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# Methods of Decoloration of Textile Wastewaters

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*ABSTRACT*

*A survey of the most widely used and, according to many researchers, the most promising textile wastewaters decoloration methods is presented. Data on decoloration rates of different dye classes, obtained by means of different methods is gathered. Where known, values of the ecological parameter dissolved organic carbon (DOC) are given as well. All of the data is gathered from the results published in the last decade.* © *1998 Elsevier Science Ltd. All rights reserved*

*Keywords*: wastewaters, decoloration, physical decoloration processes, chemical decoloration processes, biodegradation.

## 1 INTRODUCTION

Legislation about toxic substances in industrial wastewaters is becoming increasingly strict; consequently, a large number of researchers are addressing the variety of issues in this area. The greatest environmental polluter is the chemical industry, of which only a relatively small part pertains to the organic colorants industry (3–4%) [1]. However, the dye industry is a multiproduct industry, and the costs of existing dyes and the planned costs of dyes in development (testing and administration) must be determined on a relatively small sales basis. This results in further products that can satisfy the necessary financial criteria, with a consequent decreased introduction of products with improved technical properties and/or more acceptable environmental advantages.

There are several ways in which colorants cause problems in waters, viz,

(i) Depending on exposure time and dye concentration, dyes can have acute and/or chronic effects on exposed organisms.

(ii) Although visibility of dyes in rivers depends on their colour, and extinction coefficient and on the clarity of the water, they are inherently highly visible. This means that even minor releases of effluents may cause abnormal coloration of surface waters which captures the attention of both the public and the authorities.
(iii) Neglecting the aesthetic problem, the greatest environmental concern with dyes is their absorption and reflection of sunlight entering the water. This interferes with the growth of bacteria to levels sufficient to biologically degrade impurities in the water and start the food chain [2].

The aforementioned problems have encouraged efforts to minimise environmental releases, resulting in fewer dyes which cause acute effects at concentrations below visible detection.

The treatment of coloured wastewaters (mostly resulting from finishing plants) therefore is not restricted to the reduction of ecological parameters only [such as chemical oxygen demand (COD), biological oxygen demand (BOD), total organic carbon (TOC), adsorbable organic halide (AOX), temperature and pH], but also to reduction of dye concentrations in the wastewaters [3]. In general, dyes containing wastewaters can be treated in two ways: (i) by chemical or physical methods of dye removal, which refers to the process called decoloration and (ii) by means of biodegradation, which tells us more about the fate of dyes in the environment.

The present paper presents methods employed and results of studies pertaining to the elimination of dyes from wastewaters by numerous scientists over the last decade. Where possible, a comparison of different decoloration techniques from the effectiveness and economical point of view is given.

## 2 DECOLORATION

The colour of water, polluted with organic colourants, reduces when the cleavage of the –C = C–bonds, the –N = N–bonds and heterocyclic and aromatic rings occurs. The absorption of light by the associated molecules shifts from the visible to the ultraviolet or infrared region of the electro magnetic spectrum [2]. Regarding techniques for wastewater treatment physical, biological and chemical methods are known.

Physical methods include different precipitation methods (coagulation, flocculation, sedimentation), adsorption (on activated carbon, biological sludge, silikagel), filtration, reverse osmosis, etc. Biological treatments differ according to the presence or absence of oxygen. In the former case the process is called aerobic (revival of biological sludge in aeration basins) and in the latter anaerobic treatment (decay and rot in stabilising lagoons). A third

way of biological treatment also known, i.e. degradation by means of special fungi [4]. Since biological treatment simulates degradation processes that occur in the environment, it is also called biodegradation, and is reviewed in the present paper separately. Chemical treatments are those, in which chemicals needed for decoloration of wastewater are used, and include reduction, oxidation, complexiметric methods, ion exchange and neutralisation.

## 2.1 Physical methods of decoloration

There are several known methods for determining biodegradability in aquatic ecosystems, but usually they are time limited (28 days). For some organics it is impossible to achieve sufficient biodegradability in such a time. Due to their carbon chain structure, they are poorly biodegradable or resistant to environmental conditions (light, pH, micro-organisms). For such substances, determination of their abiotic reduction capability is of much greater importance.

The main abiotic mechanism for removing dyes from the wastewaters is said to be adsorption on sludge. The most important factors influencing the adsorption test are sludge quality, water hardness, duration of the test and test substance concentration. Static and dynamic removal studies involving water soluble dyes (acid, reactive) and poorly soluble dyes (disperse) have been described by Pagga *et al.* [5]. The standard Zahn–Wellens test for obtaining information on biodegradability and adsorption was found to be inadequate in a number of ways; therefore, it was modified slightly. A sludge concentration of 3 g litre$^{-1}$ suspended solids was found to be most appropriate and duration of the test should be from 24 h to 6 days (although it was found that most of the dyestuffs need 1–2 days to reach a constant adsorption degree). Furthermore, water with average hardness of 80 mg litre$^{-1}$ $Ca^{2+}$ should be used, while the test substance concentration needed, in cases where extinction measurement is used analysis of the dyes can be reduced form 1 g litre$^{-1}$ to 10–20 mg litre$^{-1}$ (which is more like the real dye concentration in the wastewater treatment plants). Based on the results, they concluded that the suggested test method of a screening test on adsorption of dyestuffs on activated sludge is useful. Its performance is easy and without problems giving reliable information about whether a dye will or will not be adequately removed in a wastewater treatment plant using activated sludge.

The second adsorbent, suitable for wastewater treatment, is dead plant and animal matter, called biomass. Biomass includes charcoals, activated carbons, clays, soils, diatomaceous earth, activated sludge, compost, living plant communities, polymers synthesised from petrochemicals and inorganic salt coagulants [6].

Biomass decoloration is a result of two mechanisms—adsorption and ion exchange, which is why the binding capacity depends on the dye molecule

size and charge, pH of medium and salt concentration. Laszlo [6] reported the decoloration of acid, direct and reactive dyes using biomass of different origin (chitin, chitosan, microbial biomass, unmodified lignocellulose biomass, chemically modified cellulose and lignocellulose). Of all the described adsorbents only a few have characteristics necessary for commercial use. Considering the price and binding capacity, quarternized lignocellulose based adsorbents are the most appropriate for treating wastewater containing acid dyes. Since this adsorbent is an ion exchange substance, the associated mechanism is described in detail in the section pertaining to chemical treatments.

