Part IV

Waste management

THE EFFECT OF A FLOCCULENT ON THE COLOUR REMOVAL PROPERTIES OF A CONDITIONED ACTIVATED SLUDGE

Gill Smart[1] and John Binkley[2]

[1] Centre for Materials Research and Innovation, Bolton Institute, Deane Road, Bolton, BL3 5AB, UK
[2] Foundation Studies, Maths and Social Sciences Building, University of Manchester, PO Box 88, Manchester, M60 1QD, UK

ABSTRACT

Colour in effluent is a problem for dyers and many small dyers need to find an easy and economic solution to the problem. Space is often at a premium and small dyers are not large enough to justify the expense of an on-site treatment plant and the local water authority will not accept coloured effluent. One of the easier solutions is to introduce a commercial flocculent into the effluent as it enters a large tank thereby incorporating the colour into flocs, which can be collected and disposed of separately. This investigation finds the optimum flocculent concentration for total colour removal, thus economizing on flocculent usage. The superior colour removal properties of conditioned, activated sludge are shown not to be the result of any residual flocculent remaining within the sludge flocs. The flocculent was added to a laboratory scale activated sludge system using a municipal activated sludge from the local sewage treatment plant and greatly improved the colour removal capabilities of the sludge.

INTRODUCTION

Industrial processes have always had a great impact on the natural environment with liquid effluent being discharged to sewer or water course. A clean-up campaign, initially by the UK National Rivers Authority (NRA) and latterly by the Environment Agency (EA) over recent years has meant that any coloured effluent discharged into a watercourse has become more noticeable. This discharge can come from the local sewage treatment works (STW) or an on-site industrial treatment plant with a discharge permit. Colour was not considered to be a problem in the past but as waterways have become cleaner, there has been an increase in their recreational use with a corresponding concern over colour (Pierce, 1994). Colour in water is visible by the naked eye at very low concentrations and also has a detrimental effect on the transmittance of light with a subsequent deterioration in the aquatic flora and fauna (Diaper *et al,* 1996).

Approximately 36% of worldwide fibre production is cotton with these figures set to remain for the foreseeable future (Anon, 2002) and much of this will be dyed with reactive dyestuffs to give the textiles the bright colours and high wash and light fastness that the consumer demands. Treating textile effluent, with its large volumes of highly coloured water, has been a source of concern to the industry for years. It is the anionic reactive dyes and some acid dyes that cause most problems. A variety of means used to treat this effluent i.e. chemical, biological or physical are available (Robinson *et al,* 2001). These dye molecules however, pass through a conventional activated sludge system at the STW virtually unchanged (Wilmot *et al,* 1998) and now in the days of 'polluter must pay' principle, the onus is on the dyers to sort the problem out at source rather than leaving it for the STW to find the solution.

Chemisolv Ltd produces coagulants and flocculants for industry where there is a particular problem with colour or other contaminants in an effluent wastestream. Chemisolv CB300 is a blend of chemicals, with aluminium sulphate ($A1_2(SO_4)_3$) as a major constituent plus a polyelectrolyte that is blended to suit a customer's own particular effluent treatment problem. Chemisolv CB300, the particular blend for Strines Textiles, was added as the treated effluent left the aeration pond prior to being transported by the Archimedean screw to the settling tank. It was added to aid flocculation of the colour laden flocs in the tank before the sludge flocs were transported to either the "Return Activated Sludge" (RAS) pipe or the aquabelt for dewatering.

EXPERIMENTAL

Activated sludge was collected from the "Return Activated Sludge" (RAS) pipe at Strines Textiles and taken into the laboratory. The "Mixed Liquor Suspended Solids" (MLSS) value was measured as 1.5% (w/v). This is much higher than the working MLSS at Strines which was approximately 0.5% (w/v) under normal working conditions. An activated sludge pilot plant was set up as described in earlier work (Smart *et al,* 2000) with a working solids content of 0.5% (w/v). Aliquots, 200cm^2, were taken from this pilot plant to treat dye solution and measure the uptake of colour by the activated sludge flocs.

The dyes used were Procion Reactive dyes supplied by BASF in their commercial form, Blue HEGN 125 and Crimson CXB. Dye solutions were made up as 1% (w/v) stock solutions in distilled water. Dye solutions were subjected to hydrolysis to mimic the spent reactive dyestuffs found in a textile effluent wastestream. The hydrolysis reaction was initiated by adding Na_2CO_3 (10g) to dye stock solution (500cm^3), the temperature of solution was increased to boiling point and maintained at that temperature for thirty minutes. Each stock solution was allowed to cool, placed in a stoppered volumetric flask, wrapped in aluminium foil and kept in a darkened cupboard to avoid any degradation of the dye by the light and to minimize evaporation.

Mini pilot plants were set up with 0.5% suspended solids, (using either Strines or Ringley Fold sludge), pH of 6.5±0.5 and aerated to give an oxygen concentration of 7 mgdm^{-3}±0.5. Dye stock solution 1%, volume 0.7 cm^3 was added to each plant to give a dye concentration of 3.5×10^{-3} % (w/v). To each plant varying quantities of Chemisolv CB300 (supplied by Strines Textiles) were added to give the following concentrations (with 0% to be used as the control): 0.1%, 0.25%, 0.5%, 1%, 2.5%, 5% and 10% (w/v). Absorbance readings to monitor the colour removal were taken at 0, 15, 60 and 180 minutes and from this % colour removal calculated, as shown by the following equation:

$$\% \text{ Colour removal} = \frac{At_0 - At_n}{At_0} \times 100$$

where,
At_0=absorbance at time=0
At_n=absorbance at time=t_n

All measurements were carried out on a double beam Camspec M350 UV/VIS spectrophotometer. Aliquots, (10cm^3) were taken from the mini-plants at intervals during treatment and centrifuged for five minutes at 5000rpm using a Camlab 1020 centrifuge supplied by Centurion Scientific to remove any turbidity which might have otherwise caused absorbance reading errors. All absorbance readings were taken at the original wavelength of maximum absorbance, λmax, for each dye against a sludge supernatant blank.

RESULTS AND DISCUSSION

Chemisolv and Strines sludge

The degree of colour removal using Strines sludge and variable concentrations of Chemisolv can be seen in Table 1 with the graphs of colour removal versus time in the presence of Chemisolv shown in Figures 1 and 2. Colour removal in excess of 80% is recorded in the mini-plant with 0% Chemisolv, as would be expected with Strines sludge which has been conditioned over the years to treat textile waste from dyeing and printing operations and the activated sludge plant has adapted over the years to treat a narrow range of pollutants very successfully. Chemisolv has been used in unusually high concentrations in these experiments to assess its effects on colour removal.

Table 1. % Colour removal at variable Chemisolv concentrations, Strines sludge

Dye	Time (mins)	Chemisolv concentration % 0	0.1	0.25	0.5	1	2.5	10
Blue	0	0	0	0	0	0	0	0
HEGN	15	86	96	109	109	102.6	35.4	-26.7
	60	87	95	104	108	102.9	32.3	-54.1
	180	79	92	106	106	100.3	31.9	-59.6
Crimson	0	0	0	0	0	0	0	0
CXB	15	78	102	109	107	84	28.4	-2.3
	60	83	104	108	108	85	32	-10.1
	180	83.5	100.5	106	105	81	32	-24.4

In the presence of the highest concentration the negative figures of -24.5% for Crimson CXB and -59.6% for Blue HEGN reveal that there has been an increase of colour at λmax within the supernatant in the treatment plant. The implication from this is that the Chemisolv is responsible for releasing colour from the sludge floc that has already previously been adsorbed prior to the set-up of the treatment plant. It is not unusual for residual colour within the sludge floc to be released. During the set-up of a pilot treatment plant the supernatant would become coloured, usually purplish, within 24 hours. The pilot plant was always set-up using sludge flocs and distilled water; therefore any colour could only come from the flocs. Strines industrial activated sludge has already been used for treating textile effluent containing reactive dye waste, therefore the flocs would hold some already adsorbed colour within them.

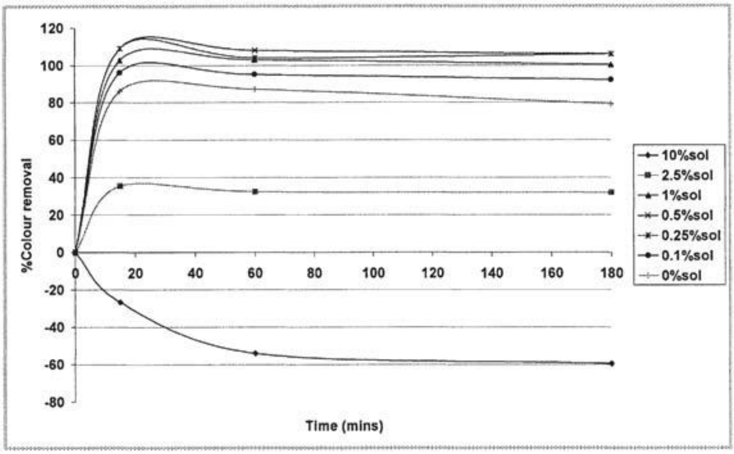

Figure 1 % Colour removal versus time Procion Blue HEGN using Strines sludge with variable concentrations of Chemisolv

When large concentrations of Chemisolv are used, i.e. 10% concentration, which is much larger than would ever be used in industry, instead of coagulation of colour and entrapment within the sludge flocs by either physical or chemical means, Chemisolv could cause the colour to be dispersed through the supernatant. Instead of allowing coagulation and flocculation to occur the large concentration is causing the sludge floc to break down and release colour already held within it. The colour removal in the presence of 2.5% Chemisolv is shown to be between 30–35% for both dyes. This suggests that at this concentration the Chemisolv is indeed holding the colour in the supernatant rather than allowing it to be adsorbed on to the sludge floc.

