-0.127	0.137	-0.578	-0.586	-0.095	0.608
		C/10	-0.112	0.127	-0.580	-0.578	-0.137	0.604
Decolourised and H_2O_2 removed waste water of (b)(second reuse)	94.48	D 65	-0.579	1.001	-1.579	-1.684	-0.812	1.958
		F 11/10	-0.553	0.754	-1.537	-1.585	-0.647	1.799
		C/10	-0.515	0.704	-1.119	-1.179	-0.791	1.510

Although the first recycling of decolorised waste waters ((a) or (b)) gave promising dyeing results, the second recycling did not give acceptable dyeing results. Waste water from a dyeing carried out using recycled waste water which had been decolourised and had removed residual H_2O_2 by method (b) was again decolourised and had removed traces of remaining H_2O_2 by method (b). The colour strength of this dyeing was 94.48% of standard dyeing and the ΔE colour difference value was 1.9 from standard dyeing under the D 65 light. Since these results were slightly outside the limits, the second reuse cycle of decolourised waste water was not promising enough under experimental conditions. Decomposition products of the dye molecule had probably increased in decolorised waste water sufficiently to cause this result. Additional treatments would be necessary for further recycling of decolourised waste waters by using photooxidation.

CONCLUSIONS

It can be seen obviously that the photooxidative decolourisation method decreases chemical oxygen demand (COD) by 71.6%, total organic carbon (TOC) by 71.4% suggesting that the decomposition of dye molecule occurs fully to CO_2 and H_2O under the experimental conditions. This ratio increases as the photooxidation time increases, therefore there may be also the probability of total removal of decomposition products after very long exposures. There is an obvious increase of biological oxygen demand (BOD) suggesting the occurrence of more biodegradable products after photooxidation. This result shows that the use of photooxidative decolourisation is beneficial before biological treatments.

There is also the probability of reuse of sodium sulphate to some degree when reactive dyeing is applied by the new "all-in" method.

Decolourised waste water is of reusable quality for dyeing after the removal of released H_2O_2 and decomposition products. Similar dyeings to standard dyeing procedure are obtained by the use of first recycled, decolorised and H_2O_2-removed waste water. However, slightly different dyeing results from the standard dyeing is obtained by the use of second recycled water.

It may thus be concluded from this research that organic compounds in waste water can be decomposed to the smaller colourless molecules, but inorganic salts such as sodium sulphate remain unchanged. Therefore, decolourised waste water and inorganic salts can be reused for textile dyeing treatments after the removal of harmful chemicals.This subject needs further investigation for successful application in industry including the investigation of the effects of different types of textile waste waters.

The author would like to thank The Research Center of Marmara University and The Association of Textile Dyeing and Finishing Manufacturers of Turkey for their financial support. Additionally, the author thank Dr. Ece Kök for academic help and Zeneca Colours for supplying the dyes.

REFERENCES

1. W Beckman, U Sewekow , ' Coloured effluents of reactive dyestuffs: Problems and methods to solve them ' , *Textile Praxis* , 1991 **46** (4), 346-52. +VI-XII.
2. B Glover,'Getting rid of colour' , *J. Soc.Dyers Col.* , 1993 **109**, 273.
3. S H Lin , C M Lin , ' Treatment of textile waste effluents by ozonation and chemical coagulation ' , *Water Research* , 1993 **27**(12), 1743-8.
4. P Cooper, ' Removing colour from dyehouse waste waters- a critical review of technology available ' *J. Soc. Dyers Col.* , 1993 **109**, 97-100.
5. U Sewekow , ' Treatment of reactive dye effluents with hydrogen peroxide /iron (II) sulfate ' , *Melliand Textilberichte* , 1993 **74**(2), 153-6, E. 68-70.
6. C Prat , M Vicente , S Esplugos , ' Treatment of bleaching waters in the paper industry by hydrogen peroxide and ultraviolet radiation ' , *Water Research* , 1988 **22**(6), 663-8.
7. M Pitroff , K H Gregor , ' Decolorisation of textile waste waters by UV irradiation with hydrogen peroxide , ' *Melliand Textilberichte* , 1992 **73,** 526-8, E. 244-6.

8. L F Clesceri , A E Greenberg , R R Trussel , Standard Methods For The Examination Of Water And Waste Water , 17 th Ed. , New York , Apha- Awwa-Wpcf, 1989.
9. B M Jones , R H Sakaji , C G Daughton , ' Effects of ozonation and ultraviolet irradiation on biodegradability of oil shale waste water ' , Water Research , 1985 19(11) 1421-8.

This page intentionally left blank

DECOLOURISATION OF TEXTILE WASTEWATER BY MEANS OF ADVANCED OXIDATION PROCESSES

S.Ledakowicz, R.Maciejewska and J.Perkowski

INTRODUCTION

The textile industry produces large quantities of highly coloured effluents, which are very toxic and resistant to destruction by physico-chemical and biological treatment methods. Textile wastewater, being non-biodegradable under both natural and sewage treatment plant conditions, is a potential nuisance to the environment. Therefore, it is necessary to find an effective method of wastewater treatment capable of removing colour and toxic organic compounds from textile effluents.

The literature indicates that ozone application, due to its high oxidizing power, may achieve at least a particle destruction or removal of many refractory organic materials[1]. Ozone is readily available, soluble in water and is easily monitored, it decomposes to O_2 and H_2O and leaves no by-products that need to be removed, and furthermore it is a disinfectant. When ozone is introduced into water-containing organics with various reactivities towards ozone, ozone may react with them directly or through oxidation of the solute by OH radicals formed in the reaction chain. The very reactive OH-radicals are also produced by activated hydrogen peroxide. Hydrogen peroxide may be activated in various ways. The different hydrogen peroxide activation processes popularly known as advanced oxidation processes (AOP) are defined as those processes which utilise the hydroxyl radical (OH) or the primary oxidant and include systems such as H_2O_2/O_3, O_3/UV, H_2O_2/UV, and Fenton's reagent.

The aim of this paper was to study the influence of ozonisation and various AOPs on colour removal of textile wastewater and to determine the kinetics of the decolourisation in particular by Fenton's reagent.

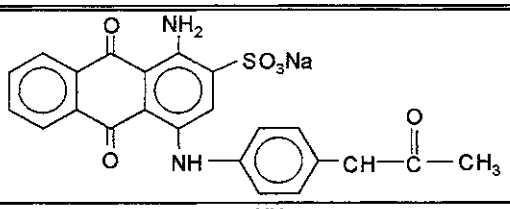
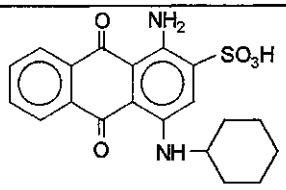
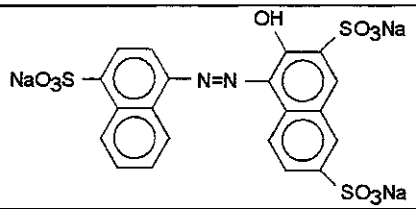
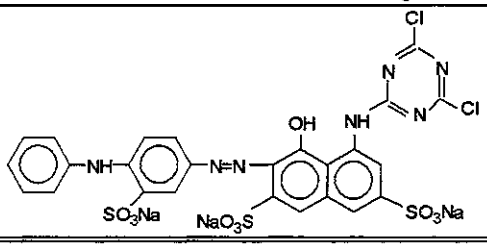
EXPERIMENTAL

Four dyestuffs were the object of three studies, two of anthraquinone type and two azo dyes. Table 1 presents the description and chemical formula of the dyes. Experimental set-up is shown in Figure 1. The tests were carried out in 1.5 litre semi-batch photoreactor (1). Ozone was introduced into wastewater via a diffuser stone. Additional mixing was provided by a magnetic stirrer. The ozone concentration was measured with an ozone-detector (6)-UV photometer. In the centre of the column was placed either a low pressure (15W), or middle pressure (150W) (Heraeus, Germany) or high pressure (2x80W) UV lamp (3) with quartz burner Q 400 (Hanau, Germany).

The different AOPs (such as H_2O_2/UV, H_2O_2/O_3, UV/O_3, Fe^{2+}/H_2O_2) were compared by observing the extent and the rate of colour reduction.

The tests were carried out at ambient temperature for a maximum time, 1-3 hours. Samples were taken every 5 min. The concentrations of dyestuffs in the liquid phase were measured by means of an UV spectrophotometer (Hewlett Packard). UV spectra were taken in the range of wavelength of 190 to 820 nm. The stopped-flow technique (Applied Photophysics, U.K.) was employed for the determination of kinetics of decolourisation of Fenton's reagent, with the use of two different Fe^{2+} salts, $FeSO_4$ $7H_2O$ and $FeCl_2$ 4 H_2O.

Table 1: Dyestuffs used in the study

Acid Blue 40 (62 125)	anthraquinone dye (technical grade)	
Acid Blue 62 (62 045)	anthraquinone dye (analytical grade)	
Acid Red 27 (16 185)	azo dye based on R-salt	
Reactive Blue 81 (18 245)	azo dye based on H-acid	

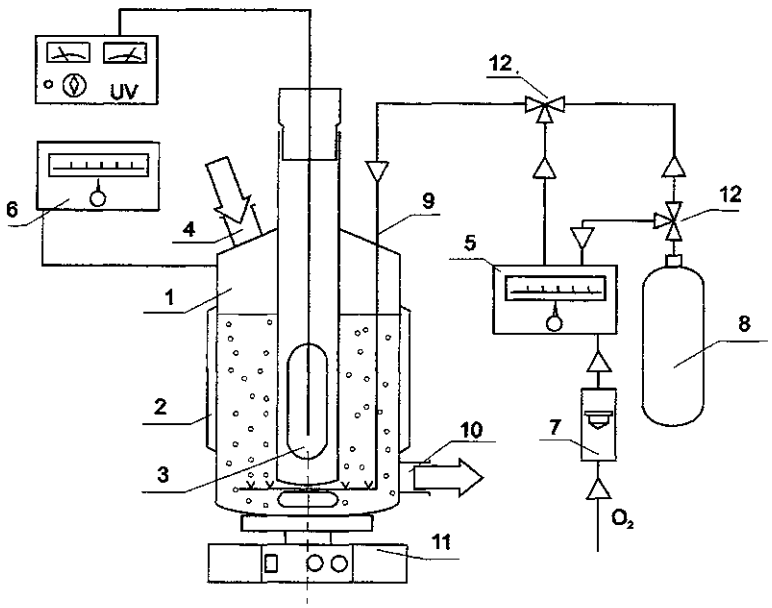


Figure 1: Experimental set-up. 1 - photoreactor; 2 - thermostated bath; 3 - UV lamp; 4 - liquid inlet; 5 - ozone generator; 6 - ozone detector; 7 - rotameter; 8 - oxygen cylinder; 9 - gas inlet; 10 - liquid sampling; 11 - magnetic stirrer; 12 - three-way valve.

RESULTS AND DISCUSSION

In our previous study [2,3] we examined the colour removal as well as COD and TOC reduction from a synthetic waste-water simulating effluents from dyehouses in the knitting industry, containing besides the dyestuff Acid Blue 62 also surfactants, salts etc. However, these additives played a minor role in colour removal, therefore in this study we only used aqueous solution of dyestuffs listed above.

It is well known that the most important factors influencing colour removal are the chemical structure of dyes and the type of degrading (oxidising) agent used. The different advanced oxidation processes were compared by observing the extent and the rate of colour removal from aqueous solutions of various dyestuffs.

UV light has an effect on the reactivity of activated hydrogen peroxide and ozone. However, UV-light has an effect not only on the formation of OH-radicals, but also on the organic components in the water. Because of their property of adsorbing UV-light, many molecules are destroyed directly by UV-light or are activated by it, thus making them more easily oxidizable. Figure 2 presents the results of decolourisation of selected dyes by UV radiation from a low-pressure mercury lamp, plotted as relative absorbance of solution versus UV light exposure. Anthraquinone dyes, in contrast to azo dyes, are resistant to decolourisation by UV. Employment of other UV lamps did not help in increasing the rate fading of anthraquinone dyes.

The OH-radicals are formed with H_2O_2 and O_3 through a complex set of reactions, resulting in the formation of two OH-radicals from one hydrogen peroxide or from two ozone molecules. Ozone alone is known as a very effective oxidising agent and it this confirmed in Figure 3, where it is evident that after 20 min. of ozonisation, the colour of both Reactive Blue 81 and Acid Blue 62 solutions disappeared. However, the hydrogen peroxide alone does not affect the coloured solution at all. Only the combination of hydrogen peroxide in combination with UV light or ozone resulted in the destruction of dyestuffs. Combination of hydrogen peroxide, in proper concentration, with UV light was successful in the case of Acid Red 27 (after 20 min. of reaction the solution was completely decolourised), see Figure 4.

The best known activating reaction of hydrogen peroxide with metals occurs with the use of Fenton's reagent. The optimum hydrogen peroxide/Fe^{2+} molar ratio was 0.21. With iron-activated hydrogen peroxide, 88% of COD was destroyed, however, 60% of COD was found in the precipitate [3]. The rate of decolourisation by Fenton's reagent is rather fast. The rate constant of the reaction of OH radicals with Acid Blue 62 was found with pulse radiolysis and is equal to $1x10^{10}$ $(Ms)^{-1}$ [4]. Further laboratory tests to find the rate constants of the reaction of OH-radicals with the other tested dyestuffs are in progress. It is evident that the initiation step of - OH-radicals creation is the slowest one, so the rate of decolourisation is limited by the rate of this reaction. The stopped-flow technique was used for determination of the reaction kinetics, see Figure 5. The pseudo-first order conditions were applied in determining of the kinetics of decolourisation by Fenton's reagent. Experiments were carried out at pH=2, with an excess of ferrous ions and the following initial concentrations of the reagents: dye 25mg/dm^3 i.e. $(3\text{-}6)10^{-4}$ M; hydrogen peroxide $0.5\ 10^{-4}$ M. The rate constant of the decolourisation was 90-100 $(Ms)^{-1}$ for ferrous sulphate, which was twice than for ferrous chloride 40-50 $(Ms)^{-1}$, while the literature data provides a value of 76 $(Ms)^{-1}$ [4]. It may be caused by different mechanisms of these two reactions.