The disadvantage of adsorption processes is that the adsorbent needs to be regenerated, which adds to the cost of the process, and is sometimes a very time-consuming procedure.

## 2.2 Chemical decoloration methods

### *2.2.1 Oxidative processes*

Because of its simple handling, oxidation is the most commonly used chemical decoloration process. In most cases the oxidising agent is hydrogen peroxide, which, due to its stability in pure form, needs to be activated. Decoloration methods differ in the way in which hydrogen peroxide is activated.

*$H_2O_2$–Fe (II) salts (Fenton's reagent).* Fenton's reagent [hydrogen peroxide, activated with Fe(II) salts] is very suitable for the oxidation of wastewaters which inhibit biological treatment or are poisonous. Besides offering advantages in COD, colour and toxicity reduction, this process also has disadvantages. Since the mechanism involves flocculation, impurities are transferred from the wastewater to the sludge, which still needs ecologically questionable land-deposition. To avoid this problem, Peroxid–Chemie GmbH developed the FSR process (Fenton Sludge Recycling System), in which Fe(III)-sludge deposition is eliminated.

According to Gregor *et al.* [3] the Fenton process is preferred for wastewater treatment in cases when a municipality allows the release of Fenton sludge to the sewer. In preclarification, the primary sludge is loaded, so with almost no effort it can be removed by mechanical separation. Furthermore, from a biological point of view, not only are the properties of the sludge improved, but it is often possible to eliminate phosphates, which also has a beneficial influence on sludge separation in the final clarification. As far as colour removal is concerned, the method is suitable for different dye classes. Reactive, direct, metal-complex, pigment, disperse and vat dyes have good decoloration rates. Low decoloration rates were observed when C.I. Vat Red (50%) and C.I. Disperse Blue (0.5%) were treated.

*$H_2O_2$–ozone.* The use of ozone for purposes of wastewater treatment began in the early 1970s [2]. Because of its instability ozone is a very powerful oxidising agent. Its oxidation potential is 2.07 (compared to that of chlorine, which is 1.36) [7]. Although the original purpose of oxidation with ozone is disinfection of potable water, it can also be used for removing many toxic chemicals from wastewaters to facilitate the decomposition of detergents, chlorinated hydrocarbons, phenols, pesticides and aromatic hydrocarbons [8].

The drawback in use of ozone for wastewater treatment is its short half-life in water—it decomposes in about 20 min. Furthermore, the time can be significantly shortened if compounds like dyes are present [9]. Its stability is affected by the presence of salts, pH and temperature. If alkaline salts are present, the solubility of ozone is reduced, while neutral salts may increase its solubility [10]. Under alkaline conditions ozone decomposes more rapidly than under acidic conditions [7]. With increasing temperature, ozone solubility decreases [11]. If ozone is used as a hydrogen peroxide activator, the rate of decoloration is increased, but additional pollution of wastewater occurs.

Decoloration by means of $H_2O_2/O_3$ combination is appliable for direct, metal-complex or blue disperse dyes [2, 3]. There are some problems with decoloration of acid [2] and red disperse dyes, though, as well as with mixtures of direct, metal-complex, disperse and reactive dye (blue dyes even more than red dyes) decoloration [3].

As far as reduction of ecological parameters is concerned (COD, BOD, TOC) there are several opinions. Gregor *et al.* [3] claim COD remains unaffected by ozone treatment. Ikehata [12] and Nebel *et al.* [13] reported a reduction in COD and BOD values, while Horning [14] indicated that these two parameters may even increase following ozone treatment. Other authors believe that COD and BOD reduction is strictly coincidental. Experiences with TOC reduction are uniform, viz, ozone treatment does not influence it.

Since oxidation of soluble compounds with ozone is not effective at a preliminary stage, Carriere *et al.* [7] suggest ozonation as a tertiary treatment, following an activated sludge process. It has been found that the dye wastewater containing other substances is lower than that of pure dye solutions (up to 20% of dye remains in the water after ozonation) [11]. Preliminary elimination of reducing agents and foaming substances enhances colour removal by ozonation [12].

*$H_2O_2$—UV radiation.* All the above mentioned problems (sludge formation and regeneration, increased pollution of wastewater caused by ozone) can be avoided by oxidation with hydrogen peroxide, activated with UV light. The only chemical used in the treatment is $H_2O_2$, which, due to its final decomposition into oxygen is not problematic. Peroxide is activated by UV light.

Factors influencing $H_2O_2$/UV treatment are hydrogen peroxide concentration, the intensity of UV irradiation, pH, dye structure and dyebath composition. In general, decoloration is most effective at pH $\approx$ 7, at higher UV radiation intensity (1600 W rather than 800 W), with an optimal $H_2O_2$ concentration which is different for different dye classes, and with a dyebath that does not contain oxidising agents having an oxidising potential higher than that of peroxide [15–17]. According to Shu *et al.* [17] acid dyes are the easiest to decompose, and with an increasing number of azo groups, the decoloration effectiveness decreases. Pittroff *et al.* [18] reported that yellow and green reactive dyes need longer decoloration times, while other reactive dyes as well as direct, metal-complex and disperse dyes are decolourised quickly. In the group of blue dyes examined, only blue dyes were not vat decolourised, yet their structure changes with the process in such a way that they can be easily filtrated. The filtrate is colourless. For pigments, $H_2O_2$/UV treatment is not suitable, because they form a film-like coating which is difficult to remove.

*$H_2O_2$–peroxidase.* For decoloration purposes, peroxidase can also be used as hydrogen peroxide activator. The effectiveness of treatment depends on the peroxidase used, its concentration, pH and on the temperature of the medium. Morita *et al.* [19] studied the decoloration of acid dye using three types of peroxidases [horseradish (HRP), soybean (SPO) and arthromyces ramosus (ARP)] as peroxide activator. By measuring the absorbence, they found that the rate constant was the greatest using ARP. The decoloration rate increased with increasing peroxidase concentration and temperature of medium and was the greatest at pH 9.5.