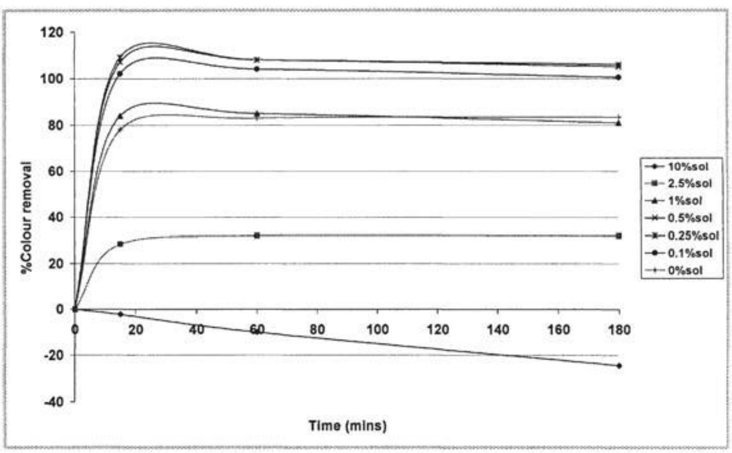

Figure 2 % Colour removal versus time Procion Crimson CXB using Strines sludge with variable concentrations of Chemisolv

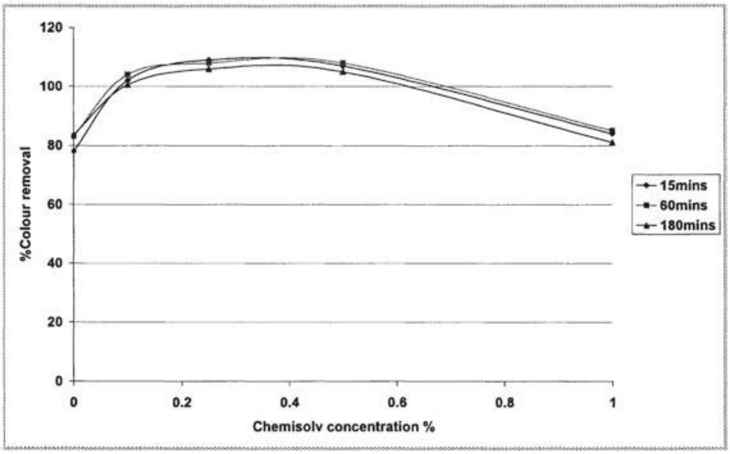

Figure 3 % Colour removal versus Chemisolv concentration with time, Blue HEGN, Strines sludge

Figures 3 and 4 show Percentage Colour removal versus Chemisolv concentration with time and it can be seen that again there is an optimum Chemisolv concentration. The optimum Chemisolv concentration is taken to be that at which 100% of the reactive dye colour is removed from the supernatant. Observation of the plot in Figure 3 shows the optimum Chemisolv concentration for Blue HEGN to be approximately 0.18% whereas Figure 4 reveals an optimum concentration of 0.2% for Crimson CXB.

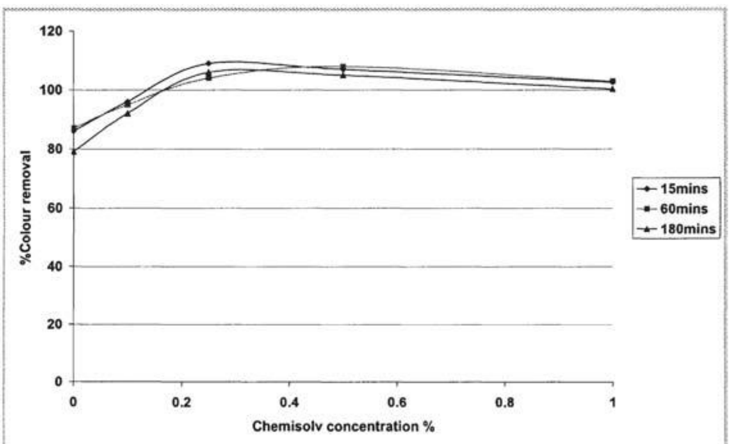

Figure 4 % Colour removal versus Chemisolv concentration with time, Crimson CXB, Strines sludge

Chemisolv and Ringley Fold Sludge

Table 2. % Colour removal at variable Chemisolv concentrations, Ringley Fold sludge

Dye	Time (mins)	Chemisolv concentration (%) 0	0.1	0.25	0.5	1	2.5	5	10
Blue	0	0	0	0	0	0	0	0	0
HEGN	15	17.6	106.1	109.8	108.5	109.2	72.4	68.7	62.9
	60	15.8	106.1	109.2	108.5	111.2	73.4	73.1	62.6
	180	14.5	106.5	110.7	110.2	109.2	78.3	76	65
Crimson	0	0	0	0	0	0	0	0	0
CXB	15	5.3	107.6	111.1	108	80.5	26.2	9.8	-2.1
	60	6.6	105.4	107.8	112.3	81.9	26.1	3.8	-1.6
	180	5.3	104	111.4	116.1	85.7	25.8	9.5	-3.9

The colour removal results obtained when dye and Chemisolv are introduced into mini-pilot containing Ringley fold sludge are displayed in Table 2. The data are plotted graphically in Figures 5 and 6 showing % colour removal versus time with varying concentrations of Chemisolv CB300 for Procion Blue HEGN125 and Crimson CXB using Ringley Fold sludge. The colour removed by the sludge in the absence of Chemisolv (i.e. the control comparator) is in keeping with the results discussed in earlier work (Smart, 2004). The Ringley Fold sludge alone is only able to remove small quantities of the reactive dye colour from the treatment plants with the results indicating colour removal of 18% for Blue HEGN and 8% for Crimson CXB, this can be seen from Figures 5 and 6 respectively.

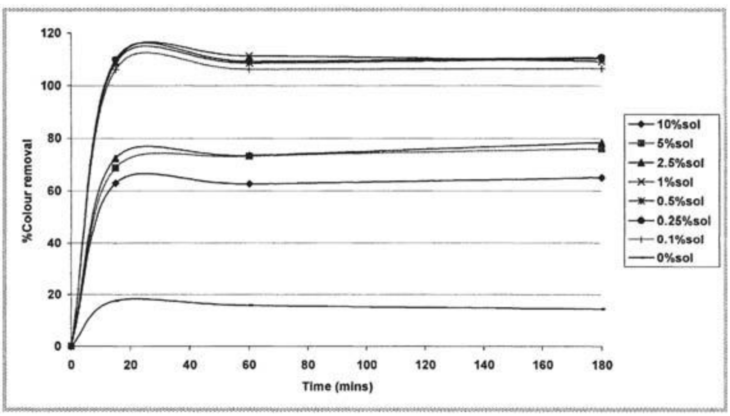

Figure 5 % Colour removal versus time Procion Blue HEGN using Ringley Fold sludge with variable concentrations of Chemisolv

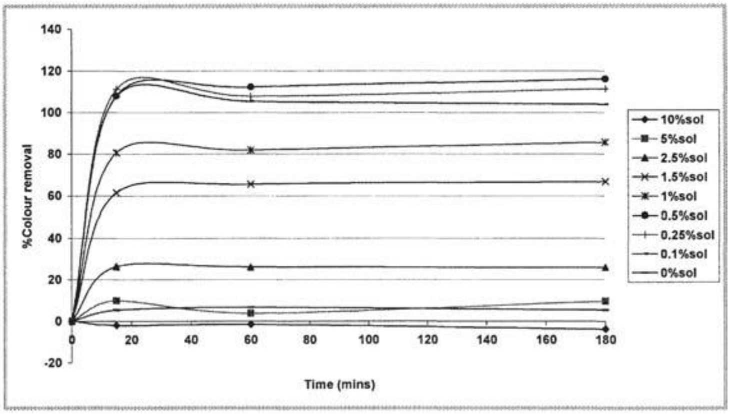

Figure 6 % Colour removal versus time Procion Crimson CXB using Ringley Fold sludge with variable concentrations of Chemisolv

Any concentration of Chemisolv higher than 0.5% reduces the quantity of colour removed from the treatment plant. It is apparent that there is an optimum Chemisolv concentration that gives maximum colour removal, beyond which its effectiveness at colour removal is reduced. A critical biosolids concentration was observed in the industrial sludge (Smart, 2004). Above this critical concentration colour removal was still effective but impaired. It was considered that this was due to an increase in floc size that reduced the overall surface area to mass ratio, thus decreasing the number of adsorption sites available on the surface for the dye. The effect could be similar here, at a critical Chemisolv concentration larger flocs are produced with reduced surface area to mass ratio and reduction in number of adsorption sites, leading subsequently to a reduction in the amount of colour removed.

In the Strines sludge it would appear that this phenomenon is occurring until, as stated earlier, there is a probable breakdown of the sludge floc with a release of the colour held within the floc. This does not seem to happen with the Ringley Fold sludge to the same extent, where there is a very slight increase of colour in supernatant in the mini-plant with Crimson CXB. The sludge flocs in the plant with Blue HEGN are still removing significant amounts of dye at 10% Chemisolv concentration although the colour removal is less than that at 0.1% Chemisolv concentration.

The optimum concentration can be seen clearly from Figures 7 and 8 which show % colour removal versus Chemisolv concentration with time for Blue HEGN and Crimson CXB respectively. The critical concentration appears to be at around 0.1%. The colour disappearance is rapid and results in coloured flocs. At the concentrations between 0.1 and 0.25% the colour disappears from the flocs during the three hour period of the treatment. The sludge flocs were examined optically after the supernatant was centrifuged off for absorbance measurements. The colour could be seen on the floc after 15 minutes reading but by 180 minutes the colour had disappeared. This was only noticed at the low concentration range. An explanation for the coloured flocs could be that initially the dye is attracted to the outside of the floc by chemical means or physical entrapment.

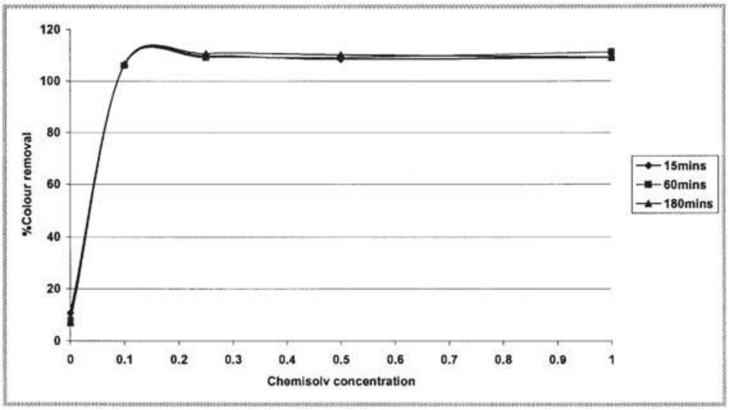

Figure 7 % Colour removal versus Chemisolv concentration with time, Procion Blue HEGN, Ringley Fold sludge

Over the three hour time period the colour is dispersed throughout the floc and therefore the colour does not appear on the outside of the floc.

The Ringley Fold sludge alone is only capable of removing less than 15% colour, while complete colour removal is apparent at 0.1% Chemisolv (although concentrations of Chemisolv up to 5% do remove a significant amount of the colour). Figures 7 and 8 indicate that the optimum Chemisolv concentration for 100% colour removal of both Procion Blue HEGN and Crimson CXB is slightly less than 0.1%, which would fit in with the data collected from extensive studies by Churchley (1999), where the optimum concentration was found to be 0.08%.

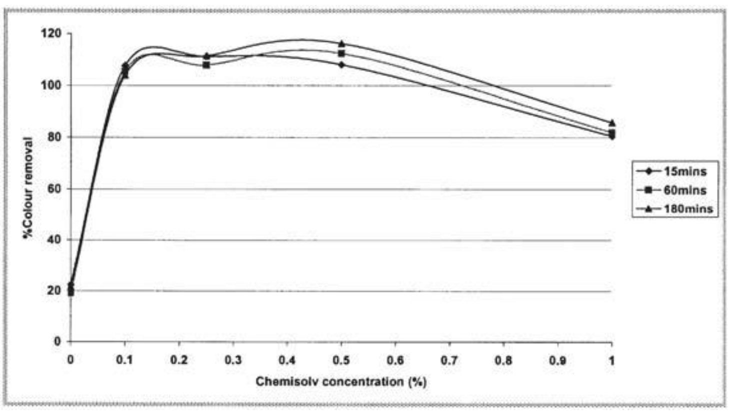

Figure 8 % Colour removal versus Chemisolv concentration with time, Procion Crimson CXB, Ringley Fold sludge

Chemisolv in the sludge floc

It was important to establish if the Chemisolv was present within the Strines sludge floc in a significant amount to be responsible for the success of the Strines sludge at removing colour. The λ_{max} was monitored in the presence of and without Chemisolv using both sludge supernatant and distilled water.

