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WASTEWATER MINIMIZATION IN DYEHOUSES BASED ON BATCH TECHNOLOGY

The paper presents a part of a complex process of waste minimization strategy in textile industry. Special attention is paid to dyehouse wastewater which is harmful to environment. The proposal of the analytical procedure for determining concentration of dyestuffs in exhausted dyeing baths is presented. This procedure enables preparing the baths according to the known formulae and would also give the possibility of recycling the baths in the course of technological processes.

The method of dyehouse wastewater pretreatment has been presented. Iron (II) sulphate (ferrous sulphate, $FeSO_4 \times 7\,H_2O$) has been proposed as a coagulant for the treatment process. It is formed in the process of production of white titanium pigment (TiO_2) as a solid waste.

1. INTRODUCTION

Changes in the Environment Protection Acts caused by limited water resources and continued worsening of water quality create a good background to the reconstruction of water management system. Increasing environmental fees, prices of water, energy and raw materials as well as market requirements for "ecological friendly" products forced us to implement the clean technologies. The main direction of modification of water management system in industry is switching from "end of pipe" solution to preventative strategy which is based on energy and raw materials recovery. As a result of implementation of such a strategy one is often able to close partly or completely water loops, reduce wastewater volume as well as to reuse energy and chemicals. One of the very interesting industries, where water management, energy savings and reduction of chemicals consumption is concerned, is textile industry.

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2. DYEING PROCESSES IN TEXTILE INDUSTRY

The textile industry uses natural and/or synthetic fibres as a raw material to produce a wide variety of finished products. Based on water consumption, one of the most important steps is complex process of dyeing. When classifying the dyeing processes, two main methods are useful:

1. by the fibre being processed:
   cotton,
   wool,
   synthetics.
2. by the method of plant operation:
   batch,
   semi-continuous,
   continuous.

Water consumption for cotton as well as for wool wet processing can reach the value up to 600 m^3 per one tone of fibre. The wet processes in dyehouses of textile industry, in general, consist of:

washing,
bleaching,
rinsing,
dyeing,
special finishing.

The batch process of dyeing is very popular in Polish dyehouses. This technology requires the preparation of different bath for each step, basing on the technological formula specific to each colour and each type of fibre. The typical dyeing apparatus consists of two tanks, in the first of them the suitable bath is prepared and in the second one, reactor, the bath is heated and dyeing processes take place. When

Table 1

The general data for dyeing polyamides fibres (400 kg) in 5 m^3 reactor

Operation (time)	Applied chemicals	Temperature in the reactor [°C]	Chemicals in wastewater
Dyeing (90 min)	dyestuffs (ca. 10 kg) detergents auxiliary compounds (organic and inorganic 5–10 kg)	100	5–20% of dyestuffs auxiliary chemicals detergents
Washing (30 min)	detergents (ca. 3 kg)	40	detergents dyestuffs auxiliary chemicals
Rinsing	–	40	detergents dyestuffs
Fixing (30 min)	fixing agents (ca. 15 kg) auxiliary chemicals (ca. 15 kg)	70	fixing agents auxiliary chemicals
Softening (20 min)	softener (ca. 8 kg)	30	softener

a particular operation is finished, the content of the reactor is removed and discharged as a wastewater, while the reactor is filled with the next bath.

The exemplary data for dyeing process of polyamides (400 kg) in 5 m^3 reactor are presented in table 1.

The dyeing operations in textile industry require large quantities of water. In these processes, the amount of auxiliary nonconsumable chemicals exceeds that of the consumable components. The former cause the dyehouse wastewater to be highly polluted with organic and inorganic substances. Dyeing wastewater is characterized by the presence of alkali, salts, unexhausted dyestuffs, fatty acids, detergents and other organic chemicals. Both colloidal and soluble dyes are normally found in the effluent. Other contaminants that may be found are: scouring agents, emulsified oils and greases, oxidizing as well as reducing agents. The parameters of the wastewater generated in the batch dyeing processes are significantly variable. The wastewater after dyeing is highly polluted, while wastewater after rinsing and washing is relatively clean.