From the results of our experiments, we can conclude that for the given dyestuff solution not every AOP is effective in decolourisation and the choice of the best method of colour removal, via AOPs, depends mostly on the chemical structure of the dyestuff.

ACKNOWLEDGEMENT

This work was supported by KBN grant No. 3 T090C 01809.

REFERENCES

1. R.C.Rice, G.W.Miller, C.M.Robson and A.G.Hill,'Ozone utilisation in Europe', *AIChE Symp. Series,* 1989 **76**(197), 117-137.
2. J.Perkowski, L.Kos and S.Ledakowicz,'Application of ozone in textile wastewater treatment', *Ozone Sci.Eng.*, 1995 **18**, 73-85.
3. S.Ledakowicz, J.Perkowski and R.Maciejewska, 'Application of advanced oxidation processes to textile wastewater' sent to *J. of AOTs.*, 1997.
4. .C.Walling,'Fenton's reagent revisited ', *Accounts of Chemical Research,* 1975 **8**, 125-131

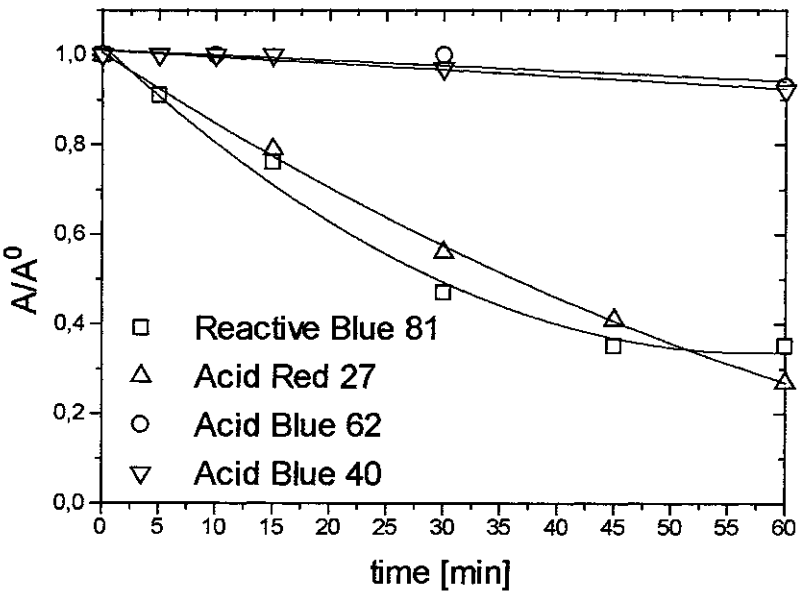


Figure 2: Colour removal by UV light (low pressure lamp , 15 W) .

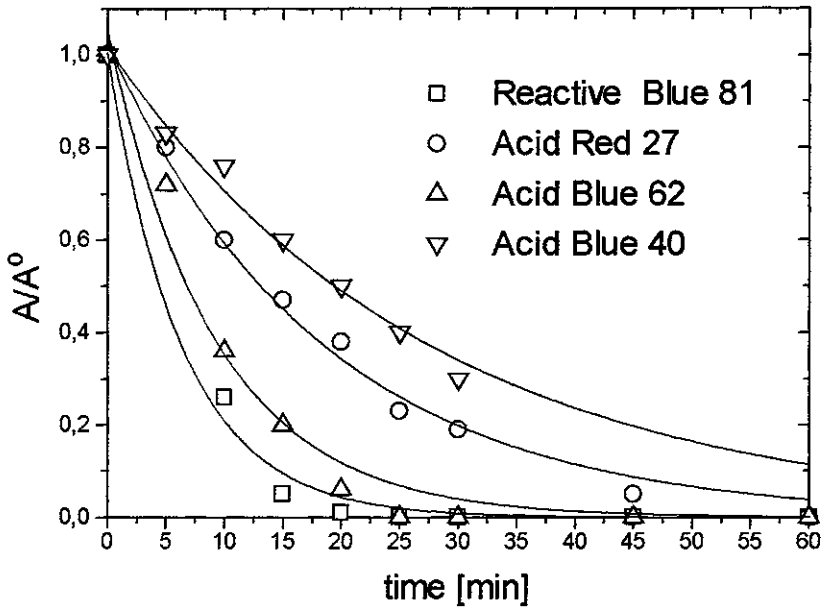


Figure 3: Decolourisation by ozone; Q_{O2} =20 dm^3/h; ozone dose=20 mg/dm^3 .

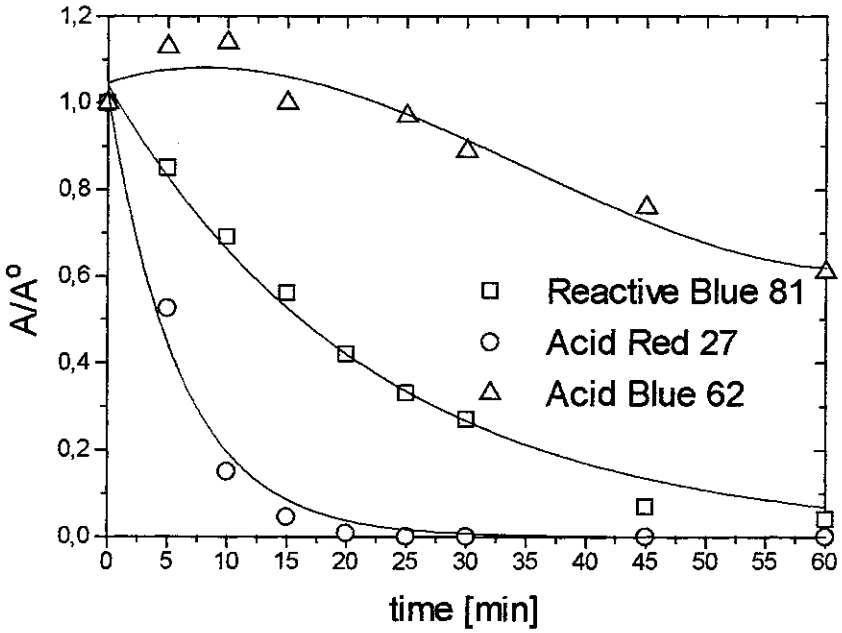


Figure 4: Decolourisation by H_2O_2/UV; C_{H2O2}= 9,79 M; Q_{H2O2}=12 cm^3/h; UV lamp (15 W).

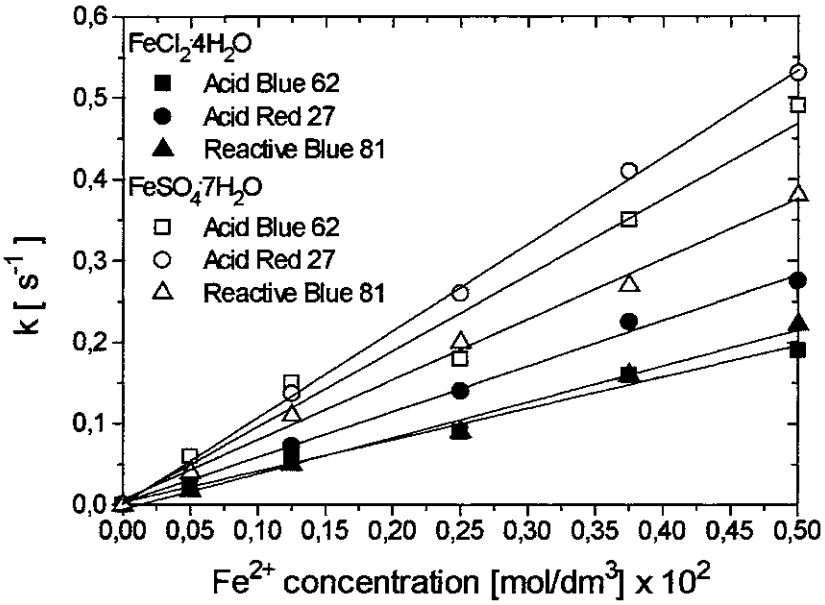


Figure 5: Kinetic constants of decolourisation by Fenton's reagent.

NOVEL APPLICATIONS OF BIOTECHNOLOGY IN THE TEXTILE INDUSTRY

Gordon Nelson

INTRODUCTION

Biotechnology encompasses a range of scientific and engineering techniques for applying biological systems to the manufacture or transformation of valuable materials or the elimination of problematic, often poisonous liquid, solid or gaseous wastes. The textile industry has been using biotechnology in a small way for over 50 years in the enzymatic desizing of cotton using amylases as an alternative to the conventional process which uses hot acids, alkalis and oxidising agents. Currently, many new applications are being or have been developed ranging from new enzyme treatments, new fibres, novel quality control methods and new environmentally friendly effluent treatment systems.

ENZYMES

Enzymes, which are biological catalysts, produced by living cells, are produced today commercially in the main by microorganisms. Enzymes increase the rate of reactions and act specifically on their target substrate. Altering pH, temperature, co-factors, substrate, and product concentration can control the activity of the enzyme. In the textile industry, as well as amylases for desizing, a range of enzymes are now available for use in scouring and bleaching, biopolishing, and biostoning. Generally the enzymes used in textile processing are hydrolases (see Figure 1), or bond breaking enzymes, however, in other industries a range of enzymes are used to synthesis valuable products (bond formation). For example the peptide based artificial sweetener Aspartame is manufactured using the enzyme thermolysin from the amino acids aspartic acid and phenylalanine[1] .

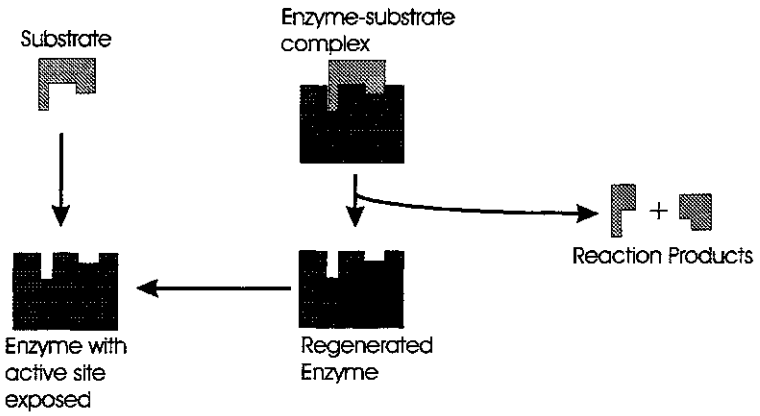


Figure 1: Hydrolase activity of enzymes

In scouring and bleaching it is often necessary to remove hydrogen peroxide before dyeing a fabric with peroxide sensitive dyestuffs. Generally, peroxide removal is achieved after thorough rinsing and possibly the addition of reducing agents. The use of the enzyme catalase allows rapid removal of the peroxide. The dyeing process can therefore, often be carried out in the original treatment bath, which aids water usage, reduces the overall treatment time and is in fact more cost-effective than the conventional reducing

agents. The possibility of completing the whole scouring and bleaching process using enzymes (Bioscour) has been examined by a number of workers, utilising pectinases, cellulases, ligninase and lipases with surfactants [2,3]. However, a commercial process is not yet available that gives, a finished cotton of comparable quality to the conventionally scoured material.

In biopolishing cotton, fabrics are treated with cellulase enzymes carefully controlled to remove the surface microfibrils which result in pill formation without reducing the overall strength of the cotton substrate significantly [4].The enzyme acts by weakening the microfibrils that are then removed with the aid of mechanical action during further wet processing. The biopolished fabric exhibits improved colour brightness, drape, softness, and overall texture without any loss of absorbency compared to conventionally treated materials.

Perhaps the most rapidly expanding application of enzymology in the textile industry is the developments in biostoning. For many years denim products have been treated with pumice stones to produce a 'stone washed' effect. The stone washing process can result in damage to the textile and residual stone trapped in the seams and pockets of the garments has been known to cause allergies. Many manufacturers had to go to the extreme of sowing the pockets up before treatment and delivery to certain clients. The use of cellulases (biostoning) has overcome many of these problems. The enzyme cleaves the fibres on the garment surface removing portions of the indigo dye that is mainly present in the surface layer. The new process can result in increased throughput and a great reduction in dust levels during fabric processing. Careful choice of the cellulase used can also allow new surface effects to be developed.

NEW FIBRES AND MATERIALS

Considerable progress has also been made in the development of new fibres and materials using biotechnology (see Table 1). Most of the work, carried out mainly in the US, has centred on improvements in cotton production and properties. In Australasia and Europe a greater proportion of the effort has gone into the more classical genetic approach to the improvement of quality and production of animal fibres such as wool and mohair, as well as attempts to produce, locally, more exotic fibres such as cashmere, alpaca and vicuna. Novel materials more akin to plastics can also be produced using a biotechnology approach. Two examples of these biopolymers include polyalkanoates (PHA) produced by Zeneca and Polylactic acid produced by Kanebo and the Shimadzu Corporation of Japan.

QUALITY ISSUES

One aspect of biotechnology, which has been neglected in the textile industry up to now, is quality control. A number of analytical techniques, based on antibody/antigen interactions and Deoxyribonucleic acid (DNA), have been available to medical researchers and forensic scientists for a considerable time. These techniques are well established and are currently the basis for most diagnostic test kits, in-house medical diagnostic procedures and are the basis for genetic fingerprinting used widely in forensic science and paternity testing.

Some of these techniques can now be applied to specific problems that are becoming more apparent within the UK textile industry.