*NaOCl.* Chemical oxidation of coloured wastewaters is also possible with Cl-compounds. Electrophilic attack at the amino group by $Cl^+$ initiates and accelerates the subsequent azo bridge cleavage. Namboodri *et al.* [20] reported the satisfactory decoloration of acid and direct dyes. Treatment of reactive dyes required longer times, while solutions of metal-complex dyes remained partially coloured. Disperse dyes do not decolourise with NaOCl. Decoloration rate increases with increasing chlorine concentration and decreasing pH of medium. According to Omura [21] dyes containing amino or substituted amino groups on the naphthalene ring, i.e. dyes derived from aminonaphthol- and naphthylamine-sulphonic acids) are most susceptible for chlorine decoloration.

However, one aspect which has come to the fore in recent years, and which is relevant to chlorine based decoloration processes, is that, for environment reasons, the future use of chemicals containing chlorine should be restricted. Since 50–60% of European chemical production directly or indirectly

depends on chlorine, the impact of such a ban could be immense, particularly for organic colorant production. However, it should be noted that although about 40% of world-wide used pigments contain chlorine this corresponds to less than 0.02% of total chlorine production [1].

## 2.3 Ion exchange

Standard ion exchange systems have not been widely used for treatment of dye-containing effluents. The reason for this is probably the general opinion that ion exchangers could not accommodate a wide range of dyes and dyeing conditions, and that they perform poorly in the presence of other additives in wastewaters. Such an opinion is erroneous, since for according to the literature, at least one successful ion-exchange treatment is known. Rock *et al.* [22] showed that a packed-bed anion exchange column in series with a nonpolar resin containing column is suitable the elimination of acid, direct and sulphur dyes. A disadvantage of such a system is the use of organic solvents for regeneration of the ion-exchanger (which is expensive).

One of the effective anion exchangers, gaining in applicability in the recent years, is quaternized cellulose. Hydrolysed reactive dye bonds to it through coulombic association of the dye sulphonate groups with resin quaternary amines, or with additional interactions (e.g. hydrogen bonding, van der Waals forces) [23]. The effectiveness of dye removal from wastewater depends on the type and number of such interactions.

Laszlo [24] reported that divalent anions (sulphate and carbonate) do not influence the binding capacity of reactive dyes. However, as chloride concentration increases, the binding rate between dye and resin diminishes, while the addition of NaOH completely prevents binding. The latter finding means that NaOH can be used as a regeneration agent of resin saturated with dye. Thus at high pH, additional cellulose hydroxyl groups and hydroxyl groups of the propyl portion of the resin quaternary amine may deprotonate, which results in increased electrostatic repulsion between dye and resin. An increase in the number of charge groups per dye molecule (from 3 to 4 or 5) at high pH should therefore decrease the number of dye molecules bound to the resin.

### *2.3.1 Complexiметric methods*

One difficulty with all the described processes is that they are not selective, so they can not be used for removal of specific chemical dye classes, only. With processes such as activated carbon adsorption or flocculation with polyelectrolytes, all organics possessing a hydrophobic part are removed, while with oxidation processes oxidising agents affect all compounds with lower oxidation potential. Thus, a selective removal process should have some advantages compared to the standard techniques.

In 1905, the synthesis of an organic compound called Cucurbituril was published; Its chemical structure was only evaluated 70 years later [25]. Cucurbituril is a macrocyclic ligand with a hydrophobic cavity and low solubility in aqueous solutions. It forms insoluble complexes with dye molecules, which makes it more effective in comparison with, for example, adsorption on activated carbon (where capacity diminishes due to adsorption of all molecules with a hydrophobic moiety) or oxidation (where all compounds with lower oxidation potentials are oxidised prior to the dye). The efficiency and selectivity of Cucurbituril has been reported by Buschmann *et al.* [26]. For decoloration purposes, Cucurbituril can be used as an aqueous solution or in the solid state. Irrespective of the form, in which it is used almost complete decoloration can be achieved with all dye classes (reactive, direct, acid, basic, disperse). Variations in decoloration rates from dye to dye may be the consequence of several factors, e.g. (i) the dye molecule does not form strong complexes with Cucurbituril, or (ii) the solubility of the formed complexes is too high. For regeneration of solid Cucurbituril, gaseous ozone ($c = 85\,\text{mg litre}^{-1}$) is the best, followed by 5% peracetic acid. The most important parameter with Cucurbituril wastewater treatment is that other organic substances present in the water do not interfere with the formation of complexes.

## 3 BIOLOGICAL DEGRADATION

Biological degradation or breakdown by living organisms (referred to as biodegradation in the following text) is the most important removal process of organics which are transferred from industry processes into solid and aquatic ecosystems. For the environmental hazard assessment of chemicals, estimation of the likely environmental concentration and comparison of the predicted concentrations with experimentally determined toxic effect levels is essential. Such screening tests are carried out with methods for (an)aerobic biodegradation of organics determination.

By far most important living organisms are heterotrophic micro-organisms. Most currently used laboratory methods for screening biodegradation involve aerobic micro-organisms which utilise molecular oxygen as the hydrogen acceptor during the respiration process. Yet, environmental conditions with lack of molecular oxygen are not uncommon. In these anoxic and hypoxic environments, micro-organisms can adjust to using sulphates, nitrates, carbon dioxide, etc., as hydrogen acceptors [27].

The simplest method for anaerobic biodegradability screening is the use of $^{14}C$ labelled test substances, but this is a long and expensive procedure. Methods based on summary analytical parameters such as dissolved organic

carbon (DOC), COD and TOC determination can also be used. However, with the testing of poorly soluble or strongly adsorbable chemicals, the use of DOC and TOC as analytical parameters is excluded. For assessing primary degradation, e.g. measurement of the chemical removal (of, for example, dyes), specific analytical methods are used. But in most cases, analysis of a specific chemical in a complex mixture with sludge is very difficult. According to Birch *et al.* [27] an ideal screening test should have the following characteristics:

- it should be easy to perform;
- it should use readily available equipment;
- it should not require a knowledge of gas solubilities;
- it should be applicable at concentrations which for most materials would be below the toxic inhibitory concentrations;
- it should use and inocolum with a low background gas production.