In practice, in textile factories, the wastewater is collected together. Taking into account the possibility of combining the different streams of wastewater based on salt content, the total amount of wastewater can be collected in two streams rather than one. Applying such a procedure, for example, in the "Zwoltex" factory, it is possible to obtain:

highly polluted stream, ca. 7% of total volume,
relatively clean stream, ca. 93% of total volume.

3. METHODS OF UTILIZATION OF THE DYEHOUSE WASTEWATER

The methods of treating the dyehouse wastewater are accurately reported in the literature. The problem of dyehouse wastewater utilization may be solved by different techniques without recovery of water, energy and chemicals as well as by those which allow recovery of water, energy and chemicals. The process of dyehouse wastewater treatment can consist of:

coagulation with mineral and organic coagulants,
adsorption on active carbon or natural sorbents,
neutralization,
aeration,
oxidation with ozone,
biological processes,
sedimentation,
flotation,
radiolysis with γ radiation,
micro- and ultrafiltration,
demineralization.

The modern approach to the problem of utilization of dyehouse wastewater should be based on evaluation of the possibility of recovering energy, water and chemicals. Such an approach is called *waste minimization assessment* and can be used for all industrial processes. Dyehouses seem to be very good objects for the implementation of a waste minimization strategy. The main reasons for this are:

high temperature of wastewater,

high content of auxiliary chemicals and unexhausted dyestuffs in wastewater,

high water consumption,

operation at batch technology.

For the implementation of waste minimization strategy, the following technical solutions should be taken into account:

switch from chemicals which are toxic and harmful to the environment to nontoxic and biodegradable compounds,

division of wastewater streams,

simultaneous recovery of chemicals, energy and water,

effective process of the wastewater treatment at the end of pipe,

processes automatization.

In order to realize these modifications, the procedure for complementing chemicals losses in dyeing processes should be established. This procedure should be based on simple measurements of exhausted baths: parameters such as colour, pH and conductivity.

In order to reduce the total amount of water and energy, it is necessary to analyse carefully the process of dyeing and to assess the possibilities of direct reuse of some streams of wastewater. For example, the water after rinsing lightly coloured fabric could be used as rinsing water for darkly coloured one. The activities mentioned above are the main points of the waste minimization strategy but this strategy should be completed with a number of the other changes which minimize the consumption of raw materials, water and energy.

Besides the technological modifications it is very important to consider:

good "house keeping",

good management system,

staff and personnel education.

The main benefits achieved by the waste minimization procedure are: decreasing of the harmful impact on the environment and saving the cost of water, energy and chemicals.

4. EXPERIMENTAL

Laboratory experiments were focused on the development of a method for calculation of dyestuffs losses in the dyeing process as well as on searching for an effective method of wastewater treatment.

A photocolorimetric method has been chosen for determining the concentrations of the dyestuffs in dyeing baths. The tests have been performed with three-component (dyestuffs) dyeing baths from the "Luxpol" textile company dyehouse. Each component, including auxiliary chemicals, has been separately investigated and a characteristic wave length of light for maximum light absorption was determined. These lengths of light wave have been chosen for later measurements of the concentration of particular dyestuffs. For each dyestuff the coefficients *a* and *b* have been determined according to equation:

$$E_\lambda^i = f^\lambda(C^i) = a_\lambda^i \cdot C^i + b_\lambda^i$$

where:

λ is the light wave length,
i is the index of particular component,
E is the extinction of single dyestuff solution,
C is the concentration of dyestuff.