Counterfeiting

One of these problems is the counterfeiting of designer-labelled products and in general top-of-the-range textiles made from speciality fibres such as cashmere. Opening up of the Asian and Eastern European economies has created opportunities for unscrupulous

Table 1: Biotechnological approaches to novel fibres and fibre properties.

Fibre or Material	Improvement	Source
Cotton	Improved insect, disease and herbicide resistance Improved strength, chemical reactivity and absorbency, reduced shrinkage, naturally coloured cottons	Agracetus Monasanto American Cyanamid Amtex Consortium
Flax	Herbicide resistance Improved retting and decortification	University of Saskatchewan Scottish Agricultural College
Jute	Biodegradable geotextiles and packaging materials	
Silk	Reduce dependence on Mulberry leaves	Chinese and Indian groups
PHA (Biopol)	Natural polyester	Zeneca
Polylactic acid	Biodegradable polylacetate fibre	Kanebo Shimadzu Corporation
Wool	Improved fibre fineness in UK	MLURI (Scotland)
Cashmere	Introduction into UK	MULRI (Scotland)
Alpaca	Introduction into UK	IGER (Wales)

textile manufacturers to abuse the well known brand names associated with many of the best Western European and US products. So much money can now be made from such counterfeiting that organised crime groups have taken over much of the business leading to the formation of specialist police and trading standards departments.

In order to protect goods in the market place it is now possible to invisibly mark products using a specially designed antigen, specific to a company or even a product line. A small independent company called Biocode Ltd., based in York was set up originally by Shell to combat counterfeiting of lubricating oils. They developed mono-clonal antibody techniques for the detection of specific marker compounds. A few parts per million of the markers can be added into or on to a product and the concentration or presence of these markers can be easily measured using simple immuno- affinity columns or lateral flow devices (see Figure 2). As well as confirming the presence of an individual product it is also possible to show dilution or blending of a product with another lower cost material. The system is extremely versatile and can even be printed on to the packaging or labels associated with the products. The label, which can give any message

the manufacturer requires, can be visualised at a later time by simply swabbing on the antibody solution containing a colour development system (See Figure 3).

Adulteration of speciality fibres

In speciality fibre processing there is another important problem associated with the purchase of the raw material. Because the demand for exotic speciality fibres such as

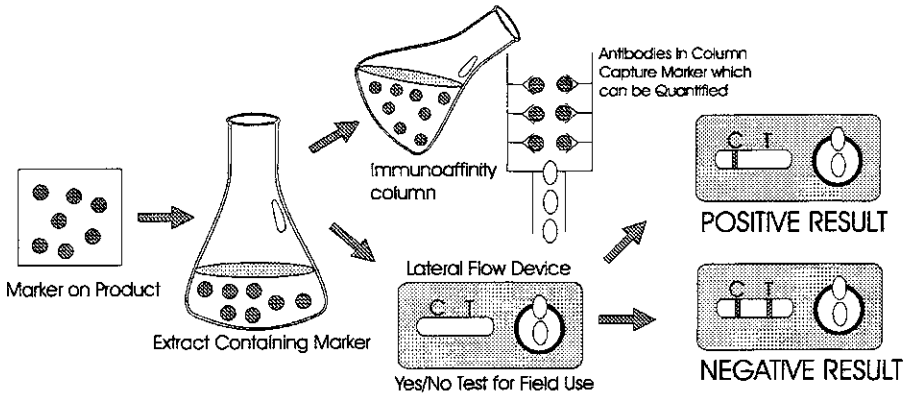


Figure 2: Mechanisms for detecting markers from commercial products.

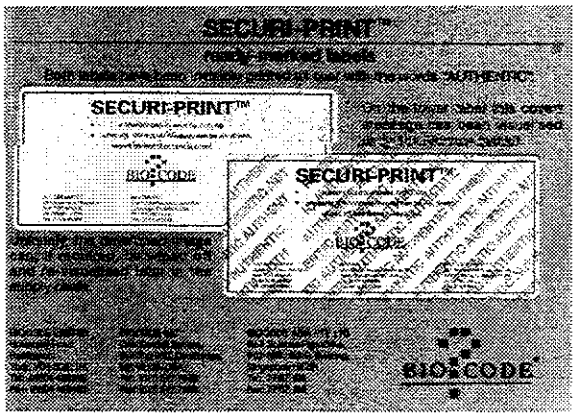


Figure 3: An example of the Securi-Print[tm] labelling system from Biocode.

cashmere always exceeds demand and the political and economic uncertainties in the fibre producing countries (e.g. China, Iran, Afghanistan etc.) the quality of the raw materials has steadily dropped due to deliberate adulteration. Today almost 50% of garments examined in test-houses appear to be contaminated or mislabelled. Garments and raw material samples, are sent for analysis by retailers, trading standards and the Camel and Cashmere Manufacturers Institute (CCMI) (an organisation set up to protect the good name of Cashmere). Up to now accurate analysis has depended on expert microscopists working with high powered optical [5] or electron microscopes [6] (see Figure 4). Microscopists make measurements of fibre diameter, presence and type of medulla and size and shape of cuticle. However, even skilled personnel working in this area are having great difficulty in positively identifying the components of fibre blends. In a recent round trial, using blind samples of known composition and origin, some well-respected laboratories failed to identify not only the blend composition, but

also failed to detect the presence of animal fibre from particular species. Little progress has been made in conventional analysis since the EC working party on Textile Names and Labelling report almost 10 years ago [8]. In their report they stated 'at the present time no method for determining the composition of internal mixtures of wool and other types of animal fibre is precise enough to allow a judgement of the stated fibre'. The most common adulterants in cashmere garments are wool and yak hair.

Other chemical and physical properties of speciality fibres have been widely

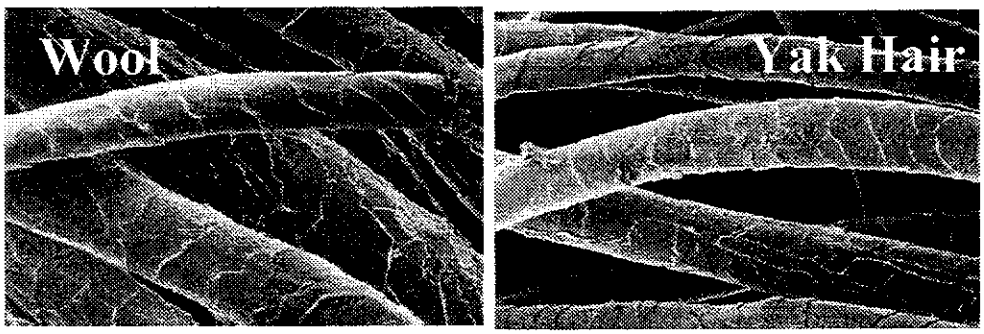


Figure 4: Scanning Electron Micrograph of animal fibre

examined as a means of fibre identification including, amino acid analysis, resolution of fibre polypeptides using one and two dimensional electrophoresis and measurement of variability of the lipid component of the fibre cell membrane complex [7,9,10]. However, although some of these techniques are useful for close comparison between specific animal species problems are found when the effects of different fibre processing regimes, local climate and diet are taken into account.

A breakthrough in speciality fibre analysis was made in 1988 when it was demonstrated that DNA (deoxyribonucleic acid) was not only present in hair roots but could be easily extracted from hair shafts (an important point when you consider that most speciality fibre is shorn not combed) [11]. High molecular weight DNA was also successfully isolated from scoured, bleached and dyed fibre in less than 2 working days and of sufficient quality to be utilised as a template in many modern molecular biology techniques [12]. DNA is therefore unique as regardless of the degree of fibre processing sufficient DNA remains for specific fibre identification. The ability to identify the presence within a fibre blend of a particular component is based on the identification and location of a particular DNA sequence that is unique to that animal species. The complete genome of an animal can be found in all animal cell types (except red blood cells) including those found in hair shafts.

Once species-specific DNA sequences are located complimentary DNA sequences can be constructed which under carefully controlled conditions specifically hybridise to the target DNA molecule giving a positive signal, confirming the presence of a particular fibre type. Species-specific DNA probes are now available for goat DNA (cashmere, mohair), yak DNA and sheep DNA. When the polymerase chain reaction (PCR) is employed to amplify target DNA molecules sufficient DNA can be obtained from a contaminating fibre to enable complete DNA sequencing of the target DNA [13]. As this sequence is unique to the target species the full sequence gives absolute confirmation of the presence of the contaminating fibre, leaving no doubt as to fibre purity. The technique is able to detect where required samples containing as little as 1% w/v of a specified fibre. Appropriate control fibre DNA samples are run alongside each test

sample containing 10% of the target fibre. For example, if you wish to determine the presence of wool in cashmere products a fibre blend will be prepared containing 10% wool / 90% cashmere and the DNA extracted. Further DNA extracts from fibre controls containing 100% cashmere, and possibly a selection of other important fibres would be included e.g. 100% yak. A positive result would be achieved if a wool specific amplification product was detected in the test sample and the 10% wool / 90% cashmere DNA control (see Figure 5). No amplification products must be detected in the other

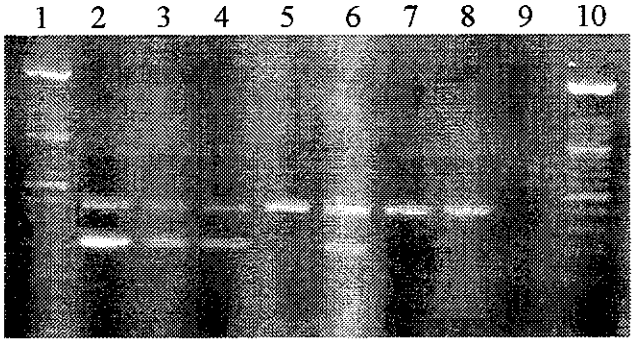


Figure 5: DNA amplification products from speciality fibres- test configuration.

Lane 1 and 10 - 100bp ladder, Lane 2 - 100% wool DNA, Lane 3 – 10% wool DNA in 90% cashmere DNA, Lane 4 – Wool DNA positive sample (1), Lane 5 -Wool DNA negative sample, Lane 6 – Wool DNA positive sample (2), Lane 7 - 100% cashmere DNA, Lane 8 – 100% yak DNA, Lane 9 – no DNA control.

control DNA samples including a 100% human blood DNA control which is present to ensure that DNA from the test operator does not give a false positive signal for any of the target species.

In addition the PCR is run as a Multiplex containing a primer set which co-amplifies a different sized product from all mammalian DNA species which confirms that DNA of sufficient quality for PCR has been extracted from the test sample. The method is designed to be simple and reproducible allowing a speedy turn around for commercial testing. For a small number of samples delivered before 10am it is likely that a result would be available next day.

Biosensors

One of the fastest growing sectors in biotechnology today is that of Biosensors [12]. Perhaps the most well known application of biosensors is in the use of glucose oxidase-based biosensors for the measurement of blood glucose in diabetic patients. These new analytical devices have the potential to replace much of the laboratory analysis carried out to ensure the quality of products manufactured by the textile industry. Real-time, on-site analysis, at a cost most manufacturers can afford, will enable complete control of the quality of raw materials, careful control of the manufacturing process and the quality of finished garments. In the textile industry the analysis and monitoring of trade effluent is vital to waste management and treatment. Accurate real time information on waste composition would allow a textile company to determine the correct treatment strategy for their waste but would also allow the company to talk to the regulators and water treatment companies from a position of authority. Biosensors can operate in a number of

ways but generally speaking a substrate to be measured comes into contact with specific binding domain on an enzyme surface or an antibody, immobilised on the surface of an electrode. Either the binding event can be measured directly or the product of the enzyme reaction can be measured (see Fig. 6). It is now possible for sensor arrays containing enzymes to be effectively printed on to inert
plastic or ceramic materials leading to individual sensor costs of only a few pence. A number of workers are applying their expertise in bio-analytical techniques to problems associated with textile waste treatment.

Sensor arrays containing localised populations of specific bacteria have been

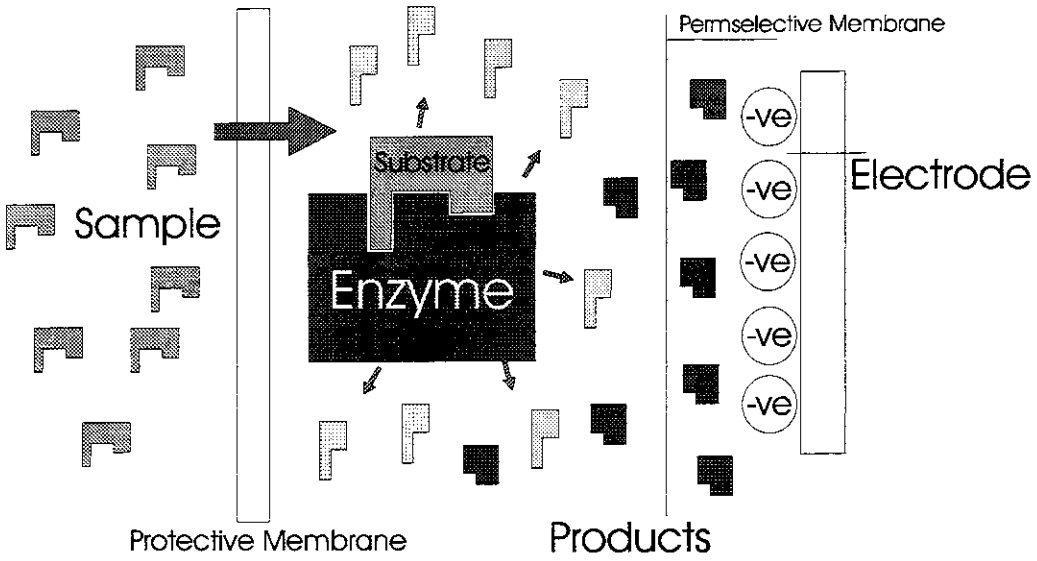


Figure 6: A schematic representation of a simple biosensor

prepared which can give estimates of the BOD within an effluent stream within 3 minutes[15]. The overall toxicity of the effluent stream can also be determined by measuring the viability of the bacterial population. The toxic load is particularly important when discharging to a local sewage treatment works. The release of toxic material into trickling filters or activated sludge tanks at the sewage treatment works could potentially put the plant out of operation for a considerable period. A number of sensors are in development for determining toxicity, many of which are based on bioluminescence. One example is Microtox® supplied by Microbics Ltd., which uses the light emitting organism *Photobacterium phosphoreum* [16]. This system is gaining some acceptance and can deliver a rapid measurement of toxicity.