Table 3. λ_{max} shift for Procion Blue H-EGN and Crimson CXB in the presence of Chemisolv.

	λ_{max} (nm) Blue HEGN	Shift nm	λ_{max} (nm) Crimson CXB	Shift nm
Dye + water	626		543	
Dye + water + 1%Chemisolv	649	23	560	17
Dye + Strines supernatant	624		544	
Dye + Strines supernatant + 1%Chemisolv	646	22	560	16

The results shown in Table 3 indicate a bathochromic shift in the absorption spectra and consequently λ_{max} for both dyes, the shift being 22nm and 16nm for Blue HEGN and Crimson CXB respectively. The fact that no change in λ_{max} was observed for either dye in the pilot plants made with "Return Activate Sludge" from Strines is a good indication that any Chemisolv present is negligible or if present is possibly 'locked' within the sludge flocs and unable to participate in the colour removal process. Therefore adsorption of the dye on to the biomass is likely to be a function of this particular conditioned activated sludge and not the result of residual Chemisolv. It can quite easily be seen that the presence of Chemisolv brings about a very significant bathochromic shift in the λ_{max} for both Blue HEGN and Crimson CXB.

The data shown in Table 4 indicates a shift in the adsorption bands at very low concentrations of Chemisolv, as low as 0.01% (v/v). There is evidence of a significant bathochromic shift in λ_{max} at this low concentration. The shift for Blue HEGN is 34nm at 0.01% and above, for Crimson CXB the same bathochromic shift of 20nm is given at 0.01% and above. This shift in λ_{max} is significant and is a good measure of very low

Table 4. Shift in λ_{max} for Procion Blue H-EGN and Procion Crimson CXB in aqueous solution with varying Chemisolv concentration.

[Chemisolv] %	λ_{max} (nm) Blue HEGN	Shift nm	λ_{max} (nm) Crimsons CXB	Shift nm
0	626		544	
0.002	627	1	545	1
0.010	660	34	564	20
0.025	660	34	564	20
0.050	660	34	564	20

concentrations of Chemisolv present within the RAS. In the absence of Chemisolv each dye solution was added to distilled water to give the correct measurement concentration and the same procedure was repeated with Strines supernatant. When absorbance spectra were run on these two solutions, λ_{max} was recorded as the same for each dye in both solutions. Since it has been established that a concentration of Chemisolv as low as 0.01% caused a significant shift at λ_{max}, this would suggest that insignificant amounts of Chemisolv are found in the Strines sludge floc, from which the supernatants are prepared for colour measurement

CONCLUSIONS

The addition of Chemisolv into the mini-treatment plants improved the colour removal properties of both sludges although the largest increase was seen the Ringley Fold sludge. The Ringley Fold sludge alone removed less than 20% of the total colour for both dyes but on addition of the optimum Chemisolv dose of 0.1% (v/v), colour removal of 100% is recorded. Total colour removal increased in Strines sludge from approximately 80% to 100% with the addition of Chemisolv. A significant bathochromic shift in the λ_{max} of each dye in the presence of low concentrations of Chemisolv show that there are no significant residual levels of Chemisolv in the Strines RAS.

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THE ANAEROBIC DIGESTION OF TEXTILE DESIZING WASTEWATER

Richard Dinsdale[(1)], Kevin Bryne[(2)] and David Tucker[(2)]
[(1)]Sustainable Environment Research Centre, University of Glamorgan, Pontypridd, UK
[(2)]Water Development Services, 142 Whitchurch Road, Cardiff, UK.

ABSTRACT

Anaerobic digestion is a biological process which converts the chemical oxygen demand (COD) present in wastewater to methane and carbon dioxide and thus can be used to reduce the treatment costs of industrial wastewaters. Textile desizing wastewater is a high strength wastewater (20,000 mgl^{-1} COD) and extremely alkaline (>pH 12) and therefore is costly to discharge to sewer and will require neutralisation to a lower pH before discharge to sewer. An anaerobic treatment stage consisting of two 50 m^3 mesophilic upflow anaerobic sludge blanket reactors (UASB) with an activated sludge polishing stage was built and operated from August 2003. This wastewater treatment plant has contributed to a COD reduction of up to 80% and a neutralisation of the pH from pH 12 to pH 7–8. The methane present in the biogas is utilised to heat the anaerobic digesters and the CO_2 produced in the biogas is used to neutralise the alkali in the wastewater. This results in an in-house wastewater treatment process with low running costs i.e. low in energy demand and chemical usage.

INTRODUCTION

In the UK with 96% of the population connected to the sewer system, trade effluent treatment is usually performed by the regional water service companies. Not only may the cost of this service be substantial but the water company may not be prepared to take certain types of waste due to the infringement of consent limits. Significant rises in trade effluent charges may also be expected to meet increased environmental standards such as the EU Water Framework Directive and other future environmental protection legislation. When the regional water companies were privatised in 1989 a pricing regime of "Retail Price Index (RPI)+ K" factor was legislated for to compensate for the increase investment required to meet increased water discharge standards. This was in contrary to other utility privatisations where a price regime of RPI—X (where X is a cost reduction factor) was imposed. Indeed the water companies have a further option to increase prices via the "pass through option" (Kinnersley, 1994). Therefore, any company discharging to sewer faces the prospect of trade effluent charges rising faster than inflation on a yearly basis. This rise in charges along with environmental legislation has increased the incentive for in-house effluent treatment. By the intelligent selection of physical and biological treatment systems, an effective and reliable on-site wastewater treatment system could be installed. This would result in a waste with a reduced treatment cost and acceptable for discharge to the water company. In many cases, anaerobic digestion can provide a better, faster and more energy-efficient effluent treatment process than other processes with typical cost savings on effluent discharge of 65% (DTI, 2001). Increasing interest has been shown in anaerobic digestion as a biological treatment system as it has significant potential advantages over aerobic treatment.

THE ANAEROBIC DIGESTION PROCESS

Anaerobic digestion is a biological process which utilises bacteria that operate without the need for a constant supply of oxygen. These bacteria convert COD to methane and carbon dioxide thus reducing the trade effluent charge for the effluent treatment. The Biochemical Oxygen Demand (BOD) of the trade effluent, although using aerobic organisms in the test assay, can be an indication of the degree of COD reduction which can be achieved by the anaerobic digestion process. However as the process differs fundamentally from the aerobic process specific anaerobic biodegradability testing on the trade effluent should be performed to give a truer indication of the degree of anaerobic treatment.

The advantages of anaerobic digestion over aerobic wastewater treatment are lower electrical power usage, the production of energy in the form of methane gas, and lower microbial cell (sludge) production. A comparison of the aerobic vs anaerobic treatment of a tonne of COD (chemical oxygen demand) removed is shown in Table 1.

Table 1. Comparison of the anaerobic and aerobic treatment of a tonne of COD.

Factor	Anaerobic	Aerobic
Electrical Input	—	1100 kWh
Methane	1.16×10^7 MJ	—
Net cell production	20-150 kg	400-600 kg

(Data From Speece, 1983)

Anaerobic digestion does have some disadvantages. Anaerobic digestion is not an all in one solution, post-treatment will usually be necessary as BOD is not usually reduced sufficiently for discharge to open water. In particular, nitrogen and phosphorus removal is limited. Industrial plants usually operate at 20–35°C although can operate efficiently down to temperatures of 10–15°C (Mergaert *et al,* 1992). This problem is usually easily overcome as most wastewaters are released at these temperatures and methane from the digestion process can be used to heat the reactor. However it means that for dilute low strength wastes (<500 mgCOD 1^{-1}) discharged at less than 10–15°C anaerobic digestion may not be the most cost effective option.

Despite these disadvantages, the cost advantage for the anaerobic process can be substantial for wastes with COD strength greater than 500 mgCOD 1^{-1} and this cost advantage increases as the COD strength increases. For a waste of 2000 mgCOD 1^{-1}, anaerobic treatment is a third of the cost of aerobic treatment and if the COD rises to 12,000 mgCOD 1^{-1} anaerobic treatment of the waste can be a tenth of the cost aerobic treatment. With increasing energy and sludge disposal costs the advantages of anaerobic digestion can only improve (DTI, 2001).

DESIZING WASTEWATER CHARACTERISTICS

Sizing compounds such as starch and polyvinyl alcohol (PVA) are applied to yarns to impart tensile strength before weaving. These size compounds must be removed before the cloth can be dyed or printed. Textile desizing effluent is produced from the processes used to remove these size compounds prior to the cloth being dyed or printed. A typical desizing process utilises sodium hydroxide/hydrogen peroxide mixture to hydrolyse the starch size and bleach the cloth with a subsequent washing stage at 80°C to wash the hydrolysed size from the cloth. This desizing process results in the production of a significant volume of hot wastewater (65–75°C), with high COD of up to 20,000 mgl^{-1} and is extremely alkaline (>pH 12). In the S. Wales region this would incur a trade effluent charge of approximately £5.70 m^3 plus neutralisation costs.

THE DESIGN PROCESS

Laboratory studies

To aid in the selection of the most suitable on-site biological treatment process laboratory trials were performed at the University of Glamorgan using a 5 litre biological aerated filter (BAF) and 5 litre UASB anaerobic reactor. Using two batches of desizing wastewater the BAF was found to give at best a 50% removal in COD whereas the UASB reactor gave up to 90% COD removal with an average of 74% COD removal over a period of 25 days of continuous operation. The residual BOD from the anaerobic reactor was found to between 200–800 mgBOD 1^{-1}. Ultimate aerobic biodegradability was found to be 80% of the total COD. The high strength of the effluent indicated that anaerobic digestion would be the most cost-effective solution. Although anaerobic digestion would be the main COD removal process utilised, an aerobic polishing stage should be implemented to further reduce the COD and remove the dissolved methane from the effluent discharged to sewer.

Neutralisation of the waste from pH 12 to pH 7 was also successfully achieved by the addition of carbon dioxide. Carbon dioxide neutralisation offers a number of advantages over mineral acid neutralisation. The main advantage is that as the anaerobic digestion process produces carbon dioxide, in-situ neutralisation using this carbon dioxide could be implemented without incurring the cost of the mineral acid dosing and consumption.