None of the existing screening tests satisfies all of the requirements, so possibilities of alternative method have been investigated.

### 3.1 Aerobic biodegradation

Aerobic biodegradation is a process that often takes place in the environment, e.g. in natural ecosystems like soil or surface waters, and it is often in associated with technical systems such as wastewater treatment plants. There is a variety of methods for the determination of the biodegradability of chemical compounds. They include removal of DOC determination (OECD [28] 301A, 301E), BOD determination (OECD 301C, 301D, 301F) and the final degradation product carbon dioxide evaluation (OECD 301B). A Very important criterion for ecological characterisation of substances is the ready biodegradability determination of chemical compounds. It is designated as readily biodegradable if the criteria are met. Firstly, OECD guideline 301 must be chosen and unadapted inoculum must be used. Secondly, in 10 days $>70\%$ DOC removal or $>60\%$ $CO_2$ of the theoretical carbon dioxide production or $>60\%$ oxygen consumption of the theoretical oxygen demand or COD must be reached. If a substance is designated as readily biodegradable, it may be expected that complete and rapid aerobic biodegradation will occur in natural environments, as well as in wastewater treatment plants [29].

For the methods based on DOC removal, it is difficult to differentiate clearly between physical or chemical elimination and microbial degradation. A solution as to how to avoid some of the disadvantages was proposed by Strotmann *et al.* [29]. They designed a combined $CO_2$/DOC test, which enables simultaneous screening of DOC removal and mineralization of a compound. The method was compared to the standard manometric

respirometry test (OECD 301F) and Zahn–Wellens test (OECD 302B) and it was found that the $CO_2$/DOC test gave reliable information on both biodegradation and elimination from water. The results can be used for the prediction of the behaviour of chemical compounds in an aerobic aquatic environment, especially in wastewater treatment plants.

However, none of the tested chemical compounds were organic dyes. These substances are most unlikely to show biodegradability in such tests. There is, however, some information about aerobic biodegradability available [30, 31], but the researchers only tested dyes with very simple structures, while highly adapted bacteria was used as inoculum. Therefore, Pagga *et al.* [32] determined aerobic biodegradability according to wastewater colour reduction (with adsorption onto activated sludge). The results showed no relationship between biological degradation and loss of colour (DOC removal did not correlate with colour removal in some cases, which was attributed to the presence of non-coloured organic components in the dyestuff). It is possible that, with some of the tested dyes, minor biodegradative changes occur to render the dye more amenable to removal (adsorption). Nevertheless, it can be expected that dyes susceptible to decoloration will be removed at least partially with biological treatment.

### 3.2 Anaerobic biodegradation

Anaerobic conditions occur naturally in the lower layers of sediments in lakes and ponds, river beds and estuaries and (deliberately) during sewage treatment of sewage sludges. This means that any material released to the environment which is slightly soluble in water and/or strongly adsorbable on solids, becomes available as a potential substrate for anaerobic organisms.

In the first step, acidogenic bacteria convert organics such as carbohydrates, fats or proteins into metabolites of low molecular weight (alcohols and short-chain fatty acids). These fermentation products subsequently utilise acetogenic bacteria and produce acetate, carbon dioxide and molecular hydrogen. Finally, methanogenic bacteria reduce acetate and carbon dioxide to methane. The produced biogas, consisting of methane and carbon dioxide, can be used to determine the level of biodegradation in anaerobic biodegradation tests.

Methods for wastewater anaerobic treatment are known, but there is still no method known for comparing anaerobic breakdown to that of aerobic degradation. Laboratory methods based on measurement of volume or pressure of evolved biogas have been published [33, 34], but they are not standardised. Furthermore, not all substances which can be anaerobically degraded will produce a sufficient amount of biogas.

Pagga *et al.* [35] organised a ring test involving 21 laboratories for determining the anaerobic biodegradation of organic compounds. The aim was to improve the existing European Chemical Industry Ecology and Toxicology Centre (ECETOC) method for determining ultimate biodegradation (which is the mechanism of the degradation of azo dyes) in such a way that it could become an International standard. The increase in headspace pressure in the closed vessels during the test was measured. At the end of the test, usually after 60 days, the dissolved carbon dioxide was determined. Biodegradation rate was calculated from the total carbon converted into biogas. With suitable analytical methods, the primary anaerobic biodegradation was assessed.

Similar work was done by Birch *et al.* [27], but like Pagga *et al.* [35] they were testing organic compounds in general only. Nothing was mentioned about organics dyes. A partial answer about anaerobic biodegradation of dyes was presented by Carliell *et al.* [36]. They studied the biodegradation of reactive dyes. Since reactive dyes are water soluble, they cannot be removed by conventional aerobic systems for wastewater biological treatment. Carliell *et al.* [36] decolourised 80% of a range of tested dyes. From a detailed study of a selected dye, it was proposed that this occurred via a reduction mechanism. The results were supported by tentative chemical identification of the dye degradation products.

A special example of reactive dyes the anaerobic removal was presented by Hu [37], who isolated *Pseudomonas luteola* bacteria. After 6 m adaptation in a coloured wastewater he obtained micro-organisms capable of reductive cleavage of azo group in the dye. Decoloration with these micro-organisms was complete within 4 days (2 days of shaking and 2 days of static incubation). TLC analysis indicated decoloration was not solely a consequence of adsorption onto adsorbent only, but also on the degradation of the dyes by bacteria.

## 4 DISCUSSION

Decoloration of dyes with Fenton's reagent (Table 1) does not depend on the neutralizing agent used, some differences are less than 10%. There are, however, some exceptions. In the case of Palanil Blue 3RT, C.I. Reactive Blue 27 and C.I. Vat Blue 14, it is important which neutralizing agent is used and according to the results, it is better to use milk of lime. Decoloration of Palanil Blue 3RT is very small even when milk of lime is used as a neutralizing agent, so for this dye, other decoloration processes are recommended ($H_2O_2$/UV or $H_2O_2/O_3$ seem to be satisfactory). It is interesting that other two dyes are both antraquinonoid. With further experiments carried out using dyes of this class, it should be possible to state whether this is a coincidence or not.