More specific sensor array systems are also in development for individual toxic materials such as phenolics or pesticides. A novel substrate-recycling biosensor has been developed based on the enzymes, tyrosinase and glucose dehydrogenase, which can detect phenol down to 0.9nmol/L. This sensor can be used successfully in wastewater streams, producing a very fast response curve [17].

The measurement of organophosphate pesticides has become increasingly more important because of the toxic effect of exposure of these compounds to farmers involved in 'dipping' sheep. The toxicity is associated with inhibition of cholinesterase, an enzyme that is important for the healthy function of the nervous system. The use of cholinesterase as the basis of a sensor not only gives accurate assessment of pesticide concentration but also by implication helps to determine the toxicological effect. Many

workers have used this approach, however, cholinesterase is not usually sufficiently stable to obtain a commercially exploitable sensor system. Recent advances in enzyme stabilisation techniques, however, have produced a cholinesterase based sensor with a shelf life of over 76 days at 37°C [18]. This sensor uses polyelectrolytes in conjunction with polyhydroxyl compounds to both hold the enzyme rigid and to replace the molecular water on the enzyme surface. The sensor is able to detect pesticides such as paraoxon at close to 10^{-11} mol/L. The sensor is so sensitive that, at a typical pesticide levels found in a river (see Table 2), the cholinesterase enzyme on the surface of the sensor is inhibited by more than 25%.

Table 2: Pesticide concentration in the River Calder

Sample	**Biosensor (% Inhibiton) (mol/L)**	**GC-MS pesticide determination**	
River Calder	26.5	Propetamphos	5.9×10^{-10}
		Diazinon	6.5×10^{-10}
		Chlorfenvinphos	8.4×10^{-11}

CONCLUSIONS

Textile processors are always on the lookout for improvements in process, productivity and quality. In the past options for improvement have generally been physical or chemical, however, a third biotechnological option is now firmly in place. Clearly in-house expertise in biotechnological areas may be lacking, but externally in the UK, there are many consultants, University Departments and Research Associations who can pass on their knowledge. Biotechnology approaches to industrial problems may often appear to be complicated, however, once installed the systems are generally easily maintained. Ultimately, the successful take-up of a biotechnology option will in all likelihood produce a more cost-effective product. It will also allow the manufacturer to operate in a more environmentally friendly manner and help him to meet the forever, tightening, legislative environmental demands.

REFERENCES

1. M. Bodansky, *Peptide Chemistry – A Practical Approach*, Springer-Verlag, 1988, p69
2. U. Robner, 'Enzymatic Degradation of Impurities in Cotton', Melliand, *Textilberichte*, 1993 **74**(2), 63
3. Y. Li and I. R. Hardin, 'Enzymatic Scouring of Cotton: Effects on Structure and Properties', *Textile Chemist and Colourist*, 1997 **29**(8), 71-76.
4. S. V. Chikkodi, 'Determining Fiber Loss in Biofinishing of Cotton and Cotton/Wool Blended Fabrics', *Textile Chemist and Colorist*, 1996 **28**(3), 28-31.
5. H. M. Appleyard, *Guide to the Identification of Animal Fibes*, BTTG, WIRA, Leeds, 1978.

6. F. J. Wortmann and W. Arns, 'Quantitative Fiber Mixture Analysis by Scanning Electron Microscopy', *Textile Res. J.* , 1986 **56**, 442-446.
7. F. J. Wortmann and H. Zahn, 'Investigation of Blends of Fine Animal Hairs by 2-Dimensional SDS-Polyacrylamide Gel Electrophoresis', 7th Int. Text. Res. Conf., Tokyo, **2**, 195-204, 1985
8. 'EEC Working Party on Textile Names and Labelling-Analysis', *J. Textile Inst.*, 1988 **79**, 155.
9. M. Bauters, 'Study of the Proteins Extracted by Formic Acid from Wool and Mohair', 7th int. *Text. Res. conf.*, Tokyo," **1**, 162-170, 1985.
10. D. E. Rivett, R. I. Logan, D. J. Tucker and A. H. F. Hudson, 'The Chemical Composition of the Cell Membrane of Speciality Fibres', *in "Speciality Fibres: Scientific, Technological and Economical Aspects,"* (A. Korner, F. J. Wortmann, G. Wortmann, and H. Hocker, Eds)., Deutches Wollforschungsinstitut, D-5100 Aachen, 1988, p128-136.
11. L. S. Meyer-Stork, J. Kalbe, R. Kuropka, S. L. Sauter, H. Hocker, and H. Berndt, 'Ein deutige Provenienzanalyse von Wolle und feinen Tierhaaren mit Hilfe der Erbsubstanz (DNS)', *Textilveredlung*, 1988 **23**, 304-307.
12. G. Nelson, P. F. Hamlyn, and B. J. McCarthy, 'Developments in DNA-based Speciality Fibre Analysis', 8th int. Text. Res. conf., Christchurch, **2**, WRONZ, 385-401, 1990.
13. G. Nelson, 'DNA-based diagnostics of speciality animal fibre', *Textile Technology International*', 1997, 110-112.
14. A. E. G. Cass, Eds. *Biosensors, A Practical Approach*, Oxford, IRL Press, 1990.
15. D. T. E. Hunt, 'Control and Monitoring of Discharges by Biological Techniques', *J. IWEM*, 1992 **6**, 269-277.
16. K. L. E. Kaiser, '*Photobacterium phosphoreum* Toxicity Bioassay. II. Toxicity Data Compilation', *Toxicity Assessment: An International Journal*, 1988 **3**,135-237.
17. A. Makower, A. V. Eremenko, K. Streffer, U. Wollenberger, and F. W. Scheller,'Tyrosinase-Glucose Dehydrogenase Substrate-Recycling Biosensor: A Highly-Sensitive Measurement of Phenolic Compounds', *J. Chem. Tech. Biotechnol.* 1996 **65**, 39-44.
18. J. J. Rippeth, T. D. Gibson, J. P. Hart, I. C. Hartley, and G. Nelson, 'Flow-injection Detector Incorporating a Screen-printed Disposable Amperometric Biosensor for Monitoring Organophosphate Pesticides', *Analyst*, 1997 **122**, 1425-1429.

This page intentionally left blank

ENZYMATIC TREATMENT OF MAN-MADE CELLULOSIC FABRICS

Jadwiga Sójka-Ledakowicz, Aneta Skaskiewicz, Rita Pyć and Edward Galas

INTRODUCTION

In recent years there has been a considerable growth of interest in biotechnology applied in finishing textile fabrics due to increasing hazards in natural environment resulting from traditional processes of chemical treatment of fibres. Because the enzymes are natural proteins, readily biodegradable, they may be favourable alternatives to many finishing chemicals. It is known that enzymes from lipase group are applied to modify wool fibres [1]. The possibilities of combining enzymatic modification with introducing special, gently acting resins to improve handle of wool fabrics [2,3] have been found very interesting.

With reference to cellulosic fibres, enzymatic surface modification is the means of: limiting the tendency to pill, imparting soft handle, smooth surface, all without the need of treating fabrics according to traditional chemical methods [4-6]. The enzymatic group of hydrolase type - acting on glycoside compounds and thus on cellulose, has found its special application in surface modification of textile fabrics from cellulosic fibres. Cellulolytic enzymes group catalyzing the hydrolytic decomposition of cellulose and its derivatives was named as cellulolytic complex.

Making cellulose hydrolysis effective and economically feasible, individual enzymes forming cellulolytic complex should remain in definite proportional quantities.

The Textile Research Institute (IW) in Lódz, Poland within a research project supported by the Polish Scientific Research Committee, carries out work on application of cellulolytic enzymes complex in surface modification processes of cellulosic fibres, especially man-made cellulosic fabrics.

Experiments have concentrated on the analysis of the share of individual enzymes forming crude cellulolytic complex in biomodification of cellulosic fibres surface and on the effects of such treatment on textile fabrics made of man-made cellulosic fibres.

EXPERIMENTAL

Cellulolytic enzymes complex was synthesized in optimal conditions at the Institute of Technical Biochemistry at the Technical University of Lódz, Poland. Isolated, characterized and improved strain of filamentous fungus named *Aspergilus niger IBT 90* was the source of cellulolytic enzymes.

In order to estimate the share of individual enzymes, from cellulolytic complex *Aspergilus niger IBT 90* , in surface modification of cellulosic woven fabrics, the hydrolysis of these fabrics has been done using isolated from this complex enzymatic proteins, i.e.:

- endo - 1,4 β glucanase [E]
- exo - cellobiohydrolase [CBH]
- β - glucosidase [β]

The treatment was carried out in the following processing conditions:

- temperature: 50°C
- pH : 4,8
- time: 180 minutes
- enzyme dose: 21,9 units of endo - glucanase per one gram of fabric

The activities of particular type of enzymes and their mixtures and a whole enzymatic complex as well, on cellulosic fabrics was estimated as measured by the amount of reducing sugars released from these fabrics and by the change of fabric weight. The analysis of the achieved results allowed to prepare the optimal composition of cellulolytic complex which was then applied for surface modification of textile fabrics from viscose and lyocell fibres. Enzymatic treatment of cellulosic fabrics was done on laboratory scale using Linitest apparatus.

Changes of saccharification degree were determined as a function of treatment time. Changes of the surface condition of cellulosic fibres after enzymatic treatment were defined using a Jeol 35C scanning electron microscope.

RESULTS AND DISCUSSION

The results have proved the efficacy of activities of cellulolytic complex *Aspergilus niger IBT 90* onto surface modification of cellulosic fibres - viscose and lyocell. The share of individual enzymes of cellulolytic complex *Aspergilus niger IBT 90* in biomodification of cellulosic fabrics was determined on the basis of reducing sugars contents, the degree of their saccharification and changes of fabric weight. The obtained results are presented in tables, see Tables 1, 2 and 3.

Result analysis indicates that the most efficient activity on tested fabrics is given by the whole complex set of cellulolytic enzymes which confirms their synergistic action. Evaluating the activity of enzymes isolated from the cellulolytic complex *Aspergilus niger IBT 90* , on tested fabrics shows that the highest activity towards cellulosic fibres is the mixture of endo - glucanase E_1 and β - glucosidase (the highest degree of saccharification was achieved). Exo - cellobiohydrolase showed the least activity.

The results obtained, confirmed the importance (dominant role) of endo - glucanase in complex enzymes applied for modification of cellulosic fibres. In order to characterize the process activities of individual cellulolytic enzymes and of the crude cellulolytic complex onto cellulosic fabrics, the analysis of soluble sugars created as the result of enzymatic treatment was performed. Such an analysis was performed according to HPLC method. The results are presented in Figures 1 and 2. Figures 3-5 show the effect of temperature and time on the weight losses on viscose and lyocell fabrics.

Hydrolyzates of tested fabrics obtained due to the usage of crude cellulolytic complex contain greater amounts of glucose (32,1 to 43,8%) but less oligosaccharides containing more that 5 glucose residues (16,9 - 19,5%), which confirms more complete hydrolysis of tested fabrics.

Microscopic tests confirmed the change of cellulosic fibre surface after modification. It can be reported that process of enzymatic treatment effects the surface development of treated fibres. Microscopic tests of changes in fibre surface indicate a significant activity of cellulolytic complex *Aspergilus niger IBT 90* on cellulosic fibres.

Experiments showed that as a result of applying the cellulolytic enzyme complex *Aspergilus niger IBT 90* in the treatment of cellulosic fabrics (made of viscose and

Table 1: The influence of enzyme type used in cellulosic fabric treatment on the contentsof reducing sugars in reaction mixture

No	Enzyme type	Concentration of reducing sugars [mg/ml]	
		Viscose fabric	lyocell fabric
1	E_1	2,05	1,45
2	E_2	1,07	0,89
3	E_1+E_2	1,84	1,31
4	$E_1+\beta$	2,59	1,67
5	$E_2+\beta$	2,24	1,55
6	E_1+CBH	1,16	0,55
7	E_2+CBH	1,05	0,50
8	E_1+CBH+β	1,42	0,80
9	E_2+CBH+β	1,26	0,73
10	E_1+E_2+CBH+β	1,48	1,02
11	enzyme complex	4,83	2,25

Table 2: The influence of enzyme type used in cellulosic fabric treatment on the degree of fabric saccharification.

No.	Enzyme type	Saccharification degree [%]	
		Viscose fabric	lyocell fabric
1	E_1	2,22	1,57
2	E_2	1,16	0,97
3	E_1+E_2	2,0	1,42
4	$E_1+\beta$	2,81	1,81
5	$E_2+\beta$	2,43	1,68
6	E_1+CBH	1,26	0,60
7	E_2+CBH	1,14	0,54
8	E_1+CBH+β	1,54	0,87
9	E_2+CBH+β	1,37	0,79
10	E_1+E_2+CBH+β	1,60	1,11
11	enzyme complex	3,47	1,73

Table 3: The influence of applied enzyme onto the weight loss of cellulosic fabrics subjected to enzymatic treatment

No.	Enzyme type	Weight loss [%]	
		Viscose fabric	lyocell fabric
1	E_1	2,98	1,53
2	E_2	1,65	1,67
3	E_1+E_2	2,07	1,64
4	E_1+β	2,98	2,17
5	E_2+β	3,44	2,02
6	E_1+CBH	2,66	2,15
7	E_2+CBH	2,09	1,71
8	E_1+CBH+β	2,46	2,5
9	E_2+CBH+β	2,18	2,04
10	E_1+E_2+CBH+β	2,72	2,15
11	enzyme comlex	2,74	1,18

lyocell fibres), treated fabrics exhibited increased smoothness, softness and silkness. These effects are obtained without impairing strength properties of treated fabrics providing that the enzymatic process parameters - pH and temperature - are strictly controlled.