Full Scale Implementation

Once the decision to use anaerobic technology was taken, a survey of the factory's desizing process was conducted to determine the current production volume and strength of the desizing effluent and an indicative value for future production volumes. This data was then used to size the biological treatment process. Anaerobic digesters are available in a number of configurations e.g. CSTR (continuously stirred tank reactors), UASB reactor etc. A selection of UASB technology was made for a number of reasons, i) the waste characteristics met the design criteria for treatment in a UASB,ii) the laboratory studies were performed using a UASB reactor and iii) the UASB is a widely used technology. The waste survey data was used to size the digesters, using the design criteria described by Lettinga and Hulshoff Pol (1991). Therefore a maximum OLR (organic loading rate) of 10 kg m^3 day^{-1} with a HRT (hydraulic retention time) of 2 days was selected, giving a total reactor volume requirement of 100 m^3. For ease of build and a degree of redundancy within the system the reactor volume was divided in to two UASB reactor systems of 50 m^3 total volume. Using the information contained in Lettinga and Hulshoff Pol (1991), the two UASB reactors were designed and constructed in GRP (glass reinforced plastic). The only modifications made to the standard UASB reactor design was the implementation of an $8m^3h^{-1}$ recycle rate to improve in reactor mixing to aid in temperature control, to reduce the impact of the high strength effluent on the granular bed and to aid the carbon dioxide neutralisation process. To balance out the wastewater flow from the factory and to try to ensure a balanced flow to the UASB reactors over a weekly period, a 200m^3 balancing tank was built into the system (see Figure 1). As the aim of the project was to ensure a process with a no or little energy or chemical inputs, and to ensure optimum usage of the biogas, a 50 m^3 gas storage system was also implemented.

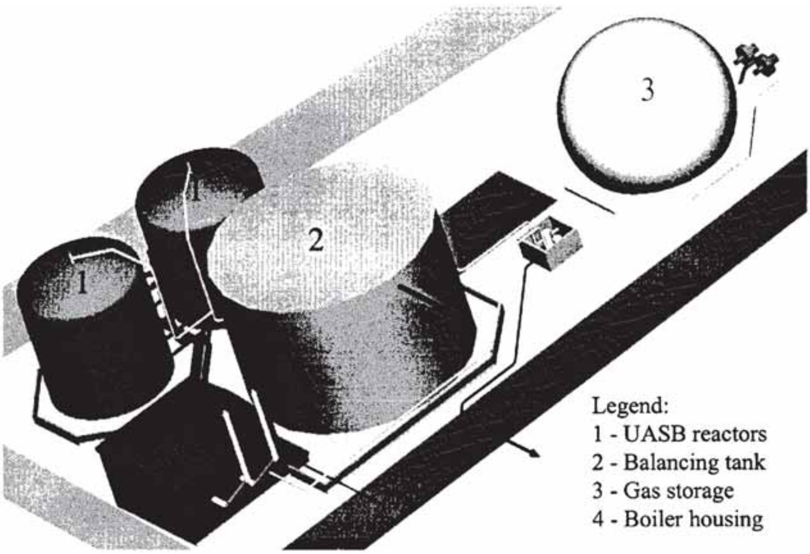

Figure 1 Layout of the Biological Treatment Plant at Treforest Textiles.

INITIAL RESULTS FROM FULL SCALE OPERATION

The digesters were seeded in August 2003 with anaerobic granules from a UASB reactor treating citric acid wastewater. The digesters are maintained at between 30–35°C largely using the biogas produced by the anaerobic digesters. From the 8 months after digester start up an OLR of 8 kg m^3 day^{-1} with a HRT of 2 days have been achieved. The effluent has been netralised to between pH 7–8 without the addition of any chemicals to achieve this. The COD removal percentage has varied between 40% and 80%.

FUTURE WORK

The future work is mainly directed at stabilising COD removals, this will be achieved by fine tuning the addition of nutrients, developing the best operational procedures for dealing with start-up after quarterly shut downs and dealing with peak loads and investigating potential inhibitors in the effluent such as hydrogen peroxide.

CONCLUSIONS

A low energy and chemical input anaerobic biological process has been developed and implemented. The effluent pH has been successfully neutralised to target levels with a reduction in COD being achieved. However with all biological treatment systems suitable operating and management procedures have to be developed and implemented over time to ensure optimal efficiency.

ACKNOWLEDGMENTS

The authors would like to thank the DTI and Treforest Textiles for their financial support to this project and Peter Jackson of Tate & Lyle for the supply of UASB reactor granules.

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EFFLUENT TREATMENT USING A SUBMERGED AERATED FILTER

Elaine Groom
A BIO-WISE Demonstrator Project, Applied Technology Unit, QUESTOR Centre (Queen's University Environmental Science and Technology Research Centre), Queen's University, David Keir Building, Stranmillis Road, Belfast BT9 5AG, Northern Ireland

ABSTRACT

In common with many companies in the textile sector William Clark & Sons Ltd produce a coloured wastewater that is highly variable in composition, which presents a challenge to treatment. The company recently chose to install a submerged aerated filter (SAF) to ensure a high rate of biological treatment in order to meet a river discharge consent. This technology, unproven in the sector, was awarded a BIO-WISE Demonstrator grant to optimise and demonstrate the effectiveness of the technology for textile effluent treatment and to assess the potential for its integration with other treatment technologies for colour removal and for treatment of wastes from a lamination process.

The plant was commissioned in 2002 and, following a period of detailed monitoring and optimisation, has consistently reduced the chemical oxygen demand (COD) and biochemical oxygen demand (BOD) of the effluent to levels required for discharge. The plant has also performed well in response to changes in effluent composition due to variations in day-to-day activities and the seasonal nature of the textile industry.

Project overview

The application of treatment technologies to textile effluent is a continuing problem. For companies needing to install or upgrade effluent treatment facilities, a number of choices exist of technologies proven to be applicable to textile effluent treatment. However, these tend not to include newer technologies that often represent a significant advance over existing processes. This is unfortunate as the textile sector contains a disproportionately high number of SMEs, a business category that can ill-afford to take risks with unproven technology, despite requiring access to the most cost-effective treatments.

Recent initiatives have tended to focus on colour removal due to changes in legislation that have allowed the introduction of colour consents for effluent discharges. For many companies however, levels of BOD and COD in effluent are a major concern as they contribute significantly to trade effluent charges. Where river discharge is possible, there is likely to be no one treatment that can deal with colour removal and remove BOD to consent levels. In comparison with other parts of Europe, the application of biological treatments to textile wastewater in the UK has been low. This has reduced the opportunities to advance the application of high rate biological treatments in this sector.

Submerged aerated filters are an example of advanced biological treatment processes that represent a significant advance over activated sludge plants and biotrickling filters but remain unproven for the treatment of textile effluents. Among the advantages of

SAFs are the high organic loading rates achievable, the small footprint and reduced cost due to availability as packaged plant with reduced civil costs. Biological treatments such as SAFs have little appreciable effect on many types of textile dye. However, the removal of BOD from the effluent may allow treatment with one of a number of technologies that would not be economic for colour removal in whole textile effluent. Thus it is possible that SAF technology will provide part of a complete treatment solution.

This project intended to demonstrate the treatment of textile effluent by a submerged aerated filter at William Clark & Sons Ltd. Funding provided an opportunity to co-ordinate the expertise of the technology provider (STG) and user (William Clark & Sons Ltd) and enable the technology to be optimised and proven under real conditions. An extensive monitoring programme was carried out jointly between the QUESTOR Centre and William Clark & Sons Ltd to produce a detailed record of effluent production and SAF performance in relation to company activities. A number of process variables and operating conditions were examined, within the range of operation of the plant, in order to optimise the performance. The company activities varied with season and produced extremes of effluent condition proving that the process is sustainable over the entire range of conditions that may be encountered. It was also demonstrated that the process can be rapidly brought into operation after shutdown periods, for example holidays, maintenance etc.

The objectives of the project were as follows:

- To design and install an advanced biological treatment plant based on SAF technology that can be optimised for the treatment of textile effluent.
- To demonstrate the robustness of the process to the variations in the effluent due to day-to-day variations in activity and the seasonal nature of the textile industry.
- To investigate the applicability of the technology to co-treatment of waste from an aqueous-based lamination process.
- To validate the sustainability of the process and examine its potential for integration with processes for colour removal.
- To demonstrate the performance of the technology to the textile industry through a dissemination programme.

Liaison between the QUESTOR Centre and STG also examined the potential for co-treatment of waste from an aqueous-based lamination process, a new and growing activity for William Clark & Sons Ltd, and the potential for integration of SAF technology with existing and emerging technologies for colour removal, including those supported by BIO-WISE. Dyeing activities at William Clark & Sons Ltd fall into two distinct seasons, therefore a range of appropriate tests at laboratory and pilot scale were carried out, running concurrently with other aspects. The project examined how a variety of treatments could be readily combined with biological treatment to give a complete, cost-effective solution to the treatment of textile wastewater.

The combined knowledge of the partners of biological treatments and the textile sector, and the specific experience of STG in the design and operation of SAF technology, provided an opportunity to optimise the configuration and operation of the technology for future application in the textile sector. The extended nature of the detailed monitoring programme ensured that data of sufficient quality was collected over a suitable timeframe to prove the technology for use within the textile industry.

EFFLUENT TREATMENT AT THOS. CHADWICK & SONS LTD

M.Madden[1] and M.Andrews[2]

[1]ENCO, Confederation of British Wool Textiles, Valley Drive, Ilkley, UK.
[2]Thos. Chadwick & Sons Ltd., Eastfield Mills, Dewsbury, West Yorks, UK.

ABSTRACT

Effluent with high COD, solids content and trace pesticide is generated by raw wool scouring. Although current methods of on-site effluent treatment reduce these contaminants before discharge the remaining concentrations are sufficient to cost the company a great deal of money for sewage treatment and to warrant severe limits on pesticide concentrations under Integrated Pollution Prevention Control legislation. It is highly likely that discharge costs will increase and pesticide limits will be lowered in the near future.

Trials with fast acting anaerobic digestion pilot plant have shown that the effluent can be further treated and that the additional use of effluent "polishing plant" can reduce contaminant concentrations to very low levels. Furthermore, the anaerobic system may provide useful methane gas with which to power the main processes on the site.

This paper shows the results of an industrially-based project that is likely to go on to become a full-scale solution to a difficult problem not only for this company but for the wool textile industry as a whole.

INTRODUCTION

The scouring of raw wool results in effluents that are rich in grease and solids and hence have a high Chemical Oxygen Demand. As well as these major components, there are traces of the process chemicals such as detergent and builders and traces of sheep dip pesticide residues. All these substances mean that wool scour effluent is subject to high discharge costs and to strict limits particularly with respect to pesticides.

Many techniques are used around the world to try to reduce the pollution potential of wool scouring effluent but in the UK, where discharge costs are extremely high and environmental legislation is strictly enforced, simpler techniques of treatment are not sufficient.

Currently the technique of choice is to coagulate then flocculate the effluent and then to separate the floc from the cleansed effluent by means of decanter centrifuge. This results in a cleaner effluent and a waste sludge that can both be discharged at a lower cost and within current environmental limits. However environmental limits are getting more and more stringent and economic pressures mean that mills are looking to further reduce costs where they can. Under these circumstances further treatment of the effluent is desirable.