**TABLE 1**
Dyes Decolourised with Oxidative Procedures

| *Dyestuff* | | | *Decoloration method* | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| *C.I. name (*commercial, where C.I. not known)* | | *Chem clas* | *Fenton's reagent* | | $H_2O_2/UV$ | | $H_2O_2/O_3$ | | *NaOCl* | |
| | | | *Decolor. (%) (milk of lime[a])* | *Decolor. (%) (NaOH[a])* | *Decolor. (%)* | *Time (min)* | *Decolor. (%)* | *Time (min)* | *Decolor. (%)* | *Time (min)* |
| Acid Yellow | 17 | monoazo | | | 98.2[17] | 40 | | | | |
| | 23 | monoazo | | 100[17] | 30 | | | | | |
| | 151 | azo | | | | | | 90[20] | 30 | |
| Orange | 7 | monoazo | | | | | | | 100[20] | 15 |
| | 10 | monoazo | | | 100[17] | 60 | | | | |
| Red | 1 | monoazo | | | 99.9[17] | 30 | | | 100[20] | 15 |
| | 14 | monoazo | | | 100[17] | 60 | | | | |
| | 18 | monoazo | | | 99.1[17] | 40 | | | | |
| | 138 | monoazo | | | | | | | 100[20] | 15 |
| | 151 | disazo | | | | | | | 100[20] | 15 |
| | 219 | — | 100[3] | 100 | | | 100[3] | 5 | | |
| Violet | 43 | anthraquinone | | | | | | | 95[20] | 5 |
| Blue | 25 | anthraquinone | | | | | | | 100[20] | 30 |
| | 186 | monoazo | 88[3] | 96.5 | 80[18] | 10 | 85[3] | 1 | | |
| Black | 1 | disazo | | | 89.9[17] | 60 | | | | |
| | 60 | monoazo | | | | | | | 60[20] | 30 |
| Direct Yellow | 4 | disazo | | | 83.2[17] | 60 | | | | |
| | 44 | disazo | | | | | 100[20] | 0.5 | | |
| | 50 | disazo | | | | | 100[20] | 0.5 | | |
| Red | 23 | disazo | | | | | 100[20] | 0.5 | | |
| | 26 | disazo | | | | | 100[20] | 0.5 | | |
| *Direct Red | 5B | — | 97.5[3] | 99.5 | | | 99[3] | 45 | | |
| Direct Blue | 1 | disazo | | | | | 100[20] | 0.5 | | |
| | 25 | disazo | | | | | 100[20] | 0.5 | | |
| | 71 | trisazo | 94.33 | 88 | 98.5[18] | 3 | 90[3] | 7 | | |
| Disperse Yellow | 3 | monoazo | | | | | 95[20] | 1 | | |
| | 64 | quinoline | | | | | 100[20] | 4.5 | | |

**TABLE 1**—*contd*

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Red | 13 | monoazo | | | | | $100^{20}$ | 0.7 |
| | 60 | anthraquinone | | | | | $100^{20}$ | 1 |
| | 279 | monoazo | $95.5^{3}$ | 100 | | | $99^{3}$ | 98 |
| Blue | 60 | anthraquinone | | | | | $100^{20}$ | 0.7 |
| *Palanil Blue 3RT | | — | $0.5^{3}$ | — | $96^{18}$ | 10 | $90^{3}$ | 31 |
| Sulphur/disperse dyes[b] | | — | | | | | $98^{2}$ | 30 |
| *Helizarin Red GR | | — | $100^{3}$ | 100 | | | | |
| *Helizarin Blue BGT | | — | $95.9^{3}$ | 97.4 | | | | |
| Reactive Yellow | 37 | monoazo | | | $85^{18}$ | 8 | $93^{3}$ | 4 |
| | 125 | azo | | | $96^{18}$ | 8 | $98^{3}$ | 2.5 |
| | 145 | — | | | | | $100^{3}$ | 7 |
| *Remazol Yellow RNL | | — | | | $85^{18}$ | 8 | $93^{3}$ | 4 |
| Reactive Red | 35 | monoazo | $100^{3}$ | 100 | $100^{18}$ | 8 | $99^{3}$ | 4.5 |
| | 195 | — | | | $100^{16}$ | 60 | $100^{20}$ | 6 |
| Blue | 21 | phtalocyanine | | | $95^{16}$ | 150 | | |
| | 27 | anthraquinone | $94.8^{3}$ | 67.1 | $100^{18}$ | 5 | $94^{3}$ | 0.9 |
| | 221 | | | | | | $100^{20}$ | 9 |
| Green | 13 | phtalocyanine | | | $93^{18}$ | 8 | $98^{3}$ | 4 |
| Reactive dyes[c] | | — | | | | | $100^{2}$ | 1 |
| *Indanthren Scarlet | | — | 51.8 | 49.9 | | | | |
| Vat Blue | 14 | anthraquinone | $83.5^{3}$ | 63.6 | $15.5^{18}$ | 10 | | |
| Vat dyes[d] | | — | | | | | $50^{2}$ | 30 |
| Azoic dyes[e] | | — | | | | | $87^{2}$ | 30 |

[a]neutralizing agent; [b]mixture of sulphur (C.I. Sulphur Blue 20, C.I. Sulphur Green 2, C.I. Sulphur Black 1) and disperse dyes (Terasil Blue GFE, Foron Black OB); [c]mixture of reactive dyes (Cibacron Yellow C5-G, Cibacron Yellow CR); [d]mixture of vat dyes (Patcovat Yellow GC, Camvat Violet 3B, C.I. Vat Blue 6); [e]mixture of azoic dyes (C.I. Azoic Coupling Component 14, C.I. Azoic Coupling Component 21, C.I. Azoic Diazo Component 32).