The results obtained suggest that the application of such a biotreatment of cellulosic fibres is advisable and further research on this subject is highly recommended.

ACKNOWLEDGEMENTS

This work has been supported by KBN (the Polish Scientific Research Committee): grant no. 3 T09B 110 12.

REFERENCES

1. D.Monlleo at all, "Die Verwendung von Lipasen zur Wollmodifizierung ", *Melliand Textilberichte*, 1994 **5**, 402-405
2. E.Heine, H.Höcker, "Enzyme treatment for wool and cotton", *Rev.Prog.Coloration*, 1995 **25**, 57-63
3. S.Fornelli, "Tellurische Behandlungen", *Melliand Textilberichte*, 1996 **4**, 230-239
4. H.Schacht, W.Kesting, E.Schollmeyer "Perspektiven enzymatischer Prozesse in der Textilveredlung", *Textilveredlung*, 1995 **11-12**, 237-243
5. R.Stöhr, "Enzyme - Biokatalysatoren in der Textilveredlung", *Melliand Textilberichte*, 1995 **11**, 1010-1013

6. H.Koo, M.Ueda, T.Wakida, "Cellulase treatment of cotton fabrics. Part II - Inhibitory effects of surfactants on cellulase catalytic reaction", *Textile Research Journal*, 1994 **64**(10), 615-618

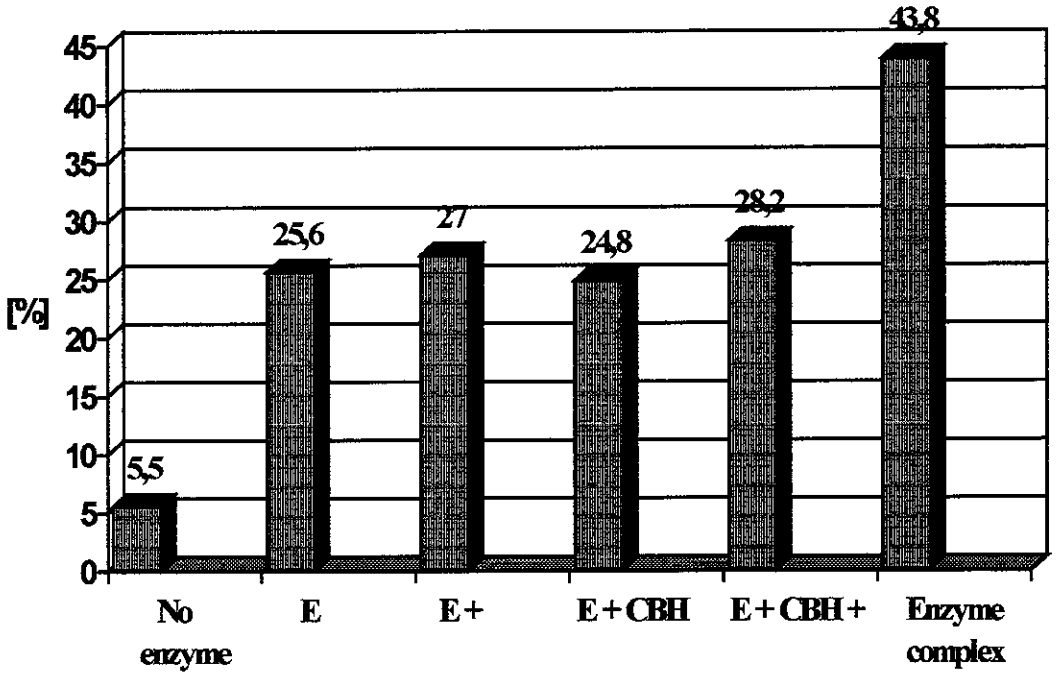


Figure 1: Glucose contents in hydrolizate created during enzymatic treatment of viscose fabric

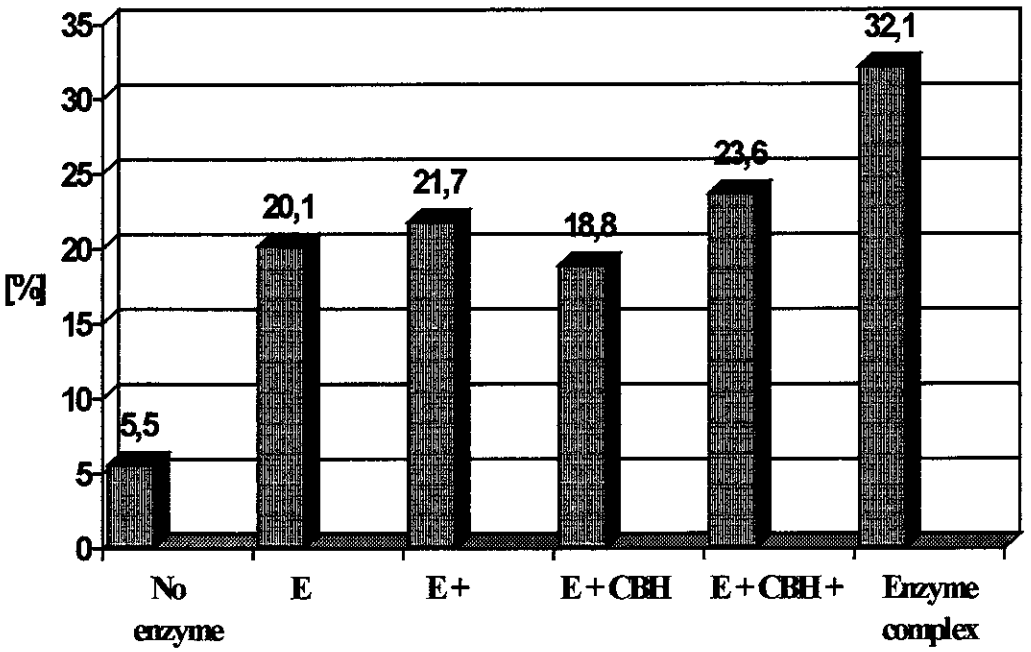


Figure 2: Glucose contents in hydrolizate created during enzymatic treatment of lyocell fabric

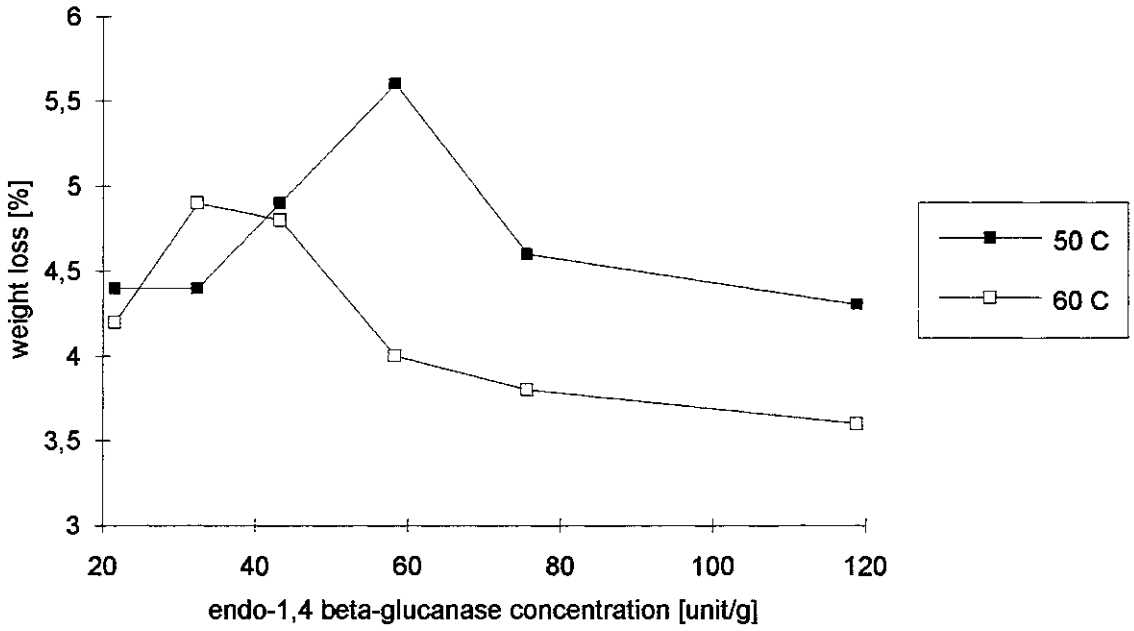


Figure 3: Weight loss of viscose fabric after enzymatic treatment (process duration is 2h)

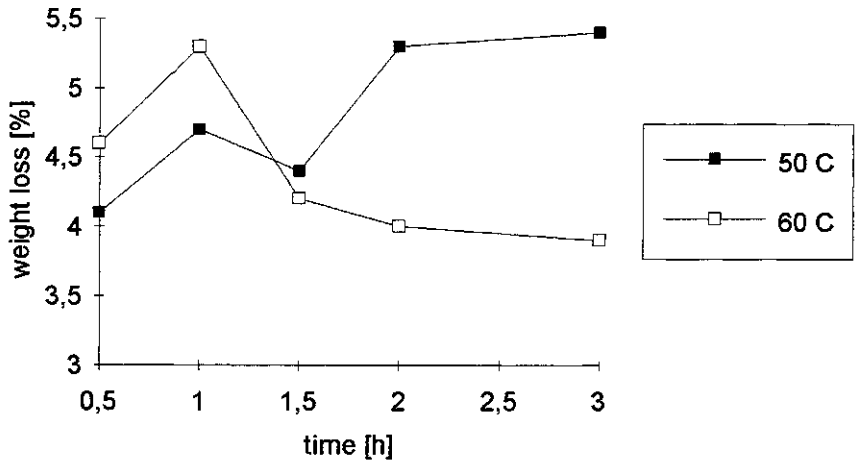


Figure 4: Weight loss of viscose fabric during enzymatic treatment (concentration of endo-1,4 beta-glucanase 58.34 unit/g)

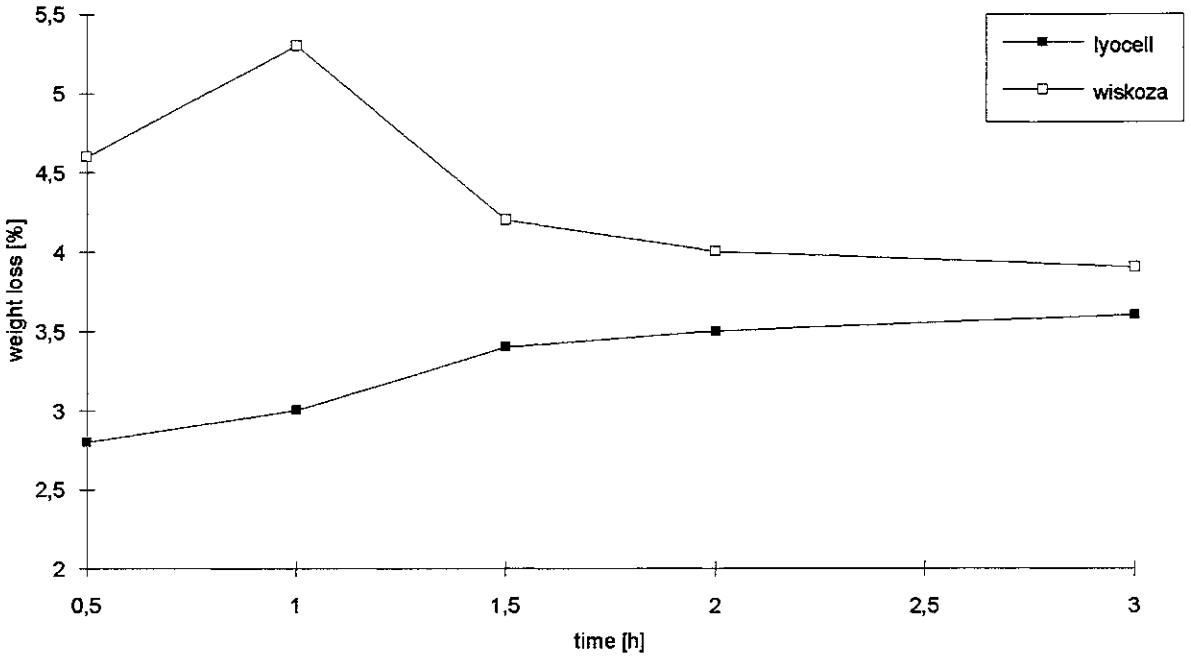


Figure 5: Weight loss of viscose and lyocell fabrics during enzymatic treatment (temperature 60 °C, concentration of endo-1,4-beta-glucanase 58,34 unit/g)

This page intentionally left blank

THE OPTIMISATION OF PROCESSES AND THE RE-USE OF WATER IN THE DYEING OF COTTON AND COTTON/POLYESTER BLENDS

Jaime I. N. Rocha Gomes and Carlos J. E. Lima

INTRODUCTION

The dyeing of cotton and cotton/polyester blends with reactive and reactive/disperse dyes, involves many steps which are mainly rinsing operations to eliminate products such as hydrogen peroxide, used in bleaching, and sodium hydrosulfite (dithionite) used in a clearing process of disperse dyes applied to polyester (reduction clearing). The elimination of these products are necessary since they affect the reactive dyes which are subsequently going to be applied in the dyeing of cotton. These extra steps however, waste water and add time to the total duration of the process, which in today's competitive and ecologically sensitive environment is a drawback.