Anaerobic digestion is a tried and tested method for treating high strength effluents worldwide. It is used in a few scouring mills around the world as the primary treatment for scour effluent but typically requires a lengthy residence time for the treatment to be successful. It has the advantages of producing only a minimal sludge since most of the organic component of the effluent is "consumed" by the biomass in the reactor and it produces methane as a by-product of that consumption which can be used as a source of power.

Past research efforts to introduce anaerobic digestion into the UK scouring industry have met with limited success. Digestion and methane production did occur but the reactors used quickly became blocked with the inorganic component of the effluent in the form of dirt and sand.

The purpose of this paper is to describe briefly trials that have been taking place at the Standard Wool (UK) Ltd wool scouring plant in Dewsbury, UK with the help of funding from the UK government's BIOWISE initiative. These trials have examined the use of anaerobic digestion of scour effluent and have utilised pilot plants designed to treat the effluent in a relatively short period compared to conventional anaerobic digestion. Pilot plant to "polish" the effluent after the main treatment has also been evaluated.

Trials have been funded for a period of two years and the project is now entering the stage where consideration of a full-scale system has begun and costing of the components is underway. Parts of the system remain confidential at this stage although once the project is completed dissemination will be much more detailed.

THE COSTS OF TREATMENT

The costs of discharge of industrial effluents to sewage treatment undertakers in the UK are governed by the use of the Mogden formula:

$$C=R+P+(Ot/Os)*B+(St/Ss)*S$$

where C=the discharge cost to sewer in pence/m3
R=reception charge at the sewage treatment works in pence/m3
P=primary treatment charge at the sewage works in pence/m3
B=biological treatment charge at the sewage works in pence/m3
S=sludge disposal charge at the sewage works in pence/m3
Os=the biological strength of combined sewage in mg/l COD
Ss=the sludge strength of combined sewage in mg/l Settled solids
All the above values are set by sewage undertakers for their area each year.
Ot=is the measured strength of the discharge in mg/l COD
St=is the measured sludge strength of the discharge in mg/l Settled solids

This formula enables easy calculation of how much an effluent will cost to discharge.

A wool scour processing 18,000T of raw wool per year at 2.5 litres of scour water per kilogram of wool would typically have effluents with Ot=80–100,000 mg/l COD and St=30–35,000 mg/l Set. Solids. Using the formula with the values set by Yorkshire Water for 2003–4 would give a discharge cost of between £1,428,955 and £1,735,939.

Currently used effluent treatment would be expected to reduce COD values by around 70% and solids values by 90%. Thus discharge at present might typically cost between £335,465 and £409,805 per year.

Clearly there is room to reduce these costs further and the trials aimed to show that a system incorporating anaerobic digestion of effluent could achieve a reduction of approximately 70% in costs.

PESTICIDES IN SCOUR EFFLUENT

The use of sheep-dip chemicals during the wool-growing season is extremely widespread. Sheep are attacked by a number of insect pests in all climates and dipping, spraying or back lining of sheep at some point is very often a necessity. Whilst most wool growing and exporting countries in the world take care to advise farmers to use the minimum amounts of chemical and at times that allow high levels of degradation of the chemical in the fleece to occur before shearing, most wools still contain measurable amounts of these chemicals. There are several types of pesticide in use for sheep dipping, but in the UK three types have attracted environmental limits because of their proven effects on aquatic environments. These are the organochlorines, the organophosphates and the synthetic pyrethroids. The first group is largely banned from use on sheep but such is their persistence in the environment that measurable traces can still be detected in wool from countries where the bans are in force. There still remains some wool exporting countries where use of this group is commonplace. The second and third groups are legally used all around the world. All these chemicals can enter the aquatic environment via the effluent from raw wool scouring and being lipophilic in nature are associated with the wool grease that is deliberately removed from the fibre during the scouring process.

In the UK, most on-site effluent treatment was originally installed to help reduce overall pollution load and thus reduce disposal costs but has had the secondary effect of reducing the micro-pollutant (trace pesticide) load by removing much of the grease from the effluent.

As legislative limits on pesticides in receiving waters have become stricter to the point where Environmental Quality Standards (EQS) are approaching analytical instrument detection limits, it has become much more important for raw wool scourers to ensure that the discharge limits imposed by the Environment Agency on their effluent discharges are adhered to. Any breaches must be reported to the Agency who ultimately has the power to order factory closure until the operator can assure the Agency that limits will be met in future.

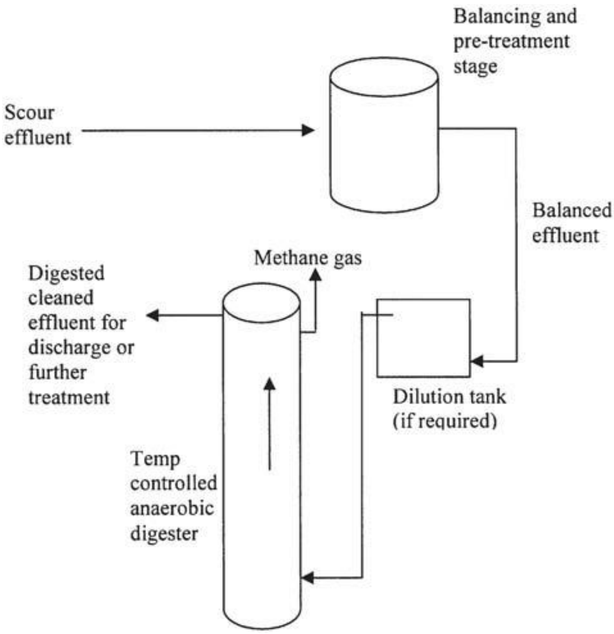
Current means of effluent treatment at UK scourers tend to reduce pesticide loads by 70–80% depending upon the sophistication of the treatment. The introduction of an anaerobic process to the treatment could result in even greater reductions in pesticide discharges and one of the aims of the trial was to show whether improved pesticide removal could be achieved by this technology.

TRIAL EQUIPMENT

Two separate systems were chosen for the trial. Parques Ltd (Netherlands) via the project partner Aquabio Ltd (UK) and the second by project partner Puriflow Ltd (UK) supplied these reactors. Both were based on the upward flow system where the effluent is introduced to the bottom of a columnar reactor with the cleansed effluent eventually being extracted from the top. The Parques reactor had a granular blanket supporting the biomass through which the effluent flowed whilst the Puriflow had a plastic medium on which the biomass grew and the effluent flowed in between. Perhaps the most important difference between the reactors was the hydraulic residence time of the effluent in the reactor. The Parques reactor, originally designed for effluent somewhat weaker than that from raw wool scouring, had a designed residence time of 15 hours whilst the Puriflow reactor was based on a residence time of 3–4 days. Increasing or decreasing the re-circulation of the effluent within the system could of course alter both these times.

The reactors were fitted with controlled heating to maintain a temperature suitable for the growth of the biomass and with pumps to feed and re-circulate effluent and, if required add extra nutrients. The plants were also fitted with a methane gas collection and measurement system.

The diagram below shows the general treatment scheme for the pilot plants.



TREATMENT

Effluent from the scour was pumped to the balancing and pre-treatment section of the system and from here to a dilution tank.

Initially both reactors were fed with very diluted effluent so that the relatively high COD load would not overwhelm the biomass within them. As time went on it was possible to increase the concentration of the feedstock until the Puriflow reactor was accepting undiluted effluent and the Parques reactor was accepting 33% diluted effluent. After anaerobic digestion in the reactors, the effluent was discharged to drain. At a later stage in the project a pilot scale membrane bioreactor plant was installed to accept effluent from the Puriflow reactor and give further treatment. The membrane bioreactor worked with a combination of an aerobic biomass and a cross flow micro-filtration membrane to treat the relatively low solids and COD load effluent. It produced a concentrate that could be recycled back into the anaerobic feedstock and permeate which was discharged to sewer.

PERFORMANCE MEASUREMENTS

The intention from the beginning of the project was to try and run the reactors in such a way as to mimic the simplest form of full-scale operation. Whilst biological treatment plants can be made to work on almost any effluent, it is often not cost-effective to consider them due to the high on-going maintenance and technical manpower required to keep them in efficient working order. This project was set up to run the pilot plants on effluent that was as little modified as possible from that currently produced and to minimise interventions such as nutrient supplementation as much as possible. The only variables the team wanted to alter were feed concentration and feed rate; the object being to achieve the fastest rate at the highest concentration.

The performance criteria set by the team were equally simple. A successful trial would be one in which the pilot plant(s) resulted in at least a 70% reduction in overall pollution load across the digester, a significant decrease in overall load compared to the current technique and demonstrated a significant reduction in pesticides concentration in the final discharge. A second criterion was to reduce the amount of chemicals used in the overall treatment of the effluent. Current methods of treatment can use very large quantities of chemicals and the cost of treatment is driven upward by this. The production of methane gas was regarded as an extra benefit only if it was of sufficient volume and quality to be of use as a fuel for the scour process. The reactor(s) had to demonstrate "robustness" i.e. the ability to survive the various pollution loads delivered to it and to recover from any malfunctions that might occur on a full-scale plant.

COD and suspended solids content, as the main pollution load characteristics, were measured at very frequent intervals through out the trial duration. The wool grease content of the effluent was also measured frequently. The wool grease is one of the largest contributors to the COD load and is also a crude way of measuring approximate pesticide removal since the pesticides are largely dissolved in the grease. The concentrations of sulphate, phosphate and nitrogen/ammonia were measured on a regular basis so that the input and output of basic nutrients to the reactors could be followed. Pesticide analysis was also undertaken once it was considered that the reactors had stabilised at an optimum treatment rate.

The performance of the MBR had no set criteria, as it was uncertain as to the level of additional treatment it could deliver. The analysis of polished effluent was expected to show a significant decrease in both COD and residual pesticide content however.

