Electrochemical Processes in Textile dyeing – State of the research and development activities

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Abstract:

Substitution of non-regenerable chemicals by electrochemical processes is a possible strategy to improve the ecological profile of dyeing processes. During the last years the technique has been developed continuously from laboratory scale experiments to full scale prototypes and full scale operation tests.
The variety of dyeing processes vat dyeing, indigo dyeing and sulphur dyeing and the different characteristics of the products required the development of optimised electrochemical systems and process concepts. In the frame of the Eureka project EUROENVIRON E! 2625 ECDVAT a pilot-scale package dyeing unit for electrochemical dyeing of yarn with vat dyes has been installed and tested in a commercial dyehouse. Dyestuff reduction was achieved using a 500 A electrolyser and a membrane filtration unit was installed to recover the used dyebath. Using electrochemical dye reduction rather than chemical reducing agents, the chemical waste is reduced by about 80% for the actual dyebath stage and by 20% for the whole process.
The new system has the great advantage that it can be regenerated and because of this there are major savings in water use and cost. Also the much lower quantities of waste products are easily biodegradable in water treatment plants, compared to the wastes released from conventional dyeing.

Keywords: vat dyeing, electrochemical reduction, recycling, cotton

1. Background

The annual production of vat dyed textiles is in the dimension of approximately 5 million tons a year. At present the application technique bases on the use of reducing agents which cannot be regenerated after their use in the dyebath e.g. $Na_2S_2O_4$, hydroxyacetone, formaldehyde sulfoxylates. A lot of optimisation has been done however the chemical principle of this technique has not been changed since more than 100 years [1].
Vat dyes yield coloured fibres with excellent colour fastness and thus are of great importance for the production of textiles with high level of quality. Reducing agents are added to the dyebath in order to reduce the dispersed oxidised dyestuff particles.
In Figure 1 an overview about the main steps during the dyeing process with vat's is shown.
The exhausted dyebath contains the oxidation products of the reducing agents and, depending on the dyeing procedure, also contains a certain surplus of reducing chemicals, which are required to ensure that the dyes remain in their reduced form during their application. Due to the different shades a dyer has to produce, in many

cases regeneration of the used dyebath is not possible. All added chemicals and auxiliaries thus have to be discharged with the dyebath.
In addition to the costs for the reducing agent, the surplus of reducing agent and follow-up products from the use can cause problems in the textile waste-water.

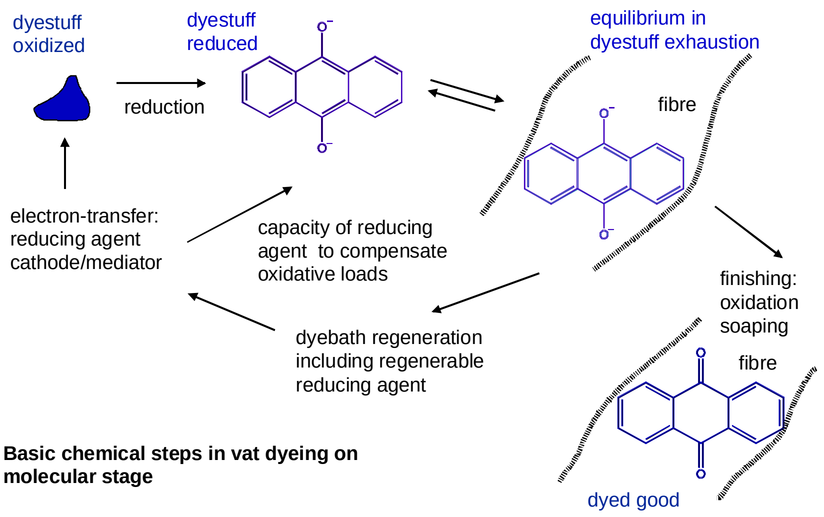

Figure 1. Basic steps in the reduction/dyeing of vat dyes

2. The Technology

2.1. The electrochemical reduction process

The reducing agent in vat dyeing represents an electron source for the reduction of dispersed dyestuff particles. In case of electrochemical dyestuff reduction electrons are transferred from an electrode (cathode) to the dispersed dyestuff. In some cases this transfer can be achieved by immediate electron transfer from the cathode to the dyestuff = direct electrochemical reduction, in case of dispersed vat dyes a regenerable redox system (mediator) is required to transport the electrons from the cathode to the dispersed dye = indirect electrochemical reduction.