Decoloration processes where the $H_2O_2$ activators are UV radiation and ozone, respectively (Table 1), are suitable for all dye classes, except for vat dyes, where decoloration is only 50% or less. Generally, the time needed for decoloration to occur varies from dye to dye, so it is impossible to make a general rule. On average, times needed for $H_2O_2/O_3$ decoloration are shorter than those for $H_2O_2$/UV. Times for the former are from 0.5 to 30 min, with the exception of C.I. Direct Red 5B (45 min) and C.I. Disperse Yellow 279 (98 min), while for $H_2O_2$/UV decoloration the shortest times for satisfactory decolouraton are 3 min and go up to 1 h or even more in the case of C.I. Reactive Blue 21 (150 min). But, with the use of the $H_2O_2/O_3$ decoloration process, wastewater is no longer polluted with dye but it becomes polluted with ozone (which is why COD reduction is not satisfactory). So, when choosing between the two methods, many considerations should be made.

The problem is similar with using NaOCl for decoloration (Table 1). The percentage of dye removed is very high, and is also achieved within a reasonable time (from 5 and up to 30 min). Again, we should be aware of the possibility that with NaOCl decoloration, wastewater might be additionally contaminated with chlorine.

There is no data available on oxidative decoloration of basic dyes.

Decoloration due to adsorption processes varies much from dye to dye (Table 2). This kind of dye removal seem to be the most appropriate for basic dyes, and decoloration varies form approximately 40 to 100%. However, very long times are needed for obtaining such results, since most dyes need to be treated for over 40 days. The worst average results are achieved with reactive dyes (only at 26% of them are decolourated more than 50%). With the decolourisation acid dyes, the most problematic seem to be C.I. Acid Red 18 and C.I. Acid Red 413, where colour removal was, even in 48 and 72 days, respectively, less than 10%. The only pigment dye that was decolourised by the adsorption process (C.I. Pigment Yellow 151) showed good results. Over 90% of colour was removed within 10 days and it would be of interest to find out if that is the case with other dyes.

Reduction of DOC is smaller than that of colour. Bearing in mind only dyes whose decoloration was greater than 50%, only 60% of these dyes showed a DOC reduction which was greater than 50%. Only for three dyes (C.I. Direct Red 254, C.I. Reactive Red 35 and C.I. Reactive Brown 31) was the reduction of DOC > 50%, although their decoloration was rather small, viz, 28, 42 and 10%, respectively. Three other dyes were tested for colour removal and DOC reduction after two different time periods (namely, C.I. Acid Red 413, C.I. Acid Blue 9 and C.I. Basic Blue 3). It was found that DOC reduction and colour removal decreased with increasing adsorption time. As a conclusion, it is difficult to say that there is any connection between colour removal and DOC reduction.

**TABLE 2**
Dyes Decolourised with Adsorption and Biodegradation Procedures

| *Dyestuff* | | | *Decoloration method* | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | *Adsorption* | | | | | *Biodegradation* | | |
| *C.I. name (*commercial, where C.I. not known)* | | *Chemical class* | *Adsorbent* | *Capacity ($mol\,kg^{-1}$ a)* | *Decoloration (%)* | *Time (days[b])* | *DOC (% of reduction)* | *Decoloration (%)* | *Time (days[b])* | *DOC (% of reduction)* |
| Acid Yellow | 3 | quinoline | activated sludge | | 0[32] | 42 | −44 | < 10[5] | 2 h | |
| | 5 | quinoline | | | | | | 40[5] | 6 | |
| | 36 | monoazo | activated sludge | | 5[32] | 42 | 11 | | | |
| | 54 | monoazo | activated sludge | | 19[32] | 42 | 0 | | | |
| | 61 | — | activated sludge | | 95[32] | 42 | 85 | | | |
| | 73 | xanthene | activated sludge | | 5[32] | 42 | 11 | | | |
| | 151 | azo | activated sludge | | 26[32] | 42 | 26 | | | |
| | 176 | azo | activated sludge | | 2[33] | 42 | 32 | | | |
| | 237 | azo | activated sludge | | 18[32] | 42 | 49 | | | |
| Orange | 3 | nitro | activated sludge | | −18[32] | 30 | −29 | | | |
| | 7 | monoazo | chitosan | 4.5[6] | | | | 100[5] | 7 | |
| | | | microbiomass | 0.05 | | | | | | |
| | 61 | monoazo | activated sludge | | 67[32] | 42 | −23 | | | |
| | 67 | — | activated sludge | | 99[32] | 24 | 76 | | | |
| Red | 1 | monoazo | chitin | 0.13[6] | | | | | | |
| | | | chitosan | 0.014 | | | | | | |
| | 18 | monoazo | activated sludge | | 5[32] | 48 | 5 | | | |
| | 73 | disazo | activated sludge | | 17[32] | 42 | 6 | | | |
| | 87 | xanthene | activated sludge | | 7[32] | 42 | −3 | | | |
| | 88 | monoazo | | | | | | 86[5] | 7 | |
| | 97 | disazo | activated sludge | | 20[32] | 42 | 17 | | | |
| | 114 | disazo | microbiomass | 0.11[6] | | | | | | |
| | 183 | monoazo | activated sludge | | 28[32] | 42 | 28 | | | |
| | 186 | monoazo | activated sludge | | 0[32] | 42 | 6 | | | |
| | 214 | monoazo | activated sludge | | 0[32] | 42 | −197 | | | |
| | 348 | monoazo | activated sludge | | 98[32] | 15 | 93 | | | |