RESULTS FROM THE PROJECT TO DATE

The results presented cover the following areas:

1) COD reduction over time for the two pilot plants—reactors only (Figures 1 and 2)
2) Grease reduction over time for the two pilot plants—reactors only (Figures 3 and 4)
3) Solids reduction over time for the two pilot plants—reactors only (Figures 5 and 6)
4) General COD reduction over the entire system—Puriflow reactor only (Table 1)
5) General Grease reduction over the entire system—Puriflow reactor only (Table 1)
6) General Solids reduction over the entire system—Puriflow reactor only (Table 1)
7) Pesticide reduction over the entire system—Puriflow reactor only (Table 1)
8) COD, Grease, Solids and Pesticides reduction in comparison to current system (Table 2)
9) Gas production and quality
10) Performance of the MBR (Table 3)

Reduction of COD during trials—measured across the anaerobic reactors

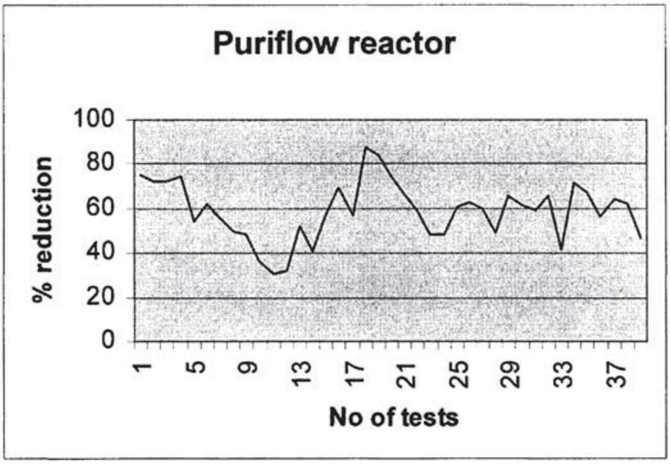


Figure 1 Percentage reduction of influent COD to Puriflow reactor

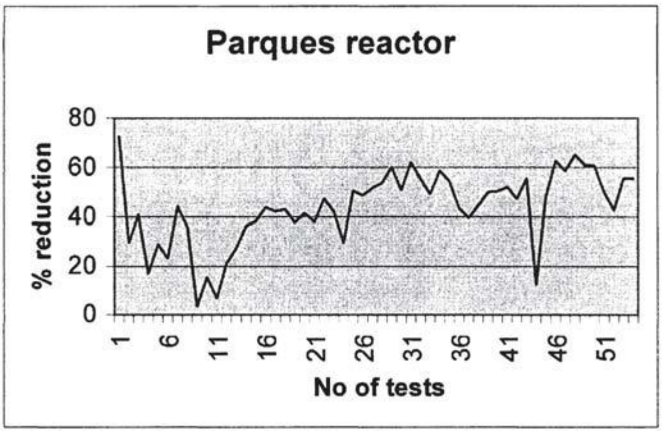


Figure 2 Percent reduction of influent COD to Parques reactor

As COD input to both reactors was increased over the trial duration the performance (reduction) of the Parques reactor appeared to improve but the Puriflow reactor gave the better performance considering the lower or zero dilution of its input.

Reduction of grease during trials—measured across the anaerobic reactors

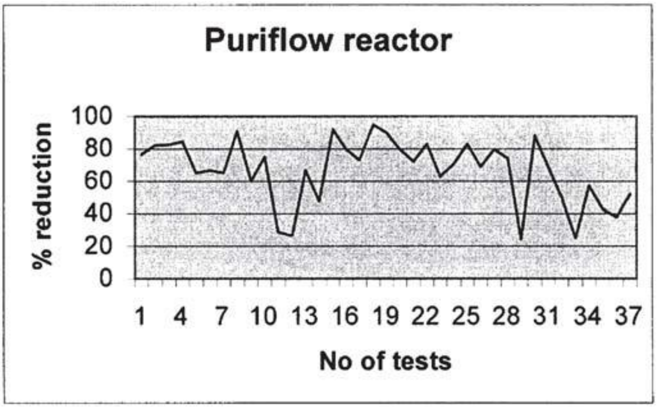


Figure 3 Percent reduction of influent grease to Puriflow reactor

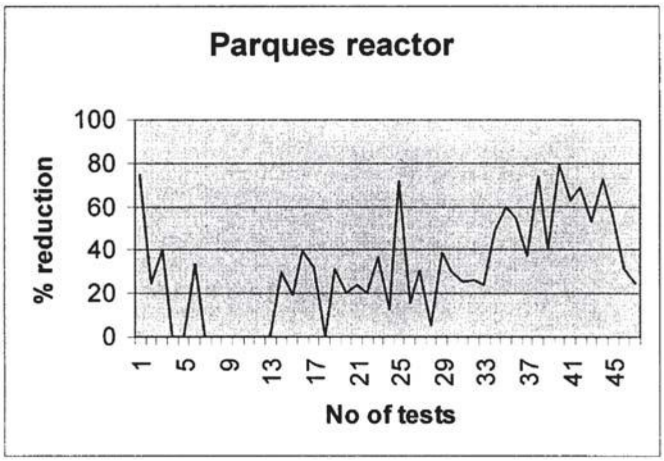


Figure 4 Percent reduction of influent grease to Parques reactor

The general trends show that grease reduction was more efficient in the Puriflow reactor despite the much higher concentration of the input. Points where the grease reduction for the Puriflow reactor dip below 40% are points at which practical problems with the pilot plant were experienced such pump breakdown or over-heating. The same is true for the point on the Parques graph where reduction seems to fall to zero.

Reduction of solids during trials—measured across the anaerobic reactors

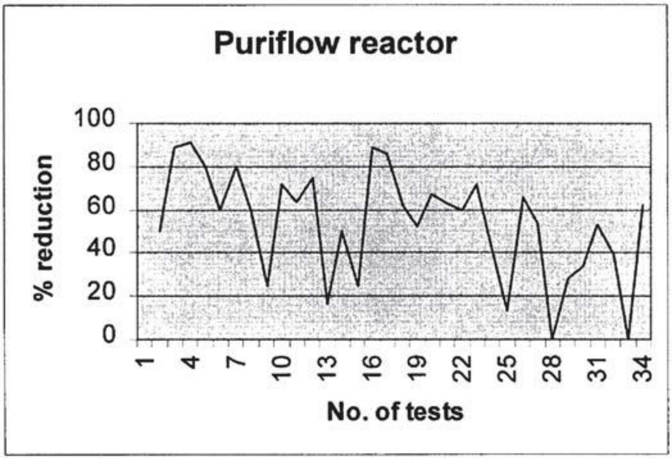


Figure 5 Percent reduction of influent solids to Puriflow reactor

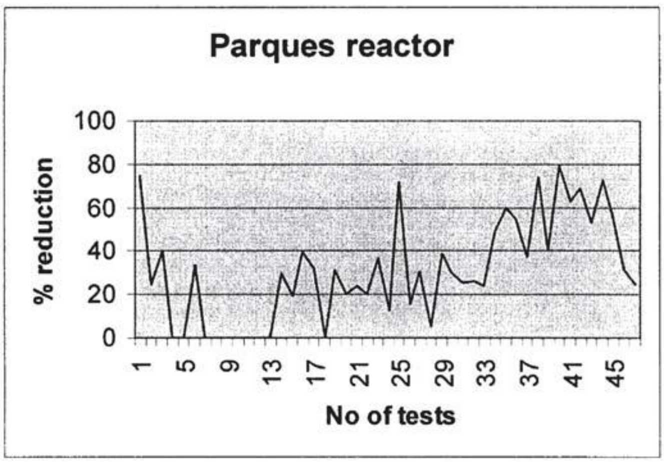


Figure 6 Percent reduction of influent solids to Parques reactor

The solids reduction in both reactors is much more variable than grease or COD reduction. The Parques reactor solids discharge actually mirrored the input closely whilst the Puriflow reactor performance has become less impressive as the input concentration has increased to 100%. These graphs do not reflect the problems experienced with solids breakthrough in the Parques reactor discussed more fully below.

Table 1. General reduction in COD, Solids, Grease and Pesticides across the whole system (from balancing tank input to Puriflow reactor discharge whilst operating at 100% effluent input.)

Parameter	Input to System	Discharge from Puriflow	% Reduction
COD	83,986 mg/l	8,749 mg/l	89.6
Set. Solids	30,679 mg/l	386 mg/l	98.7
Grease	1.59%	0.03%	98.1
OC Pesticide	9.053 ug/l	1.252 ug/l	86.2
OP Pesticide	697.43 ug/l	9.92 ug/l	98.6
SP Pesticide	252.65 ug/l	13.42 ug/l	94.7

Table 2. Comparison of reductions across the trial system with the current effluent treatment performance.

Parameter	Current Treatment Performance (% Reduction)	Trial System Performance (% Reduction)
COD	72.4	89.6
Set. Solids	85.1	98.7
Grease	88.3	98.1
OC Pesticide	68.9	86.2
OP Pesticide	76.2	98.6
SP Pesticide	25.6	94.7

(Current system values for the above parameters (input and output) are based on historical measurements for 10 typical working days)

Gas production and purity

Note that these results relate to periods during the trial when steady state treatment of effluent under minimum dilution was occurring.

Overall average volume of gas=0.3 m^3/kg COD removed

Average purity of gas—CO_2 content=15% v/v

H_2S content=<1ppm

CO content=<0.05% v/v

CH_4 content=80% v/v

Balance of volume is made up by nitrogen.

Performance of the MBR system

Table 3. Reductions of pollutants as a result of using an MBR "polishing" system fed with effluent discharged from the Puriflow reactor.

Parameter	Input to System (ex Puriflow)	Discharge from MBR	% Reduction
COD	8,749 mg/l	3,065 mg/l	64.9
Set. Solids	386 mg/l	50 mg/l	87.0
Grease	0.03%	0.0094%	68.7
OC Pesticide	1.252 ug/l	0.205 ug/l	83.6
OP Pesticide	9.92 ug/l	0.45 ug/l	95.4
SP Pesticide	13.42 ug/l	0.49 ug/l	96.3

CONCLUSIONS FROM THE TRIALS

During the trials it has been clear that the Parques pilot plant with its short hydraulic retention time was not able to deliver the same reduction in overall load as the Puriflow plant. The graphs showing COD, Solids and Grease reduction with time show that the fast throughput system achieved reasonable results especially given the speed of treatment. However the plant only ever operated on diluted effluent feed and seemed unable to cope when dilution was reduced. For the purposes of the project, the aim was to select a technique of anaerobic digestion that could reduce its input load by 70% and thus improve the overall load reduction of the system in comparison to the current treatment. The Puriflow pilot plant came close to this target and is thought likely to achieve and even exceed it at full scale. The plant was linked with an MBR pilot scale system to measure whether any further worthwhile reductions in load could be attained.

Robustness was also an important selection criterion and during the trials it was clear that the Parques plant was more susceptible to changes in input load than was the Puriflow plant. Despite the use of a balancing tank to try to "smooth" out any sudden changes in effluent characteristics the short hydraulic retention time of the Parques plant meant that it had little time for its biomass to adjust to even slightly changing conditions. It was also shown that the Parques plant was more difficult to return to steady state running after practical problems such as temperature excursions in the biomass. One of the major problems with the Parques plant was, however, the distribution of solids within the reactor. The design of the effluent circulation within the reactor itself meant that solids were lifted from the lower parts of the reactor column by rising bubbles of gas and became lodged in the gas take-off ports. This meant that the reactor had to be regularly cleaned and it became clear that the short residence time and the reactor circulation could not cope with the effluent strength despite prior dilution.

The longer the period of time that can be allowed for digestion, the more effective an anaerobic reactor system is likely to prove but it is obvious from the results that some portions of the feed effluent are more easily digested than others. Grease reduction across the whole system (Puriflow reactor) is excellent and is significant for both reactors measured in isolation but there is clearly another component of the effluent COD that is not being digested so quickly. This is highly likely to be suint. Suint is essentially the sweat of the sheep dried on to the wool that is to be scoured. It is made up principally of organic potassium salts that have a characteristic dark brown colour in solution. This coloration is evident in the discharge from the anaerobic reactors and is indicative of suint presence. Being water-soluble it likely that the salts would need to be exposed to the anaerobic conditions for longer than used in these trials in order to be digested or degraded.