In the Eureka Project E!2625 ECDVAT – ElectroChemical Dyeing with VAT dyes - package dyeing electrochemical dyeing was realised for package dyeing where the added reducing agent is replaced by the cathodic electron transfer which is performed in an electrochemical cell [2].
Figure 2 shows a flow scheme the technical unit for package dyeing of 110 kg yarn (X-cones). The 500 A cell is coupled to the dyeing apparatus and the dyebath is reduced electrochemically. The oxidised dyestuff is added to the dyebath and reduced therein by means of the mediator.
The redox potential required for proper dyestuff reduction is formed by cathodic reduction and permits the dyer to adjust the redox potential in the dyebath by control of the cell current. At the point of completed dyestuff reduction, the cell current is lowered to the minimum height required to maintain the redox potential within well defined limits. In this phase typical values of cell current are around 50 – 100 A.
The dyebath and the reductive rinse contain mediator and thus are collected in the regeneration tank (used dyebath in Figure 2). Reuse of the mediator system respectively dyebath is possible after removal of the oxidised dye by nanofiltration.

The dyeing process is completed with oxidation, soaping and rinsing.

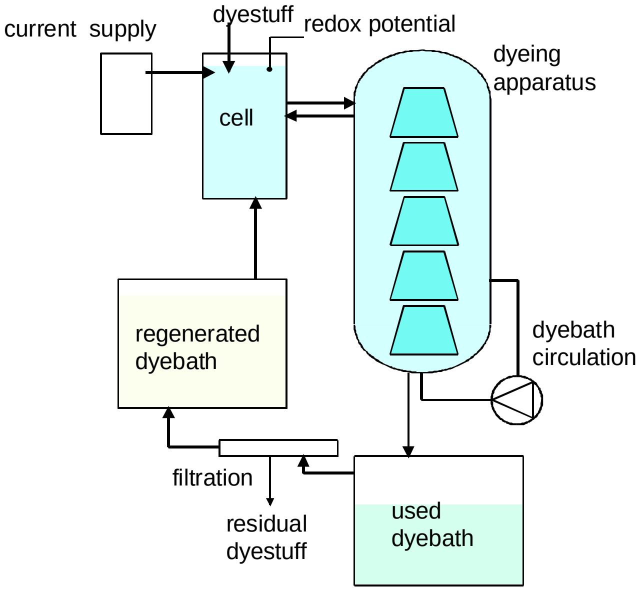

Figure 2. Scheme of the installation: Package dyeing apparatus, circulation through cell, regeneration of used dyebath by Nanofiltration

Figure 3. Installation of ECDVAT dyeing unit at Getzner Textil AG. 1 Storage tank, 2 cell current supply, 3 cell, 4 exhaust fan, 5 dyebath circulation, 6 dyeing apparatus

This installation included the following main elements (Figure 3):
Electrolysis cell for indirect electrochemical reduction of dispersed dyestuff:.
A new designed 500 A multi cathode electrolyser was developed for this application. Particularly the relative low current densities required high cathode area. A special construction had to be designet to run the electrolyser at the relative high dyebath temperature of nearly 80°C. Minimum cell volume had to be realised to keep liquor

ratio of dyeing as low as possible. At present the 500 A cell required a filling volume of 160 l for normal operaiton.
Figure 4 shows front view of the electrolyser and in Figure 5 a top view inside the specially designed flow cell is shown.
Relevant technical data of the installation are summarised in Table 1.

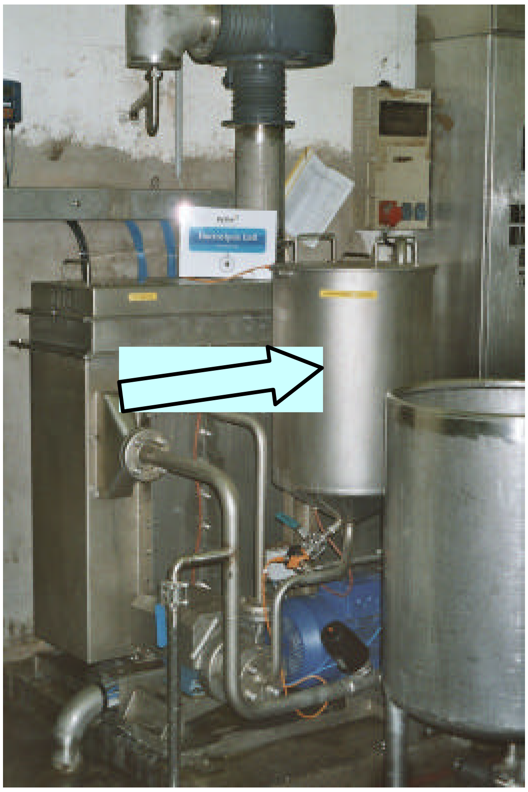

Figure 4. Electrolyser (the arrow indicates the flow of the dyebath through the cell)