*continued*

**TABLE 2**—*contd*

| *Dyestuff* | | | *Decoloration method* | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | *Adsorption* | | | | | *Biodegradation* | | |
| *C.I. name (*commercial, where C.I. not known)* | | *Chemical class* | *Adsorbent* | *Capacity ($mol\,kg^{-1}$ a)* | *Decoloration (%)* | *Time (days[b])* | *DOC (% of reduction)* | *Decoloration (%)* | *Time (days[b])* | *DOC (% of reduction)* |
| | 413 | monoazo | activated sludge | | 7[32] | 72 | 15 | | | |
| | | | | | 83 | 42 | 97 | | | |
| Blue | 9 | triarylmethane | activated sludge | | 0[32] | 42 | 45 | | | |
| | | | | | 33 | 33 | 24 | | | |
| | 13 | triarylmethane | mod. cellul.[c] | 0.013[6] | | | | | | |
| | 15 | triarylmethane | activated sludge | | 100[32] | 42 | 4 | | | |
| | 25 | anthraquinone | chitin | 0.45[6] | | | | | | |
| | | | chitosan | 0.032 | | | | | | |
| | | | unmod. cell.[d] | 0.05–0.1 | | | | | | |
| | 41 | anthraquinone | activated sludge | | 84[32] | 24 | 84 | 19[32] | 28 | 33 |
| | 92 | monoazo | activated sludge | | 38[32] | 42 | 10 | | | |
| | 113 | disazo | activated sludge | | 98[32] | 41 | 70 | | | |
| | 354 | — | | | | | | 90[5] | 3 h | |
| Green | 25 | anthraquinone | activated sludge | | 14[32] | 42 | 29 | | | |
| | 108 | azomethine | activated sludge | | 43[32] | 42 | 28 | | | |
| Brown | 100 | — | activated sludge | | 75[32] | 24 | 20 | | | |
| | 159 | — | activated sludge | | 86[32] | 42 | 74 | 40[32] | 49 | 41 |
| | 248 | nitro | activated sludge | | 100[32] | 42 | −280 | | | |
| | 311 | azo | activated sludge | | 84[32] | 41 | 67 | | | |
| Black | 1 | disazo | activated sludge | | 18[32] | 35 | 30 | | | |
| | 2 | azine | activated sludge | | 75[32] | 42 | 96 | 7[32] | 21 | 2 |
| | 48 | anthraquinone | activated sludge | | 61[32] | 42 | 80 | | | |
| | 84 | monoazo | activated sludge | | 28[32] | 42 | 36 | | | |
| *Lanasyn Black BRI ABK | | | unmod. cell.[d] | 0.13–0.14[6] | | | | | | |
| Acid dyes[e] | | — | quart. cell.[f] | 0.6–0.7[6] | | | | | | |
| Basic Orange | 22 | quinoline | activated sludge | | 100[32] | 42 | 100 | | | |

**TABLE 2**—*contd*

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 40 | azo | activated sludge | | 48[32] | 42 | 22 | | | |
| Red | 22 | azo | activated sludge | | 85[32] | 10 | 95 | | | |
| | 46 | monoazo | activated sludge | | 98[32] | 42 | 95 | | | |
| Violet | 19 | quinoline | activated sludge | | 54[32] | 42 | 19 | | | |
| Blue | 3 | oxazine | activated sludge | | 37[32] | 42 | 30 | | | |
| | | | | | 46 | 42 | 10 | | | |
| | 22 | anthraquinone | activated sludge | | 100[32] | 42 | −100 | | | |
| Direct Yellow | 27 | monoazo | activated sludge | | 44[32] | 42 | −267 | | | |
| | 44 | disazo | activated sludge | | 73[32] | 48 | 70 | 45[32] | 21 | 47 |
| | 132 | disazo | activated sludge | | 0[32] | 41 | −12 | | | |
| | 133 | disazo | activated sludge | | 37[32] | 41 | 19 | | | |
| Orange | 46 | stilbene | activated sludge | | 52[32] | 42 | −86 | | | |
| | 60 | stilbene | activated sludge | | 55[32] | 42 | 49 | | | |
| Red | 7 | disazo | activated sludge | | 50[32] | 42 | 20 | | | |
| | 23 | disazo | activated sludge | | 92[32] | 42 | 54 | | | |
| | 28 | disazo | unmod. cell.[d] | 0.01[6] | | | | | | |
| | 81 | disazo | activated sludge | | 0[32] | 41 | 20 | | | |
| | 254 | disazo | activated sludge | | 28[32] | 42 | 56 | | | |
| Blue | 10 | disazo | activated sludge | | −1[32] | 42 | −17 | | | |
| | 14 | disazo | activated sludge | | 86[32] | 48 | 75 | | | |
| | 15 | disazo | activated sludge | | 25[32] | 41 | −7 | | | |
| | 71 | trisazo | activated sludge | | 100[32] | 42 | 27 | | | |
| | 86 | phtalocyanine | mod. cellul.[c] | 1.0 | | | | | | |
| | 151 | disazo | activated sludge | | 100[32] | 42 | 44 | | | |
| Direct Brown | 9 | — | activated sludge | | 68[32] | 42 | 53 | | | |
| | 106 | poliazo | activated sludge | | 100[32] | 42 | −71 | | | |
| Black | 19 | poliazo | activated sludge | | 94[32] | 42 | 93 | 25[32] | 28 | 37 |
| Direct dyes[g] | | — | quart. cell.[f] | 0.6–0.7[6] | | | | | | |
| Disperse Yellow | 5 | monoazo | | | | | | >90[5] | 1 | |
| Orange | 29 | azo | | | | | | >90[5] | 3 h | |
| Red | 4 | anthraquinone | | | | | | >90[5] | 1 | |
| | 60 | anthraquinone | | | | | | >90[5] | 3 h | |
| Mordant Yellow | 30 | monoazo | activated sludge | | 48[32] | 42 | 77 | | | |
| Blue | 13 | monoazo | activated sludge | | 83[32] | 42 | 5 | | | |