The solids in the effluent are to some extent removed by the anaerobic digesters but the most effective part of the system in this respect is the balancing and preparation technology. Without solids reduction in front of the reactors it would not be possible to run the anaerobic components at such a relatively high rate of through-put.

The pesticide removal of the pilot system is excellent and is a significant improvement over the current treatment plant. It is known that the organisms within a biomass will tend to adapt to digest and degrade the substances they are regularly exposed to and again a longer retention time will aid in this process of adaptation. In the anaerobic reactors the biomass is breaking down the grease by digestion and the pesticides are suffering the same fate.

There has been no evidence of “breakthrough” of grease, pesticides or solids from the Puriflow reactor during its running period and this indicates that there is no or only very gradual build-up of sludge (undigested material) in the reactor. The structure of the reactor will allow, on a full-scale plant, the removal of small quantities of sludge build up in the base by simply opening a valve to remove consolidated material in the base. This material may then be de-watered.

The gas produced by the Puriflow reactor was remarkably high quality and consultation with CHP engineers confirmed that the gas could be used to power a CHP engine that would supply electricity to the main process or supply green electricity to the grid. Green electricity attracts favourable tariffs and this could provide some income to offset running costs of the effluent plant.

The MBR system did produce some excellent results especially in the area of pesticide concentration reduction. However the COD reduction was relatively poor and it was noted that the suint content of the effluent from the MBR was similar to that of the influent feed. It could be that membranes with reduced pore size might help solve this but the throughput rate of the MBR would decrease in this case.

THE POTENTIAL FUTURE

If the full-scale version of the pilot plant was to perform in the same way as described in this report then the following cost comparisons could be made:
(note: current system average discharge COD=21,020 mg/L and SS=2,042 mg/L)

Current treatment—discharge to sewer cost=£6.35/m^3
New system—discharge to sewer cost=£2.72/m^3
New system with additional MBR—discharge to sewer cost=£1.21/m^3

For a discharge of 45,000m^3 per annum (18,000T wool at 2.5L/kg discharge rate) the above values translate into:

Current treatment=£285,750 per annum (+£65,000 current chemical costs)
New system=£122,400 per annum—an annual saving of £163,350 (not inc. chemicals)
New system+MBR=£54,450 per annum- an annual saving of £231,300 (not inc. chemicals)

The value of gas produced can only be crudely estimated by scale-up but would be in the region of £ 30–40,000 for a 45,000m^3 discharge.

There is thus considerable scope to cover the cost of some of the installation of such a new system despite the fact that such a system would be relatively expensive because of its uniquely custom designed and built nature.

Once costs have been covered (estimated pay back about 4–5 years for the option without MBR) the new system would immediately begin to add its cost savings to the company bottom line and would in addition improve the environmental profile of the company by reducing pesticide discharges and by producing green electricity or reducing on-site imports of electricity.

PROTECTIVE PROPERTIES OF TEXTILES DYED WITH NATURAL DYES

Deepti Gupta
Department of Textile Technology, Indian Institute of Technology Delhi, Hauz Khas, New Delhi-110016, India

INTRODUCTION

Now and in the future consumers will accept only special textile materials; these are textiles which enable differentiation of products, are multi-functional, technologically perfect and are available at a reasonable price. Today's customers are becoming more and more aware of problems caused by microbes—from the meat we eat to the clothes we wear. Exposure to sun is leading to increased incidence of skin cancer. Therefore claims for protection are increasingly. Researchers are now looking for natural products, which do not have any ill-effects on the general population and are easily degradable. Consequently, there is increased research activity to find solutions based on natural products for most protective finishes.

Interestingly, most of the plant materials used for natural dyes are also attributed to have medicinal properties. Hence, it was decided to undertake systematic research to study the special properties of natural dyes after they have been applied on textiles. In preliminary studies carried out by the authors [1] these dyes had shown good absorption in the ultra violet region of electromagnetic radiation. Hence, they could be expected to provide good sun protection (UPF).

There is no information available on the protective properties and behaviour of these products once they are dyed on to textile substrates. In this study, a series of experiments was conducted to screen the commercially natural dyes for UV absorbing and anti microbial activity and to study the effect of various dyeing parameters on these properties.

MEDICINAL PROPERTIES OF DYE PLANTS

Many natural dyes form a part of the Indian pharmacopoeia and are known to be effective antioxidants, anti-tumor and anti-diabetic agents. This paper presents a brief review of the reported medicinal properties of some plants which are known to be important sources of dye.

Ahmad and Beg [2] tested the ethanol extracts of 45 Indian medicinal plants traditionally used in medicine for their anti microbial activity against certain drug-resistant bacteria and a yeast *Candida albicans* of clinical origin. The plant extracts were tested against *Staphylococcus aureus, Salmonella paratyphi, Shigella dysenteriae, Escherichia coli, Bacillus subtilis* and *Candida albicans*. Broad-spectrum anti-microbial activity was observed in 12 plants, *T. chebula* being one of them. Qualitative photochemical tests, thin layer chromatography (TLC) of certain active extracts demonstrated the presence of common photo-compounds in the plant extracts including phenols, tannins and flavonoids as major active constituents.

Studies have been carried out with plants belonging to *Acacia* family. Naik et al report that the extract of *A. catechu* contains catechu tannic acid, catechin and quercetin [3]. These compounds are responsible for the colour characteristics as well as imparting powerful astringent and anti-oxidant properties to the extract. Kambizi et al studied the methanol extracts of *A nilotica* and found that they show significant inhibition against Gram-positive and Gram-negative bacteria [4].

Alkaloid constituents obtained from the roots of ***Berberis vulgaris*** have been used as medicine in rheumatic and other chronic inflammatory disorders [5]. The same plant yields a fluorescent yellow basic dye which is very bright but fleeting. Another yellow/red dye of historical significance is ***Carthamus tinctorius*** or Safflower. The aqueous extract has antioxidant properties according to Hiramatsu et.al [6]. A potent antioxidant has also been isolated from the safflower oil cake making it a good candidate for development of anti-inflammatory drugs. [7].

Many home remedies based on ***Curcuma longa*** or turmeric are still used in India. Turmeric owes its characteristic yellow color to three major pigments; curcumin (50–60%), demethoxy curcumin (20–30%) and bis (demethoxy) curcumin (7–20%) [8]. Scientific evidence has shown that it possesses bactericidal, anthelmintic activity and reduces cholesterol levels when given orally. Nowadays, curcumin is used in clinical trials for AIDS patients [9,10]. The chemical investigation on volatile oils of *Curcuma longa* [11], indicated it to be a good antifungal material. Turmeric also has pronounced anti-oxidant and anti-inflammatory effects and is anticipated to act as an anti-tumur promoter [12].

Rheum emodi is an important medicinal plant, which finds an extensive use in Ayurvedic and Unani systems of medicine. A recent publication [13], deals with a variety of biological properties of the compounds isolated from various *Rheum* species. A US patent discloses the insect-controlling activity of the ooze of *Rheum* genus, against sanitarily injurious insects [14].

Roots of ***Rubia cordifolia*** roots are a source of deep red shades on cotton. Coloring matter comprises of a mixture of hydroxy anthraquinones. Prominent among them are purpurin (trihydroxy anthraquinone) and munjistin. Roots are credited with tonic, astringent, antidysentric and antiseptic properties. They are used in rheumatism and form an ingredient of several ayurvedic preparations [15]. It has recently been credited with anti-tumur activity [16].

Quercus infectoria galls contain tannic acid (gallo tannic acid) as the principal constituent (50–70%) which are often used in dysentery and diarrhoea. [17]. A study by Redwane [18] et al. indicates the efficacy of extracts and fractions of *Quercus* galls as larvicidal agents and their possible use in biological control of *Culex pipiens,* the urban nuisance mosquito. ***Terminalia chebula*** contains tannin, gallic acid and chebulenic acid thus it acts as an effective purgative, astringent and blood purifier. The aqueous extract acts as an anti-oxidant, and protects the human body from liver cirrhosis, atherosclerosis, cancer etc [3]. It was found to inhibit lipid peroxide formation and to scavenge hydroxyl and super oxide radicals in vitro [19]. Bacterial species like *H. pylori E. coli, V.cholerae, V. vulnificus* etc were also inhibited by *Terminalia chebula* extracts.

Punica granatum (Pomegranate) is an important source of yellow dye. Researchers have reported the antibacterial, anti-fungal, anthelmintic and anti fertility activities of the various extracts of different parts of this plant [20,21]. Machado et al. [22] studied ethyl acetate extract of *Punica granatum* against multi resistant bacteria, *Staphylococcus aureus* by disc diffusion method. A mixture of ellagitannins isolated from the plant demonstrated antibacterial activity against all *S. aureus* strains tested. Significant activity was shown by the methanolic extract against *P. vulgaris* and *B. subtilis* [23].

MATERIALS AND METHODS

Scoured cotton fabric in plain weave was used for the study. Fabric thickness was 0.33 mm with a cover factor of 81.

Ten natural dyes procured from M/s Alps Industries Ltd, Ghaziabad, India were used for the study. The dyes used were *Rumex maritimus, Quercus infectoria, Mallotus phillipinensis, Rubia cordifolia, Rheum emodi, Kerria lacca, Acacia catechu, Terminalia chebula, Punica granatum* and *Acacia nilotica.* All chemicals used were of LR grade.

Dyeing and mordanting of test samples

Cotton fabric was dyed using 10% (owf) shade, at 80°C for 30 min using 1:30 MLR at neutral pH. Samples were also prepared with specific dye-mordant combinations as reported in Table I. Pre-mordanting, simultaneous mordanting—dyeing and post-mordanting were used. After dyeing, the samples were soaped with 0.5 gpl Lissapol N and rinsed in water.