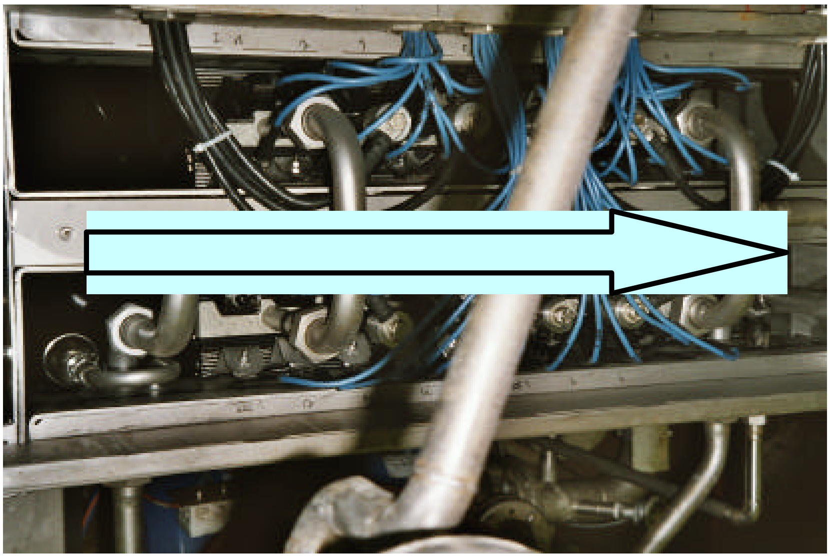

Figure 5. Top view of electrolyser (arrow indicates flow direction of dyebath)

Table 1. Technical data of the installation

Dyeing apparatus	
Capacity	112 kg yarn
Temperature	77°C
Storage tank for regenerate	3000 l
Storage tank for used baths	3500 l
Electrolyser	
volume	160-200 l
cell current	500 A
cell voltage	10 – 15 V
current efficiency at 300 A	79 %
power	5 – 7.5 kW
energy consumption per 1 h	5 – 7.5 kWh
Catholyte = Dyebath	wetting agent $Fe^{2+/3+}$-complex as mediator [3]* NaOH
Anolyte	40 g/l NaOH
Filtration	
Permeate flow	1 m^3 / h

* The production of the iron-complexes used for the indirect electrolysis was made by DyStar.

2.2. Coupling of a dyeing unit to an electrolyser:

The adaptation of an existing dyeing apparatus to electrochemical dyeing required specially designed equipment and new steering concepts. While working as a normal batch dyeing apparatus during pre-treatment, scouring, bleach processes etc., the installation should permit easy coupling of the apparatus to the cell for electrochemical dyeing. The modification of an existing 112 kg dyeing apparatus was chosen as a strategy to keep high flexibility in use of the existing apparatus and to minimize risks of failure to acceptable dimensions.

2.3. Recycling of dyebath with Nanofiltration:

A key process for the ecological profile and the economic benefits is the regeneration of the used dyebath by nanofiltration. For this purposes a nanofiltration unit for dyestuff removal had to be designed and installed and storage tanks for used dyebaths before filtration and for storage of recycled liquors had to be built up.

Figure 6 shows the nanofiltration unit used for dyebath filtration. A general phase scheme of the process is given in Table 2

Figure 6. Full scale nanofiltration unit for dyebath regeneration

Table 2. Schematic presentation of a typical dyeing process including dyebath regeneration

Cell and filtration	Dyeing apparatus	Process step
	X	Scouring, bleaching, rinse of goods, drain of last rinse bath
X		Storagetank with regenerated dyebath filled
X		Filling of cell and preparation of reductive rinse in storage tank (approx. -850 mV)
X	X	Filling of dyeing apparatus and cell with regenerated dyebath
		Addition of replenishments
X	X	Addition of dyestuff
X	X	Electrochemical reduction/dyeing (defined program: redox potential, time, temperature)
X	X	Rinse with reductive bath
X		Collection of used dyebath
	X	Rinse with water
X		Collection of used reductive rinse
	X	Start oxidation of dyeing
X		Reductive rinse of cell
X		Oxidation of used dyebath (pressurised air) and reductive rinse in storage tank
	X	Soaping and rinse of dyeing
X		Oxidation completed, start filtration to remove dispersed vat dye

3. Results

3.1. The technical installation

The scale up based on more than 200 electrochemically laboratory scale dyeing experiments (2 – 3 kg capacity each) however the fact that a production scale unit was built first time included a considerable risk. Particularly the lack of information available on the lifetime of cost intensive components and on handling and maintenance of the equipment during full scale production could be studied only during operation of the installation.