After completing this procedure, the system of equations describing the dependence of the dyestuff concentrations in a three-component bath on the extinction of exhaused bath has been derived:

$$E_{\lambda 1} = f^{\lambda 1}(C^1) + f^{\lambda 1}(C^2) + f^{\lambda 1}(C^3),$$
$$E_{\lambda 2} = f^{\lambda 2}(C^1) + f^{\lambda 2}(C^2) + f^{\lambda 3}(C^3),$$
$$E_{\lambda 3} = f^{\lambda 3}(C^1) + f^{\lambda 3}(C^2) + f^{\lambda 3}(C^3).$$

Based on this system of equations and measurements of extinction for exhausted dyeing bath, it is possible to calculate the concentrations of dyestuffs. Exemplary data obtained for dyeing bath for the colour called "MARINE" (M), which consists of dispersed dyestuffs such as Resolin Rot K-2BLS 200% (R), Resolin Dunkel Blau K-RLS 300% (DB) and Resolin Schwarz K-BLS 150% (S) are presented in figures 1–4.

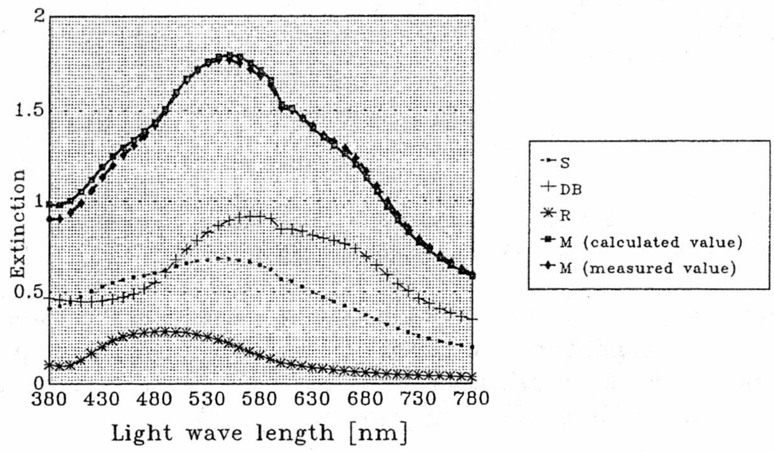

Fig. 1. Dyestuff component spectrum of the "Marine" colour dyeing bath

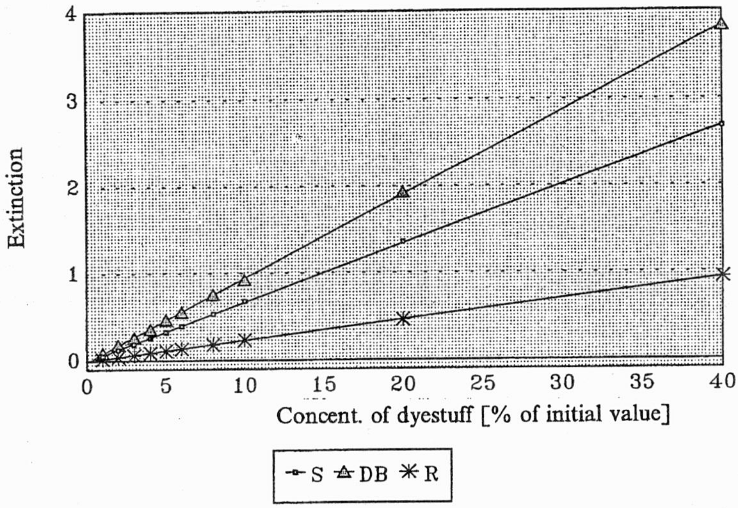

Fig. 2. Extinction of the solutions of the component dyestuffs of the "Marine" colour dyeing bath vs. concentration at light wave length $\lambda = 544$ nm