They can be avoided altogether, in certain circumstances, such as dyeing cotton in very dark colours, which does without bleaching if the cotton is of good quality and impurities have been previously eliminated, and dyeing polyester in light colours, which can do without the clearing process since the amount of dye resting on the surface of the fibre which needs to be cleared is not enough to affect the fastness. These cases make up only a very small proportion of dyeings in most dyehouses.

In the last few years, products such as enzymes were introduced to eliminate hydrogen peroxide and save on rinsing and time, without affecting the dyeing.

In this work a different approach was used, by avoiding these two processes before dyeing, and applying an oxidative process with hydrogen peroxide after dyeing, which serves both as a bleaching process for cotton and as a clearing process for disperse dyes (oxidative clearing). This process can be also referred as post-bleaching when applied only to cotton.

For water saving alone, another approach, alternative or simultaneous with Post-bleaching/oxidative clearing, can be applied: water re-use. In this project it was used together with post-bleaching/oxidative clearing so that water is saved in both, since the dyehouse where it was applied suffers from water shortage in the drier months.

For water re-use, the water must have certain characteristics acceptable for the dyeing and washing processes. There are many different alternatives to obtain water in this condition. The safest is the ultrafiltration of the effluent and the re-use of the water filtered in this way. The problem is that it is an expensive process, mainly due to the membrane and energy costs, and therefore not justifiable for textile industries, unless some other products are also recovered, as is the case with indigo dyeing.

In this project, an alternative approach was used: separation of the most polluted effluents from the least polluted ones, and physico-chemical treatment for removal of the colour and auxiliaries present in the effluent to be re-used.

Simultaneous post-bleaching and oxidative clearing

Post-bleaching

In previous works it was shown how post-bleaching with hydrogen peroxide, cotton dyed with reactive dyes, was a process which made it possible to save either more on chemicals and labour[1] or more on energy[2], depending on the specific type of textiles or processes we are considering, which in these cases was respectively jig dyeing of woven cloth and pad-batch dyeing of knitwear. In the first case it was calculated as 12% for chemicals and 48% for labour respectively, and in the last case savings in energy were found to be as much as 50% due to the fact that intermediate drying is avoided . In both cases, dyes were tested and screened so as to have the least possible alteration in colour due to the action of hydrogen peroxide on more sensitive dyes. Nevertheless, it was not possible to do a lot of colours due to this problem.

More recently in the work that served as a basis for the present work at the textile Tintrofa dyeing plant [3], post-bleaching was taken a step further, by applying a protecting agent developed specifically for the protection of reactive dyes to peroxides and perborates, and developed together with a chemical industry, Indinor, who supplied the product for this project.

It was found that dyes based on the triazine reactive group, provided the dyes were treated with the protecting agent, were resistant to post-bleaching, and the alteration in colour for three colour recipes were insignificant.

For the cotton component of the polyester/cotton blends, it was also found that the protective treatment for the post-bleaching protected the reactive dyes to the perborate present in the ISO105CO6-C2 test, giving better results than when not used.

Oxidative clearing

In the present work, the emphasis is on the advantages obtained when oxidative clearing polyester/cotton blends mainly due to the elimination of the reduction clearing process. The ecological advantages are expressed mainly through the conductivity values of the effluent which are greatly reduced so as to comply with the limits imposed by the local water treatment entity. Other advantages are economical and are expressed mainly as the water saved through the elimination of rinsing operations when doing post-bleaching and oxidative clearing, all in one, for polyester/cotton blends.

For the polyester component of the polyester/cotton blends, it was found that the oxidative clearing could substitute the reduction clearing, with the same results in fastness, and in some cases better, such as was the case for some dyes with thermomigration fastness.

INDUSTRIAL APPLICATION AND RESULTS

Post-bleaching and oxidative clearing

Comparative post-bleaching tests, with and without the protecting product, Nortex Fix, were carried out on the same machine and on the same knitwear.

Post-bleaching was as follows:

Time	30 minutes
Temperature	100°C.
Sodium Carbonate	4 g/l
Hydrogen Peroxide	1 ml/l (50%)

The protection treatment which preceded the post-bleach was as follows:

Time	30 minutes
Temperature	80-100°C.
Nortex Fix	1-2% o.w.f.
Trisodium Phosphate	2 g/l

The classical and the Post-bleaching sequences applied are represented on Figure 1

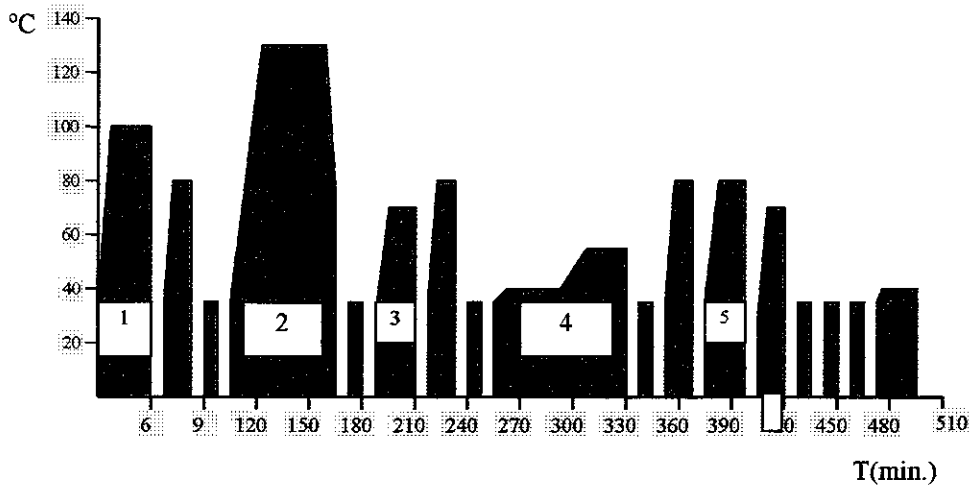


Figure 1: Sequence of operations in the dyeing of polyester/cotton blends

Classical: 1-bleach; 2- PE dyeing; 3- Reduction clearing; 4-CO dyeing; 5- soaping

Post-bleach: 2-PE dyeing; 4- CO dyeing 5- soaping+Nortex Fix; 6-Post-bleach

Water saved

In a previous assessment of saving in water it was found that the oxidative clearing process saved about 40% when compared to the classical sequence of polyester/cotton

dyeing[4]. In a typical dyehouse polyester/cotton blends may account for 50% of the fibres dyed, such as was the case in this work Of these, 30% were being processed by the post bleaching/oxidative clearing sequence after a period of 8 months. The total water consumed was measured and it was verified that it was possible in polyester/cotton blends to economise at 8.5 % water /dyeing lot by this time (Table 1 and Figure 2).

Table 1: Water consumed (average of 14 machines)

	Oct 96	**Jun 97**	**water saved**
Post-Bleaching (% of P/E dyeings)	0	30	-
Water (m^3/dyeing lot)	41.3	37.8	8.5 %

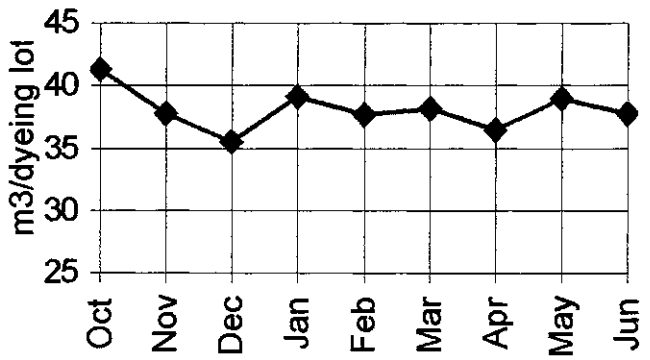


Figure 2: Evolution of water consumption

Effluent separation and treatment

The effluent separation was done based on the conductivity measurements, since a high conductivity might affect the dye affinity and the washing off processes, and COD values, which is a indirect indication of the load of auxiliary products.

In Table 2 are represented some values of conductivity of the work which immediately preceded this work[4], which together with COD values were useful to programme the effluent separation for recycling.

After dyeing tests, the conductivity for recycled water was set at a maximum of 2000 µS/cm and machines were programmed to discard effluents with a conductivity much higher than 1000 µS/cm , and a COD value above 300 mg/l, although other factors were

taken into consideration such as the presence of cations and colour. The dyebath itself was discarded, since it is heavily loaded with colour and salt, but many of the rinsing baths can be re-used since the colour they still contain, can be mostly eliminated by the physico-chemical treatment.

Table 2: Conductivity of effluents from reduction-clearing and post-bleaching

	pH	Conductivity µS/cm	COD mg/l
POST-BLEACH			
1st wash after post-bleach	10,4	1011	290
REDUCTION CLEAR			
Sample 1 (red)			
1st wash after Reduction clearing	12,3	6200	-
Sample 2 (navy)			
1st wash after Reduction clearing	11,7	2650	313
2nd wash	11,0	844	110
3rd wash	10,2	441	59
Sample 3 (navy)			
1st wash after Reduction clearing	12,0	4650	650
2nd wash	11,8	2760	390
SOAPING AND WASHING OFF			
Sample 1 (red)			
2nd wash after soaping	7,74	483	51
3rd wash	7,49	410	49
Sample 2 (brown)			
1st wash after soaping	7,64	309	37
2nd wash	8,00	304	34
3rd wash	7,75	288	34
4th wash	7,69	280	17

The treatment plant consisted of a homogenising tank, a coagulation/flocculation unit and a flotation unit where most of the substances in the dyebath are extracted, including dyes. These are treated with a decolourising agent, and if there is colour remaining it is eliminated in an activated charcoal column.

The floatation process is a physico-chemical process consisting of flotation of flocculated products by pumping air into the tank, and scraping the solids from the top. The cleaner effluent is then mixed with water coming in from the river at a percentage that can go up o 50% depending on how much water is being recycled. In this way it is ensured that some dissolved substances, such as electrolyte, does not accumulate too rapidly by recycling. Even so, it is advisable after a number of cycles, depending on the conductivity of the recycled effluent, that the cycle be interrupted and fresh 100% river water be used.

In Table 3, the values of the effluent before the treatment and after, show that the conductivity increases slightly (but still within the limits for recycling) the COD values are reduced by more than 50% and the colour is not visible, showing the flotation process' high efficiency as compared with the precipitation-decantation process. This

was one of the reasons why this method was chosen, but other advantages were appraised, such as occupation of a smaller floor space and a quicker treatment.

Table 3: Effluent characteristics after separation (with 25% recycling)

	Conductivity μS/cm	**CQO mg/l**
Before floatation treatment	1275	410
After floatation treatment	1790	184

Total benefits

Since the water intake is from the river and there is at present still no charge, the costs which are most important in the area where the dyehouse was situated, are the effluent treatment costs, which are about £0.30/m^3 average. Since this dyehouse was using annually 700,000 m^3 of water, for a saving of 8.5 % with the introduction of the post-bleaching/oxidative clearing sequence, we can estimate an annual saving of £17,850. With recycling a further 25% saving can be achieved, saving a further £0.20/m^3 (since the indoor treatment costs about £0.10/ m^3) which represents an annual saving of £32 250 , making up a total value of just over £50,000 saved in a year. For this dyehouse the main benefit however is guaranteeing a constant supply of water throughout the year. For other dyehouses, the benefit in value might be higher with a greater proportion of post-bleaching/oxidative clearing processing or greater recycling.

Higher fastness of the textile articles and lower conductivity of the effluent are also important benefits of the post-bleaching/oxidative clearing sequence.

CONCLUSIONS

Post-bleaching polyester/cotton knitwear blends and the separation and re-use of cleaner effluents after a physico-chemical treatment, was shown to be a process which generates economy of water, so much so as to interest a dyehouse to implement it as a standard procedure.

REFERENCES

1. J I N R Gomes, G M Vasconcelos-Almeida, "Economy and Effectiveness of Post-bleaching Reactive Dyeings" *Journal of The Society of Dyers and Colourists*, 1986.102, 349-352
2. J I N R Gomes, "Optimisation and automation on continuous and semi-continuous dyeing of cotton knitwear", *VI National Conference de Textile Technology*, Rio de Janeiro, Brasil, July 1991.
3. J I N R Gomes, "Post-bleaching cotton and cotton polyester blends made safe and as a way to avoid Reduction clearing" annual international conference of AATCC, *American Association of Textile Chemists and Colorists*, Nashville 13-18 - Book of papers , September 1996

4. J I N R Gomes and C J E Lima " The optimisation of the reuse of water and Economy of Water and Time, through the application of a clean Technology such as Post-bleaching to Cotton and Cotton /Polyester Blends", *Aachen Textile Conference*, Aachen, Germany, November 1997

Acknowledgements: We thank Indinor, Indústrias químicas SA, for supplying Nortex Fix, and Tintrofa, Tinturaria da Trofa Lda, Portugal, for the collaboration.

This page intentionally left blank

UREA REDUCTION IN REACTIVE DYE PRINTING

Miroslav Prášil

INTRODUCTION

In reactive dye printing urea acts as a swelling agent for cellulose, it disaggregates and solubilises dyestuffs, retards evaporation of water during drying, and increases condensation of water during steaming. The typical reactive dye printing recipe is in the Figure 1.

Urea, on its own is not toxic but it enhances a process known as overfertilization of water. This is a process in which water is enriched with nutrients, resulting in the production of plant biomasses, and also in the consumption of oxygen, resulting in the anaerobic disintegration of dead biomasses. It is essential to keep down the usage of urea.