Table I. Recipes used for dyeing of test samples

Dye	Mordanting method			Time & temp
	Pre-	Post-	Simultaneous	
A catechu	---	---	$CuSO_4$ 0.25%	80°C, 30 min
A catechu	---	---	$FeSO_4$ 2% $CuSO_4$ 2%	80°C, 30 min
R cordifolia	Alum 8%	---	---	80°C ,30 min
Q infectoria	---	$FeSO_4$ 0.5%	---	RT, 20 min
M philippinensis	Alum 8%	---	---	80°C ,30 min
Kerria lacca	Alum 10% Tartaric acid 5%	---	---	80°C ,30 min
Kerria lacca	---	---	$SnCl_2$ 2% Oxalic acid 10%	80°C ,30 min
Kerria lacca	---	$CuSO_4$ 1%	---	80°C ,30 min
R emodi	Alum 8%	---	---	80°C ,30 min
T chebula	Alum 8%	---	---	80°C ,30 min
P granatum	Alum 8%	---	---	80°C ,30 min
A nilotica	---	---	Alum 5%	80°C ,30 min
R maritimus	---	---	Alkaline dyebath $CuSO_4$ 2% TSP 5%	80°C, 15 min 80°C, 15 min 80°C ,15 min

Studies on UV-absorption of dyes

The UV spectra of dyes in solution were recorded using a Pharmacia Biochrom 4060 UV-Visible spectrophotometer. Scans were analysed for their absorption characteristics with a view to see if the absorption characteristics of dyes in solution could be used to predict the UV protection provided by dyes on fabric. On fabric, the transmittance measurements from 280–400 nm were taken on each specimen. Fabrics are assigned a UPF rating number and also a protection category depending on how much UV radiation they block out, as shown below in Table II:

Table II. UPF ratings and protection categories

UPF Rating	Protection Category	% UVR Blocked
15 - 24	Good	93.3 - 95.9
25 - 39	Very Good	96.0 - 97.4
40 and over	Excellent	97.5 or more

UPF values of fabric samples were measured on SDL UV protection measurement system based on a Campsec M350 UV-Visible spectrophotometer, using the standard AS/NZS 4399:1996. This system is equipped with an integrating sphere for diffused transmittance measurement and calculates the UPF value directly.

Determination of anti-microbial activity of selected natural dyes

The bacterial strains for testing were procured from MTCC (Microbial Type Culture Collection) Chandigarh. Testing for antimicrobial activity of dyes was carried out using AATCC test method 100 (colony counting method). The commercial antimicrobial agent Fabshield AEM 5700 was obtained from Rossari Biotech India Pvt Ltd, to be used as a reference.

RESULTS AND DISCUSSION

UV absorbance of dyes in solution

In evaluating sun protection efficiency, the critical zone is that between 280–320nm or the UV B region. These are high intensity rays which are known to cause skin carcinomas following extended exposure. UVC rays (200–280 nm) are absorbed by the ozone layer and do not reach the earth, while UVA (320–400) does not penetrate deep into the skin and is less harmful. To study the efficiency of dyes, their absorbance spectra in UV-Vis region was recorded. Shapes of the curves and areas under the peaks in various UV regions were analysed. Results are reported in Table III.

Table III. Analysis of the UV specra of natural dyes in solution

Dye	λ max (nm)	% of total area under the curve		
		UVA	UVB	UVC
R. maritimus	280	31.4	28.3	40.2
Q. infectoria	270	19.9	30.1	50.0
M. philippinensis	280	37.1	27.3	34.3
R. cordifolia	260	35.0	26.8	38.1
R. emodi	270	35.2	26.4	38.5
K. lacca	295	35.6	26.5	37.8
A. catechu	280	32.5	23.1	44.4
T. chebula	275	27.1	29.3	43.6
P. granatum	275	31.0	21.7	47.2
A. nilotica	280	49.2	22.4	28.4

It can be seen that λ_{max} for five dyes namely *R. maritimus, M. philippinensis, K. lacca, A, catechu and A. nilotica* lies in the UV-B region. All dyes absorb approximately 20–30% radiations in UV-B region, which is adequate for providing good UV protection. Hence it can be expected from this analysis that the selected natural dyes can act as good UV absorbers and are suitable for use in sun protective clothing.

UPF values of cotton dyed with Natural Dyes

Absorption characteristics of dyes in solution can be but indicative of behaviour or fabric. To study the actual protection provided, cotton fabric was dyed with two natural dyes *Q. infectoria* and *T. chebula.* These two dyes were selected for initial studies because they had greatest absorptions in the UVB region, shown in Table II. Secondly, these dyes have good affinities for cotton unlike most other natural dyes and can be dyed with as well as without use of mordants.

Detailed experiments were carried out using higher concentrations of these two dyes in combination with 3 mordants, alum, copper sulphate and ferrous sulphate. The undyed blank sample having a mean UPF of 4.91 was used as a standard for comparison. Results are reported in Table III. It can be seen that there is a dramatic increase in the UPF values for all samples when dyeing is carried out in combination with mordants. All samples offer good to excellent protection from UV radiation even at very pale shades. Maximum UPF values are obtained when dye concentration is between 9% and 12% owf. The SD values are low, implying uniform dyeing and reproducibility of results. The dyed and mordanted samples were also washed as per ISO 2 and the UPF values of washed samples were recorded. The values are reported in Table IV. It can be seen that after washing samples provide protection of a very high order implying that the protection is durable in nature.

Table IV UPF and K/S values of cotton samples dyed with natural dyes

Sample no	Dye	Conc. of dye (% owf)	Mordant	UPF	Std Dev.	Rated UPF	K/S	UPF after washing
1	QI	6	---	21.1	3.08	15	0.72	-
2	"	9	---	21.8	5.13	15	0.75	-
3	"	12	---	26.4	4.61	20	0.79	-
4	"	15	---	30.1	2.36	25	0.82	-
5	TC	6	---	16.1	0.25	15	0.76	-
6	"	9	---	20.6	1.04	15	0.95	-
7	"	12	---	22.1	1.19	20	1.02	-
8	"	15	---	24.5	0.89	20	1.06	-
9	QI	6	Alum	45.1	1.87	40	1.26	37.5
10	"	9	"	45.4	5.24	40	1.3	42.9
11	"	12	"	56.5	9	45	1.36	45.5
12	"	15	"	65.8	16.3	50	1.61	58.3
13	TC	6	"	35.5	0.778	30	2.2	33.2
14	"	9	"	43.8	13.5	40	2.59	41.5
15	"	12	"	49.3	3.7	45	2.98	46.1
16	"	15	"	52	3.92	45	3.52	50.9
17	QI	6	$CuSO_4$	36.3	3.1	30	1.5	31.9
18	"	9	"	36.7	0.31	35	1.7	33
19	"	12	"	39.5	1.6	35	1.88	37.8
20	"	15	"	40.2	1.8	35	1.92	39.1
21	TC	6	"	21.9	2.65	20	1.84	21.9
22	"	9	"	27.5	0.895	25	2.21	25.7
23	"	12	"	30.9	2.6	25	2.52	25.9
24	"	15	"	34.4	0.36	30	2.55	29.1
25	QI	6	$FeSO_4$	33.8	3.5	30	1.56	26.1
26	"	9	"	35.5	1.06	30	2.05	35.3
27	"	12	"	39	0.457	35	2.70	36.8
28	"	15	"	43.5	4.7	35	1.59	39.2
29	TC	6	"	26.9	4.62	25	1.69	23.3
30	"	9	"	28.1	2.6	25	2.12	27.4
31	"	12	"	35.1	2.8	30	2.21	31.2
32	"	15	"	49.9	4.8	45	3.38	39.4

K/S values of samples were also recorded. No relationship could however, be established between the depth of shade (K/S) and UV protection (UPF) provided by the dyed fabric. It is most likely that the chemical structure of the dye decides the UV absorption characteristics of dyes and therefore light shades can also impart good protection. Detailed studies on structure—property relationship can yield more information about this phenomenon.

Determination of antimicrobial activity of natural dyes on cotton fabric

The above study showed that Q. infectoria has good UV absorption properties. Hence it was decided to carry out studies on the antimicrobial activity of this dye against two bacteria, namely *P. vulgaris* and *E.coli*. Since most recipes for dyeing with this dye are based on the use of copper sulphate and ferrous sulphate as mordants for colour development, the effect of mordants and their concentration on antimicrobial activity was also studied. The commercial antimicrobial agent Fabshield was used as control.

Quantitative evaluation of antimicrobial activity on a solid substrate can be carried out suitably by colony counting. This method was employed to test the anti microbial efficacy of *Q. infectoria*. Results are listed in Table V and the effect of dye concentration on anti microbial activity is shown in Figure 1.

Table V Effect of dye concentration and mordant on antimicrobial activity of *Q Infectoria* on cotton fabric

Microbe	Sample type	Number of CFU ($x\ 10^5$/ml)	Reduction in CFU (%)
E.coli	Control	539	--
	Fabshield-treated fabric	20	96.6
	0.5% shade	545	0
	6% shade	466	13.9
	12 % shade	422	22.3
	15 % shade	14	93.5
	15% shade + 2% $CuSO_4$	348	33.9
	15% shade + 2% $FeSO_4$	512	4.8
P.vulgaris	Control	899	--
	Fabshield-treated fabric	14	94.3
	0.5 % shade	907	-0
	6 % shade	910	-0
	12% shade	885	1.4
	15 % shade	4	91.7
	15% shade + 2% $CuSO_4$	869	7.2
	15% shade + 2% $FeSO_4$	810	9.8

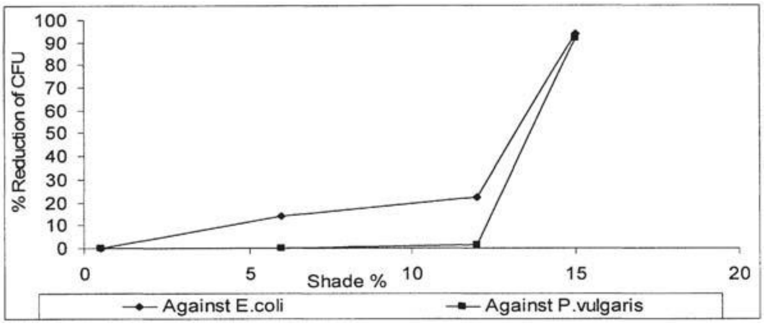


Figure 1 Antimicrobial efficacy of *Q. infectoria* against *E. coli* and *P. vlulgaris* on cotton fabric

It can be seen that the antimicrobial activity of fabric dyed with *Q. infectoria* increases with increase in the shade %. At 15% shade there is a sharp increase in activity with the fabric showing 97.4% reduction in CPU for *E.coli*. No activity is seen against *P.vulgaris* at less than 12% shade, while there is very high activity at 15% shade where the reduction in CPU is ~99.5%. The antimicrobial activity is better than that of standard antimicrobial agent—Fabshield.

An interesting observation was that the antimicrobial activity decreased significantly or was lost completely when mordant was used in combination with the dye. Loss in activity was found to be higher when $FeSO_4$ was used as a mordant. This could be because of the complex formation between dye and metal salts. The only functional groups present on these dyes are hydroxyl groups. Hydroxyl groups ortho to the chromophore are involved in co-ordinate bond formation with the mordant. If these same groups are responsible for the antimicrobial activity- when they get complexed no free groups are available to act on the microbes. Hence better is the complex formation, faster is the dye but lesser is the antimicrobial activity.

CONCLUSIONS

From the current study it could be established that natural dyes can indeed impart multifunctional properties to cotton fabric. Besides imparting fast and harmonious shades on cotton, *Quercus infectoria* can provide durable UV protection of a very high order. The fabric at the same time has a bactericidal effect and shows activity which is as good as that of commercial antimicrobial agents. Concentration of dye required is quite high being about 12 to 15% to make the fabric both UV protective and bactericidal. This is probably due to the low exhaustion of the dye on cotton. Mordants have a positive effect on UV absorption but a negative effect on antimicrobial activity. Further work needs to be done with natural dyes on different fibrous substrates to elucidate their protective properties.

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