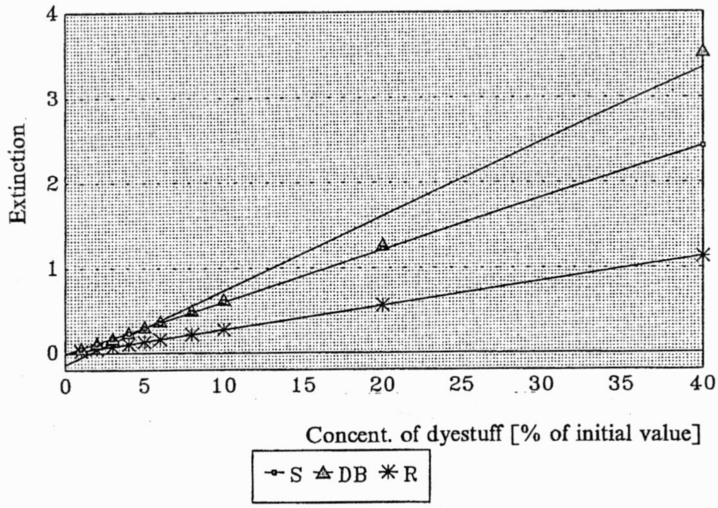

Fig. 3. Extinction of the solutions of the component dyestuffs of the "Marine" colour dyeing bath vs. concentration at light wave length $\lambda = 488$ nm

Calculations of dyestuff concentrations in exhausted dyeing bath show a relatively high degree of consumption of dispersed dyestuffs in the dyeing process. The concentrations of dyestuffs in exhausted bath have been found to be 1–8% of the initial concentrations of dyestuffs in original dyeing bath.

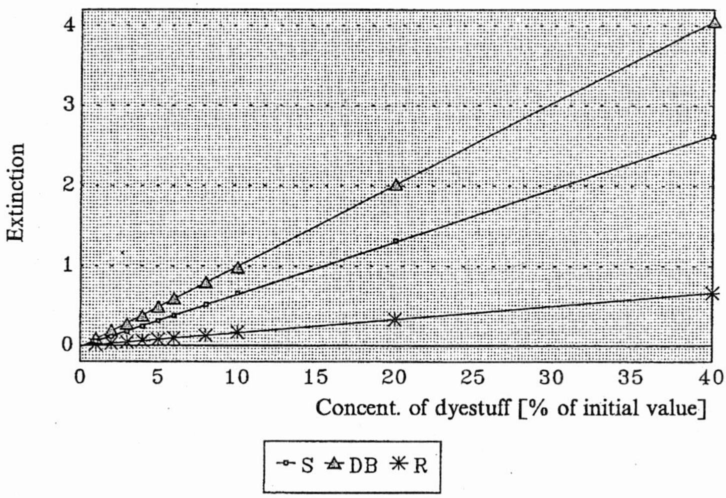

Fig. 4. Extinction of the solution of the component dyestuffs of the "Marine" colour dyeing bath vs. concentration at light wave length $\lambda = 574$ nm

For the final treatment of dyehouse wastewater, the coagulation method has been chosen. Based on the previous experiments conducted in the Chair of Water Environment Engineering, iron (II) sulphate (ferrous sulphate, $FeSO_4 \times 7H_2O$) has been chosen for wastewater coagulation. One of the sources of this coagulant is a process of white titanium pigment (TiO_2) production. In this process, pure and polluted iron (II) sulphate can be formed. Both can be used for dyehouse wastewater coagulation.

Laboratory tests of classical coagulation with iron (II) sulphate, lime and flocculant were carried out with wastewater from two different dyehouses (table 2):

1. Dyehouse wastewater from the textile works "Luxpol" situated in Stargard Szczeciński about 40 km from Szczecin.

2. Dyehouse wastewater from the textile works "Zwoltex" situated nearby Łódź – the centre of textile industry in Poland.

Table 2

The basic wastewater data

Source of wastewater	Reaction [pH]	COD [mg O_2/dm^3]	Conductivity [mS/cm]	Dry residue [mg/dm^3]
"Luxpol"	5.9	1 082	0.68	770
"Zwoltex"	8.8	761	7.2	4 155

The colour reduction was chosen as a parameter for determination of the optimal dosage of coagulant and lime. Based on the results of the colour reduction versus dosage of the coagulant, the optimal dosage of pure and polluted iron (II) sulphate for each wastewater was represented by the functions shown in figures 5 and 6.