Complex thickening

urea	150 g
soda ash	20 - 30 g
Tiskan 90 (anti-reduction agent)	10 g
water	785 - 795 g
thickener (eg. Lamitex S)	25 g
	1000 g

Printing paste

dye	30 - 60 g
complex thickening	940 - 970 g
	1000 g

Figure 1: Typical reactive dye printing recipe

METHODS OF UREA REDUCTION

There are three methods of reducing or completely substituting the amount of urea in reactive printing pastes.

Two phase printing method

Paste, that does not contain an alkali or urea, is applied first. Then just before steaming the material is treated with an alkali. This method is not well known around the world

because of it's complicated technology and the requirement of an anti-corrosive protection on the machine equipment.

Substitution of urea by other chemicals

This could have been ideal if there existed an easily available chemical which could substitute urea. Unfortunately, besides all efforts put by producers of textile auxiliaries, such a chemical still does not exist. However, at the present moment, there exist some chemicals which may partially substitute urea. For example, there exists an agent, based on polyacrylic acid, which is able to substitute urea by up to 70% during cotton printing. The problem, however, is that there is a lower colour intensity during printing.

Application of moisture on the substrate

Here a paste that does not contain urea is applied and then just before fixation the textile is moistened. The amount of water applied is around 30% of the the total mass of the dry textile.The most efficient ways of moisture application are:

- spray -system - water is sprayed on to the textile by means of a rotating disc.
- foam moisture application - just before entering the steamer, foam is applied on to the substrate.

INDUSTRIAL STUDY

The results from the plant experiments are shown in the Figures 2 and 3, which give the colour intensity for Ostazin dyes for varying amounts of urea (0 - 150 g/kg) when printed from a standard recipe. The route for conventional method is:

Preparation → Print (with varying amounts of urea) → Dry → Steam → Wash - off → Dry.

The route for spray system is :

Preparation → Print (with varying amounts of urea) → Dry → WECO moisture application controled to give 20 % moisture → Steam → Wash - off → Dry.

The route for foam moisture application is:

Preparation → Print (with varying amounts of urea) → Dry → STORK foam application controlled to give 20 % moisture → steam → wash - off → dry.

CONCLUSION

The whole area of urea reduction in the print paste is undergoing considerable study at the present time. Application of moisture prior to fabric entering the steamer only partially substitutes urea. When the paste is completely free of urea, problems with uneven - printing may occur.

BIBLIOGRAHY

1. J. R. Provost, Effluent improvement by source reduction of chemicals used in textile printing, *J.Soc.Dyers.Col.*, 1992 **108**, 260.
2. J. R. Easton, J. R. Provost, Pollution control and the textile printer, *International Dyer*, 1993, 21.
3. M. Prášil and J. Odvárka, Pollution Source Reduction in Textile Printing, *IFATCC congress*, Vienna, 1996, 344.
4. M. Prášil, Textile Finishing and Ecology, *EMF conferenc,e* Sozopol, 1997, 76.

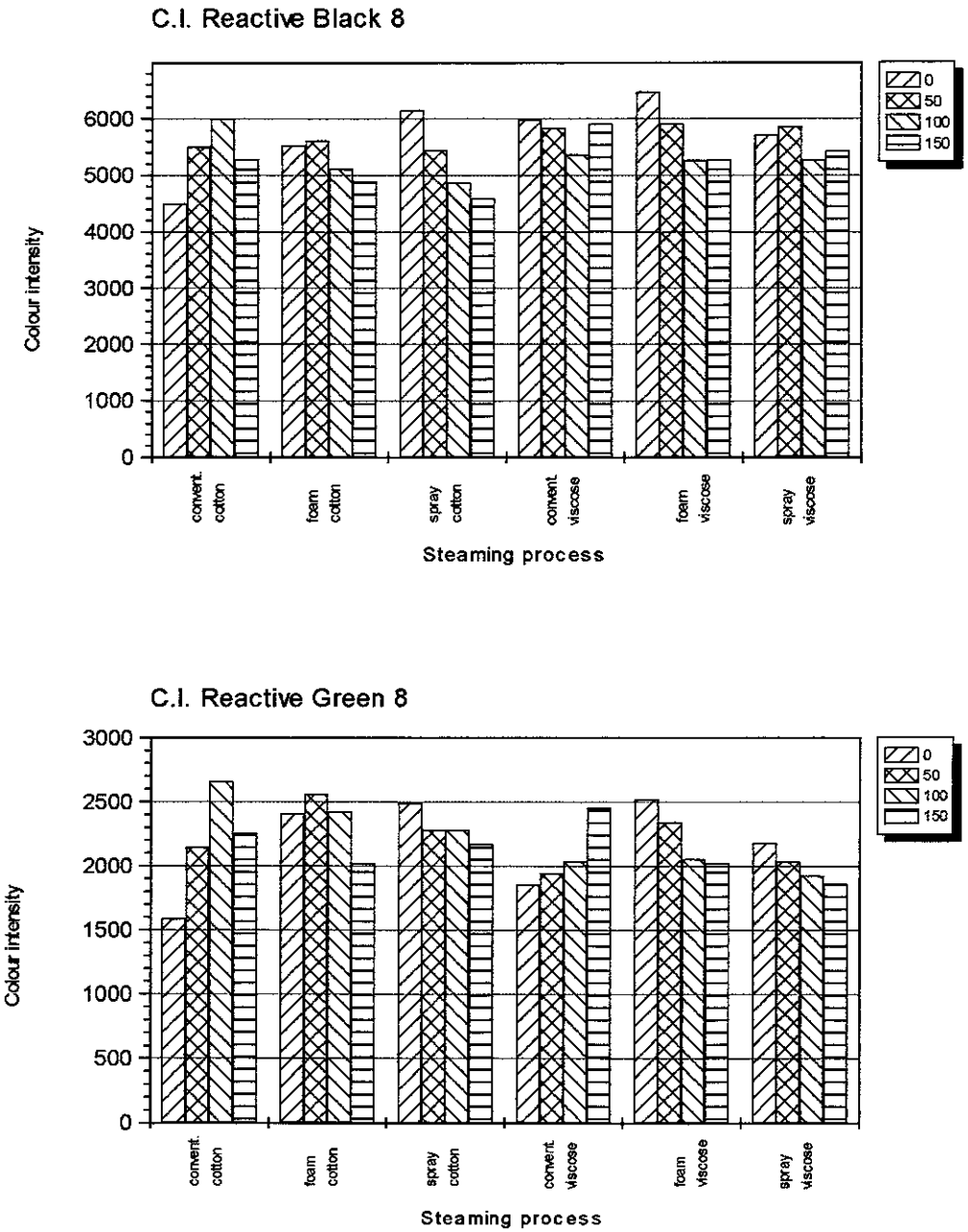
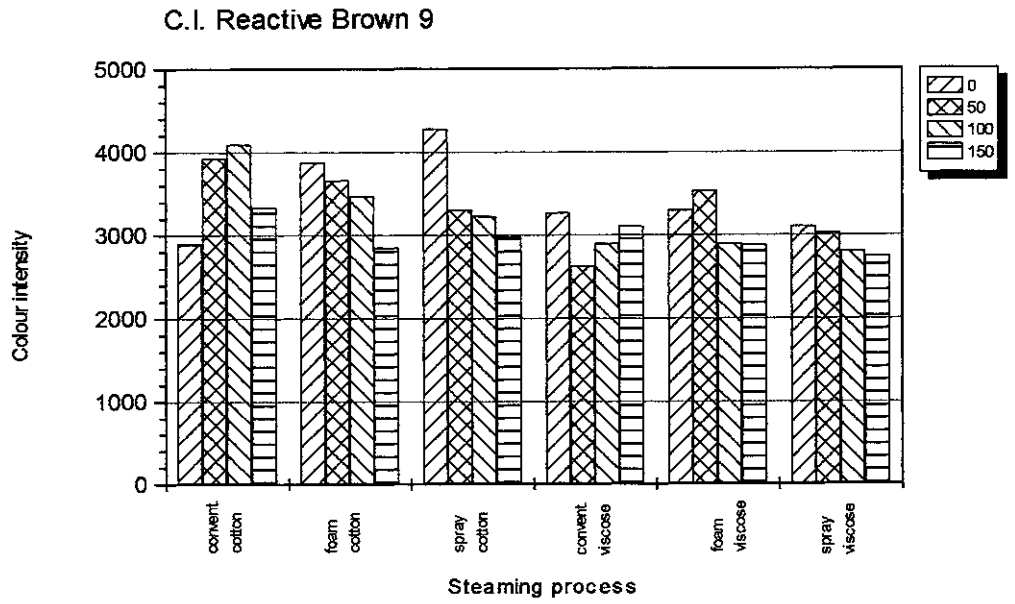


Figure 2: Diagram of the colour intensity for printed cotton and viscose with C.I. Reactive Black 8 and Green 8 for different steaming process and varying amounts of urea (0 - 150 g/kg).



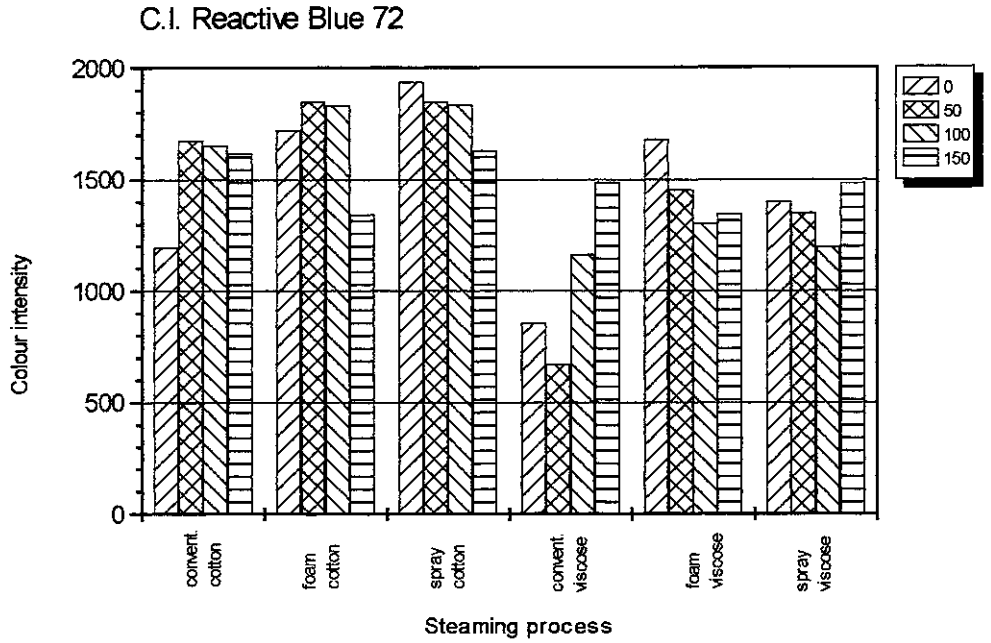


Figure 3: Diagram of the colour intensity for printed cotton and viscose with C.I. Reactive Brown 9 and Blue 72 for different steaming process and varying amounts of urea (0 - 150g/kg).

DISTRIBUTION OF FIBROUS PARTICLES EMITTED DURING SIMULATED HANDLING OF BASALT WEAVES

Jiøí Militký, Vladimír Kovaèiè and Vladimír Bajzík

INTRODUCTION

For usability, acceptable health and safety effects and comfort, it is important to include human aspects already in the development of new kinds of fibres and handling techniques. There is a need for research on fibre emission characteristics in production and handling of fibre-enforced materials in order to control the emission. For economical and health reasons such research should be integrated in the development of new materials.

The non-polymeric multifilament fibres as basalt ones are now very attractive for technical textiles and composites preparation [1]. Some characteristics of these fibres are similar to asbestos. Since the mechanisms for asbestos carcinogenicity are not fully known it can not be excluded that new fibres may also be hazardous to health.

Based on the results of workshop held by April 1988 at Oak Ridge National Laboratory the fibrous fragments with diameter of 1.5 μm or less and length of 8 μm or greater should be handled and disposed of using the widely accepted procedures for asbestos. Fibres falling within the following three criteria are of concern [2].

a) The fibres are respirable. Diameters of less than 1.5 μm (some say less 3.5 μm) allow fibres to remain airborne and respirable.

b) The fibres have a length/diameter ratio R greater than 3. Short stubby fibres (particles) do not seem to cause the serious problems associated with asbestos.

c) The fibres are durable in the lungs. If fibres are decomposed in the lungs, they do not cause a problem.

Most nonpolymeric fibres have diameters significantly larger than 3.5 μm, but break into long thin pieces.

Emission of particles, including fibres, occurs frequently during handling. This study is focused on the complex effect of friction, bending and tensile forces simulated by abrasion experiment on the distribution of fibrous fragments length.

It is assumed that fibrous fragments lengths L are in nature independent stochastic variables fully characterized by distribution function F(L) or probability density function f(L). The failure of non-polymeric fibres such as basalt is frequently caused by volume nonhomogenities and therefore the unimodal distribution is expected. Generally, the number of modal values is an indicator of presence of specific kinds of defects (obviously surface defects and volume ones).

For experimental fragment lengths (L_i) i = 1.....N it is then necessary to use special techniques for [4]:

a) estimation of number of modal values by thnonparametric method;
b) comparison of experimental fragment lengths distribution with some theoretical ones; and
c) estimation of parameter for selected fragment lengths distribution.

In this contribution the suitable techniques for solution of these problems are presented. Complex analysis of basalt fibres fragment lengths distribution is described.

ANALYSIS OF FIBROUS FRAGMENTS DISTRIBUTION

On the base of preliminary analysis of the large sample of basalt fragment lengths it has been proved that corresponding distribution is unimodal and positively skewed to the right. This type of distribution can be well approximated by a Weibull one [3]

$$F(L) = 1 - exp\ -(\frac{L - L_o}{A})^C \qquad (1)$$

or a Lognormal one [4]

$$F(L) = \int_{-\infty}^{P} \{(x - L_0)^2\ 2pA^2\}^{-1}\ exp\ [-\frac{\{\ln(x - L_0) - C\}^2}{2A^2}\ ]\ dx \qquad (2)$$

where F(L) is distribution function (cumulative frequency), L_0 is threshold (minimal) fragment length, A and C are scale and shape parameters.
In sequence, the sample containing N experimentally measured independent fragment lengths (L_i) i = 1.....N is analyzed.