**TABLE 2**—*contd*

| *Dyestuff* | | | *Decoloration method* | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | *Adsorption* | | | | | *Biodegradation* | | |
| *C.I. name (*commercial, where C.I. not known)* | | *Chemical class* | *Adsorbent* | *Capacity (mol kg$^{-1}$ a)* | *Decoloration (%)* | *Time (days$^b$)* | *DOC (% of reduction)* | *Decoloration (%)* | *Time (days$^b$)* | *DOC (% of reduction)* |
| Pigment Yellow | 151 | monoazo | activated sludge | | 96[32] | 10 | 95 | | | |
| Reactive Yellow | 2 | monoazo | microbiomass | 0.08[6] | | | | | | |
| | 19 | monoazo | | | | | | 89–90[36] | 6.5 h | |
| | 17 | monoazo | activated sludge | | 53[32] | 28 | 10 | | | |
| | 23 | monoazo | activated sludge | | 84[32] | 30 | 85 | | | |
| | 37 | monoazo | activated sludge | | 35[32] | 28 | 38 | | | |
| | 42 | monoazo | activated sludge | | 40[32] | 28 | −45 | | | |
| | 95 | azo | | | | | | 0[36] | — | |
| | 155 | — | activated sludge | | 3[32] | 42 | 47 | | | |
| Orange | 12 | monoazo | | | | | | 90–95[36] | 23 h | |
| | 13 | monoazo | | | | | | 85–90[36] | 50 h | |
| | 19 | monoazo | activated sludge | | 37[32] | 28 | 15 | | | |
| Red | 19 | monoazo | activated sludge | | 23[32] | 42 | −6 | | | |
| | 24 | azo | activated sludge | | −1[32] | 42 | 26 | 90–97[36] | 32 h | |
| | 35 | monoazo | activated sludge | | 42[32] | 30 | 69 | | | |
| | 45 | azo | activated sludge | | 7[32] | 42 | −12 | | | |
| | 133 | xanthene | activated sludge | | 53[32] | 30 | 20 | | | |
| | 141 | disazo | | | | | | 85–90[36] | 4.5 h | |
| | 180 | azo | quart. cell.[f] | 0.361[24] | | | | | | |
| | 185 | azo | activated sludge | | 11[32] | 42 | −3 | | | |
| | 198a | — | | | | | | 85-90[36] | 2 h | |
| | 218 | — | | | | | | 90-95[36] | 32 h | |
| *Reactive Red G | | — | | | | | | 37.4[37] | 4 | |
| Reactive Blue | 19 | anthraquinone | activated sludge | | 35[32] | 28 | 24 | | | |
| | 21 | phtalocyanine | activated sludge | | 72[32] | 28 | 64 | 85–90[36] | 4.5 h | |
| | 38 | phtalocyanine | | | | | | 40[36] | 4.5h | |
| | 49 | anthraquinone | | | | | | 7–10[36] | 2 h | |

**TABLE 2**—*contd*

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 72 | phtalocyanine | | | | | 25–30[36] | 50 h |
| | 170 | monoazo | activated sludge | | 30[32] | 41 | −4 | |
| | 220 | azo | | | | | 90–95[36] | 1 h |
| Green | 12 | phtalocyanine | activated sludge | | 47[32] | 42 | 27 | |
| Brown | 11 | azo | | | | | 90[36] | 23 h |
| | 31 | azo | activated sludge | | 10[32] | 42 | 58 | |
| | 48 | — | | | | | $< 10^5$ | 2 h |
| Black | 5 | disazo | activated sludge | | 60[32] | 28 | −53 | 80–85[36] 4.5 h |
| | 8 | monoazo | activated sludge | | 6[32] | 42 | 47 | |
| | 39 | disazo | | | | | 70–75[36] | 5.5 h |
| Blue PB (reactive) | | — | | | | | 98[36] | 2 h |
| * Black SG (reactive) | | — | | | | | 75–80[36] | 7.5 h |
| * Reactive RBB | | — | | | | | 93.2[37] | 4 |
| * Reactive RP2B | | — | | | | | 92.4[37] | 4 |
| * Reactive V2RP | | — | | | | | 88[37] | 4 |
| Reactive dyes[h] | | — | quart. cell.[f] | 0.6–0.76 | | | | |

[a]For quaternized cellulose the capacity is in eq $kg^{-1}$; [b]where decolouration time is not in day the appropriate time unit is stated; [c]chemically modified cellulose and ligno-cellulose; [d]unmodified ligno-cellulose biomass; [e]not specified which acid dyes; [f]quaternized (ligno)cellulose; [g]not specified which direct dyes; [h]not specified which reactive dyes

The best results in colour removal due to biodegradation (Table 2) were shown by disperse dyes, all of which decolourised more than 50% within 1 day. Also, 74% of reactive dyes were decolourised satisfactorily (> 50%), but the times required were longer (4 days). On the other hand, DOC reduction is very poor, since it never exceeded 50%.

There are 13 dyes of different dye classes, as shown in Tables 1 and 2, that were decolourised with one or more of the oxidative procedures and with adsorption or biodegradation processes. Those dyes are C.I. Acid Yellow 151, C.I. Acid Orange 7, C.I. Acid Red 1, C.I. Acid Red 18, C.I. Acid Blue 25, C.I. Acid Black 1, C.I. Direct Yellow 44, C.I. Direct Red 23, C.I. Direct Blue 71, C.I. Disperse Red 60, C.I. Reactive Yellow 37, C.I. Reactive Red 35 and C.I. Reactive Blue 21. It is interesting to note that all these dyes were decolourised 90% or more by oxidative processes, while only four dyes equally well removed (> 90%) by adsorption or biodegradation processes. Also, the times needed for oxidative decolorations to occur were much shorter (in min) than those needed for the other two methods (times in hours or days). So, from this point of view, would seem the economical reasons much more sensible for dyes to be removed by oxidation processes, while adsorption and biodegradation tests are more of a pointer of what might happen to the dye if it is accidentally released to environmental waters.

## 5 CONCLUSION

Although it is estimated that dye releases from a typical textile dyehouse could result in a total dye concentration in receiving waters of 10 $\mu$g litre$^{-1}$ only [38] (lower detection limit is 100 $\mu$g litre$^{-1}$), this should not diminish efforts for wastewater pollution reduction. In this way it is possible to:

- reuse wastewater, which is an advantage not only from the environment-protection point of view, but from an economic one also;
- reduce surface waters pollution;
- diminish the bioaccumulation possibility of dyes and other chemicals used in dyeing processes, in the environment.

It is difficult to define a universal method that could be used for the elimination of all organic substances from wastewaters. Nevertheless, it is the obligation of all polluting industries to choose a method, which would be, regarding their production program, the most appropriate wastewater treatment. As shown, the choice is anything but small!

In the future, is would be advantageous to find a rule by which it would be possible to determine the most appropriate treatment method according to

the dye structure (its chromophore or reactive group). One of the ways which our group is researching is optimisation and modelling by means of an artificial neural network.

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