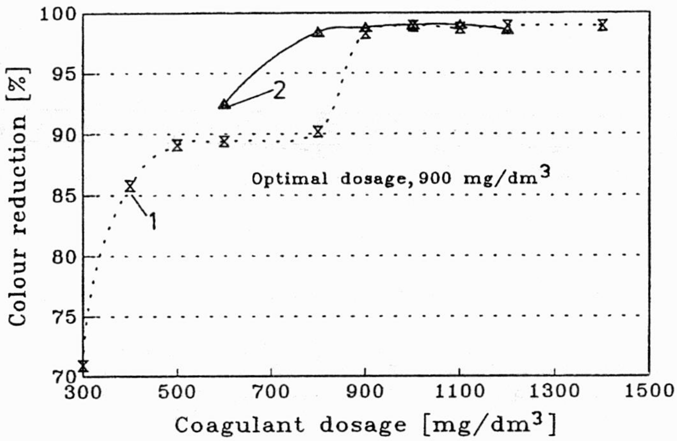

Fig. 5. Colour reduction vs. coagulant dosage for the "Luxpol" dyehouse wastewater
1 – pure $FeSO_4$, *2* – polluted $FeSO_4$

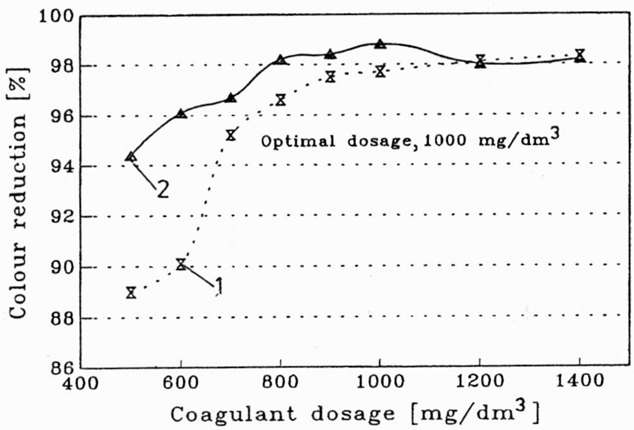

Fig. 6. Colour reduction vs. coagulant dosage for the "Zwoltex" dyehouse wastewater
1 – pure $FeSO_4$, *2* – polluted $FeSO_4$

After the optimum dosages were determined, the samples of each wastewater were purified with the same (optimal) dosages of pure and polluted ferrous sulphate. A flocculant was also used to improve the process of coagulation and sedimentation. The dosage and type of the flocculant were determined in additional laboratory tests. Magnafloc 919 flocculant was found as the best for the wastewater tested. The final results, i.e. a reduction in both COD and colour, are presented in figures 7 and 8.

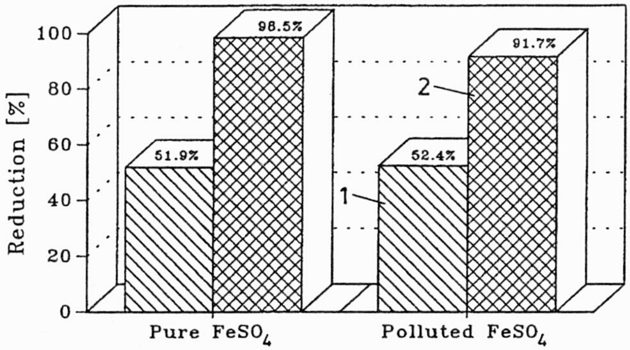

Fig. 7. Colour and COD reduction at the optimal dosage of coagulant for the "Luxpol" dyehouse wastewater
1 – COD reduction, *2* – colour reduction
Dosages: $FeSO_4$ – 900 mg/dm^3, $Ca(OH)_2$ – 380 mg/dm^3, Magnafloc 919 – 2 mg/dm^3