Nonparametric density estimation

The number of modes (local maxima) on the strength probability density function is important from point of view of evaluation of kinds of fragmentation mechanisms (or kinds of defects causing the fibre failure).

Classical nonparametric estimators of the histogram lead often to artifacts. It is well known that histogram quality is critically dependent on the number and lengths of bins (class intervals). For approximately symmetric distribution a suitable number of bins L is given by [4]

$$L = int\ [\ 2/\sqrt{N}\ ] \qquad (3)$$

where int[x] is integer part of number x.

For nonsymmetrical distributions the bins of variable length have to be used.

Especially for complicated shapes of sample distribution the smooth kernel density estimator

$$f(L) = \frac{1}{N * H}\sum_{i=1} K\left[\frac{L - L_i}{H}\right] \qquad (4)$$

is suitable. In this equation H is bandwidth, which controls the smoothness of f(L) and K(x) is kernel function, which is symmetric around zero, and also has the properties of probability density function.

The choice of kernel function form is not critical. The biquadratic kernel is usually sufficient [4]

$$K(x) = 0{,}9375\ \left(1 - x^2\right)^2 \qquad for\ -1 \le x \le 1 \qquad (5)$$

$K(x) = 0$ *elsewhere*

The quality of kernel estimator f(L) is controlled mainly by the selection of parameter H. If H is too small, the estimator is too rough; if it is too large, the shape of f(L) is flattened too much. For nearly normal distributions the optimal bandwidth can be calculated from the expression

$$f(L) = \frac{1}{N}\sum_{i=1}^{N} K\left[\frac{L - L_i}{H_i}\right] \qquad (6)$$

where s is sample standard deviation. For complicated density shapes the Lejenne, Dodge and Koelin procedure can be adopted [5]:

(1) From eqn.(4) an initial guess of probability density function $f^0(L)$ is calculated. The constant bandwidth H is computed as

$$H^0 = 2{,}34\, s\, N^{-1/2} \qquad (7)$$

(2) The final estimator of probability density function with nonconstant bandwidth H_i is constructed The local bandwidth H_i is calculated from

$$H_i = H^0\left[f^0(L_i) \Big/ \max f^0(L_i)\right]^{-A} \qquad (8)$$

Parameter A is defined in the interval $[0,1]$ and controls the smoothness of f(L). The parameter A is usually chosen to be equal to 1/3. For complex sample distribution (polymodal) it is useful to construct f(L) with various values A and select the one corresponding to the greatest visual smoothness.

Comparison of sample distribution with theoretical ones.

Given a sample of measured independent fragment lengths, it is often necessary to find whether the data can be regarded as a sample from the population with a given theoretical distribution.

To compare the closeness of the sample distribution to a given theoretical one the quantile - quantile plot (Q-Q plot) is useful.

The Q-Q plot allows comparison of the sample distribution being described by the empirical $Q_E(p_i)$ quantile function with the given theoretical one characterized by theoretical quantile function $Q_T(p_i)$.

The empirical $Q_E(p_i)$ function can be simply approximated by sample order statistics of fibrous fragments length $L_{(i)}$ which are ordered sample values. These order statistics are $100p_i$%-th quantiles of sample distribution for [4]

$$p_i = \frac{i}{(N+1)} \qquad (9)$$

For a given theoretical fragment lengths distribution the quantile function $Q_T(p_i)$ is inverse to the cumulative density function.

For a Weibull distribution defined by eqn.(1), the quantile function has the form

$$Q_T(p_i) = L_0 + A\left[-\ln(1-p_i)\right]^{\frac{1}{C}} \tag{10}$$

For a Lognormal distribution has the quantile function the form

$$Q_T(p_i) = L_0 + \exp\left[A\Phi^{-1}(p_i) + C\right] \tag{11}$$

where $\Phi^{-1}(.)$ is quantile function of standard normal distribution. When the theoretical and sample distribution are the same then

$$Q_T(p_i) = L_{(i)} \tag{12}$$

The eqn.(12) shows that:

a) For a Weibull distribution the dependence of $L_{(i)}$ on $[-\ln(1-p_i)]^{1/C}$ will be straight line.
b) For a lognormal distribution and selected L_o, the dependence of $\ln(L_{(i)}-L_o)$ on $\Phi^{-1}(p_i)$ will be straight line.

For given shape parameter C or threshold L_o it is then simple to compare the sample distribution with the Weibull or Lognormal ones. In practice the Weibull Q-Q plot is constructed for set of C values and Lognormal plot for set of L_o values. The C or L_o value leading to the best straight line is selected as optimal.

The Q-Q plot can be created by the same way for other theoretical strength distributions, too.

Parameter estimates of strength distribution

Based on theoretical findings or Q-Q plots the suitable strength distribution f(L) can be specified. This function contains some model parameters (for above mentioned distributions the parameters are L_o , A, C). The estimation of these parameters can be realized by using of sample values of fragment lengths L_i by the maximum probability method.

For measured, independent fragment lengths L_i having probability density f(L) the likelihood function has the form

$$L = \prod_{i=1}^{N} f(P_i) \tag{13}$$

By maximizing of L or ln L the maximum probable estimates can be computed.

For above selected distributions the maximization of ln L leads to three nonlinear equations from which the parameters L_o , A, C can be iteratively refined.

A more simple technique is based on quantile function comparison. For example the parameters L_o , A, C of Weibull distribution can be estimated by minimizing the criterion

$$S = \sum_{i=1}^{N} \left\{ L_i - L_0 - A*\left[-\ln(1-p_i)\right]^{\frac{1}{C}} \right\}^2 \tag{14}$$

This is typical problem of nonlinear least squares and minimization can be performed by nonlinear regression software [4]. The lognormal distribution can be treated in the same way.

Converting the parameter estimation task to the problem of nonlinear regression enables the use of specific criterion for selection of the best distribution. A suitable one is the Akaike information criterion, AIC defined as

$$AIC = N * \ln\left(\frac{S^*}{N}\right) + 2 * M \qquad (15)$$

Here M is number of estimated parameters and S^* is minimal value of S (see eqn. (15)).

EXPERIMENTAL PART

The weave from basalt filaments was used. The fragmentation was realized by the abrasion on a propeller type abrader for a time of abrasion of 60 seconds. It was proved by microscopic analysis that basalt fibres are not split and the fragments have cylindrical shapes. Fibrous fragments were analyzed by the image analysis, system LUCIA M. Only the fragments shorter that 1000 μm were analyzed. Results were lengths L_i of fibrous fragments. For comparison the diameters D_i of fibrous fragments were measured as well.

RESULTS AND DISCUSSION

Kernel nonparametric density estimator of the distribution of fibrous fragments lengths is shown on Figure 1 (as a dotted line). The solid line represents a normal distribution with mean value and variance computed form data. It is clear that the number of modes Mo = 1 and normal distribution are quite different from the data-based nonparametric one.

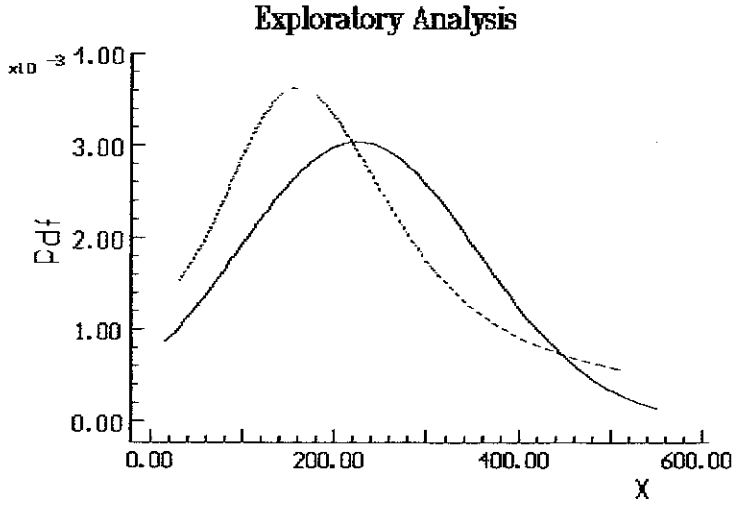


Figure 1: Kernel nonparametric density estimator of the distribution of fibrous fragments lengths (dotted line) and normal approximation (solid line)

Basic statistical characteristics fibrous fragments lengths are

mean value $L_M = 224.16$ μm

standard deviation $\sigma_L = 131.56$ μm

skewness $g_1 = 0.6705$

kurtosis $g_2 = 2.8139$

These parameters show that the distribution of fibrous fragments is unimodal and positively skewed. By the direct investigation using microscope it has been found that no splitting occurs and fragments have the same diameter as the fibres. The distribution of fibre diameters is positively skewed as well.

Basic statistical characteristics of fibres diameters are:

mean value $D_M = 11.08$ μm

standard deviation $\sigma_L = 2.12$ μm

skewness $g_1 = 0.641$

kurtosis $g_2 = 2.92$

By use of a Q-Q plot it has been proved that the best approximation of fibrous fragment lengths distribution is the Weibull one.(see Figure 2.)

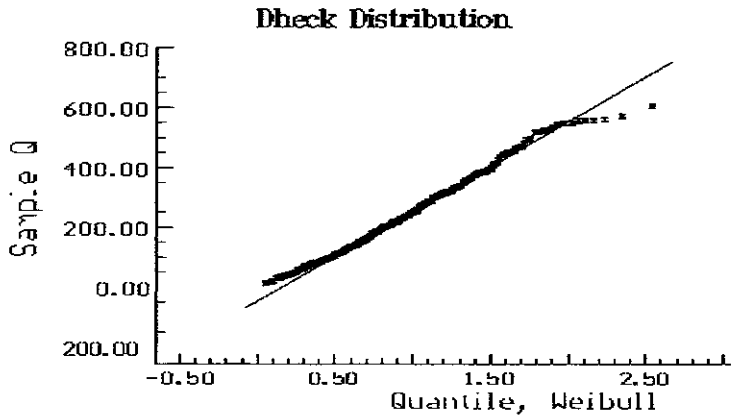


Figure 2: Q-Q graph for Weibull distribution (C = 2)

For estimation of parameters L_o , A, C the maximum probability method maximizing eqn. (13) has been used. The probability density function with optimal parameters (smooth curve) is compared with a raw nonparametric estimate as a Rosemblatt moving histogram (as a rough curve) on the Figure 3. The agreement of both shapes is very good.

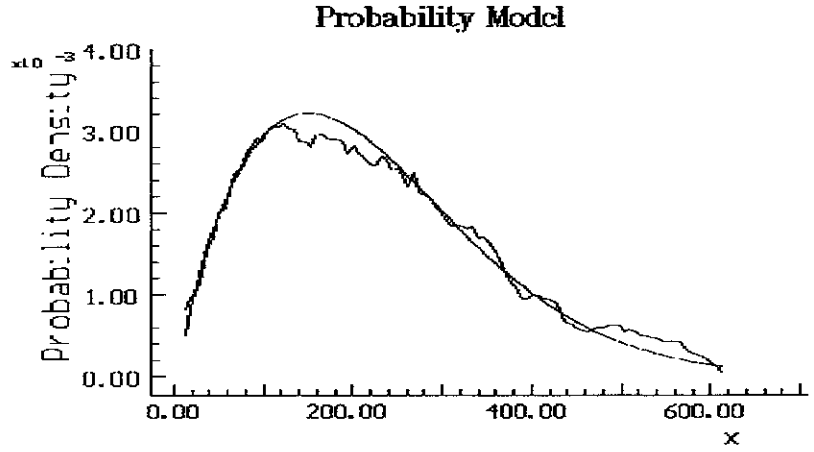


Figure 3: Comparison of optimal PDF(smooth curve) with a Rosemblatt moving histogram (rough curve)

Maximum probability parameter estimates for a Weibull distribution are in Table I.

Table 1: Parameters of strength distribution

Distribution	L_o	A	C	ln L
Weibull	8,687	246,82	1,618	-2469

The value ln L^* represents the maximum of the log probability function. It is evident that the Weibull distribution is more suitable for the description of fibrous fragments length distribution. A unimodal distribution of the Weibull type has been found also for strength distribution of basalt fibres [1].

It is known, that from point of view of their cancer-promoting hazard the length/diameter ratio R is very important. For basalt fibres fragments is ratio R = 224.16/11.08 = 20.231. Therefore the handling of basalt fibres has to be carried out with care.

CONCLUSION

Above mentioned techniques allow complex analysis of fibrous fragments length data. The basalt fibres are attractive for replacing classical asbestos or other nonpolymeric ones. The health problems with this class of fibres are not known. Very long thin fragments of basalt fibrous fragments are dangerous when inhaled. Theoretical treatments like the above help in controlling and minimising concentrations and hazards during the handling and processing of potentially dangerous (and polluting) fibrous materials.

REFERENCES

1. Militký J., Kovaèiè V.: Proc. *25th. Textile Research Symposium* at Mt. Fuji, August 1996
2. Weddell J.K. 'Continuous Ceramic Fibres', *J. Text. Inst.*, 1990 **81,** 333.
3. Weibull W. *J.Appl. Mech.*, 1951 **8**, 293.
4. Meloun M., Militký J. and Forina M. *Chemometrics for Analytical Chemistry, vol. I,* Ellis Horwood, Chichester, 1992
5. Lejenne M., Dodge Y., Koelin E.: Proc Conf. *COMPSTAT 82,* Toulouse, vol. III, 1982, p173