Approximately 150 dyeings were performed in the project, which corresponds to an amount of approximateyl 15 tons of cotton yarn. The project led to important data about quality of dyed yarn, process costs, dimensions of apparatus and cell, lifetime of sensitive parts e.g. membranes and thus will form a basis for further development of the technique and further introduction of the process in vat dyeing.

3.2. Installation and lifetime

The electrochemical cell represents a critical component of decisive importance. The electrolyser reached the projected cell data (cell voltage, current efficiency). Lifetime of components membranes and electrodes was much better than expected. Automatic handling and cleaning processes could be established successfully. Function of chosen measuring devices (redox potential) and steering concepts could be verified.

3.3. The environmental concept – Recycling and savings

To become an environmentally feasible technology two main topics have to be treated:

Proper function of mediator recycling and lifetime of mediator components. After a dyeing process the used dyebath is collected in a storage tank and reoxidized by air oxygen and the precipitated dyestuff is removed by the filtration unit. Soluble components pass the filtration unit and can be stored in the storage tank ready for reuse. Only losses of volume of mediator solution due to the handling and processing of the baths have to be replenished. Thus savings can be expected from the regeneration of the chemicals in the exhausted dyebath, because after its oxidation the residual dyestuff can be removed by filtration.

Table 3. Chemical consumption and savings, IN-process, 100 kg Co, liquor ratio 1:10

Colour depth	**EC-reduction 0,3 - 4 %** conc.	weigth	**Dithionite 0,3 %** conc.	weigth	**2 %** conc.	weigth	**4 %** conc.	weigth
Dyeing:								
complexing agent	13,6 g/l	2050 g						
dithionite			3 g/l	3000 g	5 g/l	5000 g	8 g/l	8000 g
NaOH	32 ml/l	2100 g	14 ml/l	6160 g	19 ml/l	8360 g	24 ml/l	10560 g
Reduct. rinse:								
dithionite	-	-	-	-	2 g/l	2000 g	2 g/l	2000 g
NaOH	-	-	-	-	2 ml/l	880 g	2 ml/l	880 g
Total amount		**4150 g**		**9160 g**		**16240 g**		**21440 g**
Savings				**55 %**		**75 %**		**80 %**
Water – Dyeing		150 l		1000 l		2000 l		2000 l

only process chemicals considered,
losses during recycling of mediator c. 15 % of dyebath volume

Table 3 shows savings expected for a 100 kg yarn package dyeing apparatus. The calculation is performed as minimum savings because only process chemicals NaOH and $Na_2S_2O_4$ are considered for the comparison with the EC-reduction. Losses of 15% of the dyebath volume are considered to appear in the case of EC-reduction due to losses during dyebath filtration and losses from the transportation of a residual amount of dyebath by the wet yarn into the washing/rinsing baths.

4. Summary

The technical concept realised in E!2625 ECDVAT defines a new state of the art with clear potential to be defined as a BAT (best available technology) for vat dyeing.
The use of electrochemically regenerable redox systems offers the following advantages:
For the dyehouse:
- simple control of the dyeing conditions by measurement of redox potential
- control of potential by regulation of the cell current
- well defined dyeing conditions and good reproducibility
- stable concentrations of chemicals in the dyebath result in constant dyebath exhaustion
- savings of chemicals, water and energy will lead to economic advantages
- lowered chemical load in the wasted water
- the ecological profile of the dyeing process will be improved and sustainability increased
- no use of hazardous chemicals (e.g. reducing agent Na-dithionite).

The demonstrated application of electrochemical techniques in textile dyehouses represents a pioneer development for a wider application of electrochemical concepts.
Examples for related electrochemical concepts are:

- Electrochemical dyeing with indigo (prototype in full technical scale has been built, in exhaust dyeing full scale operation reached) [4]
- electrochemical dyeing with sulfur dyes (full scale prototype reached) [5]
- electrochemical decolourisation of dyehouse effluents (technical process in full scale in operation) [6]
- electrochemical bleach (prototype in full technical scale has been built) [7]

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