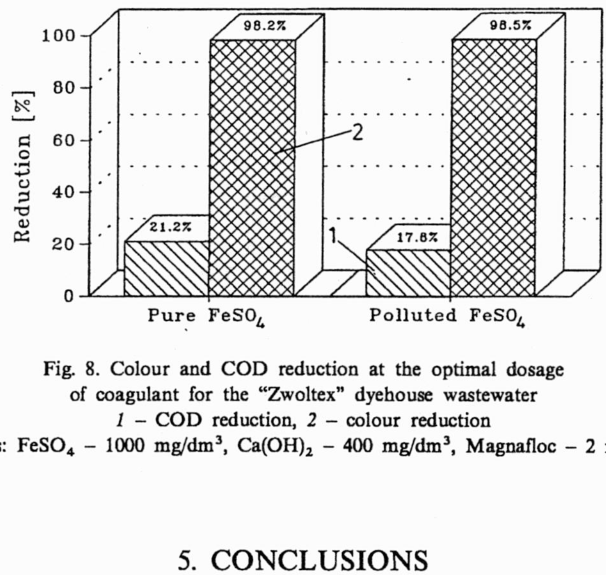

Fig. 8. Colour and COD reduction at the optimal dosage of coagulant for the "Zwoltex" dyehouse wastewater
1 – COD reduction, *2* – colour reduction
Dosages: $FeSO_4$ – 1000 mg/dm^3, $Ca(OH)_2$ – 400 mg/dm^3, Magnafloc – 2 mg/dm^3

5. CONCLUSIONS

The procedure proposed for determining the amount of dyes in the exhausted dyeing baths would enable preparing the baths according to the known formulae and would also give the possibility of recycling the baths in the course of technological processes. The mentioned steps will allow for the partial closing of the technological water loop and which finally results in the reduction of the dye quantities used during dyeing as well as in substantial reduction of the volume of generated wastewater.

The implementation of the efficient method of pretreating dyehouse wastewater could decrease the impact of the textile industry on the environment. Iron (II) sulphate seems to be a good coagulant for dyehouse wastewater coagulation. The main reasons for applying this method to wastewater treatment are relatively high degree of purification of dyehouse wastewater as well as cheap and easily available coagulant. External use of waste iron (II) sulphate for coagulation of wastewater is also a part of a strategy of waste minimization for the producers of white titanium pigment (TiO_2).

ZMINIMALIZOWANIE ILOŚCI ŚCIEKÓW W FARBIARNIACH

Przedstawiono część kompleksowego procesu zminimalizowania ścieków w przemyśle tekstylnym. Szczególną uwagę zwrócono na ścieki z farbiarni, które są szkodliwe dla środowiska. Zaproponowano procedurę analityczną umożliwiającą określenie stężenia barwników w zużytej kąpieli barwiącej. Procedura ta pozwala przygotować kąpiele zgodnie z przyjętym przepisem i umożliwia wielokrotne ich użycie w procesie technologicznym.

Opisano metodę wstępnego oczyszczania ścieków farbiarskich. Jako koagulant zaproponowano siarczan żelazawy ($FeSO_4 \times 7\,H_2O$), który powstaje jako odpad stały w procesie produkcji bieli tytanowej (TiO_2).

МИНИМИЗАЦИЯ КОЛИЧЕСТВА СТОЧНЫХ ВОД В КРАСИЛЬНЯХ

Представлена часть комплексного процесса минимизации сточных вод в текстильной промышленности. Особенное внимание уделено сточным водам из красилен, которые вредны для среды. Предложена аналитическая процедура, дающая возможность определения концентрации красителей в использованной красильной ванне. Эта процедура позволяет приготовить ванны согласно принятым нормам и многократно их использовать в технологическом процессе.

Описан метод предварительной очистки красильных сточных вод. В качестве коагулянта предложен сульфат железа(II) ($FeSO_4 \times 7H_2O$), который образуется как отброс в процессе производства титановых белил (TiO_2).