CURRENT SITUATION AND FUTURE PERSPECTIVES FOR TEXTILE EFFLUENT DECOLOURISATION

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ABSTRACT

Textile dyes are an important class of synthetic organic compounds and are therefore common industrial pollutants. They are produced in large scale and may enter the environment during production or later on during fibre dyeing. Due to the stability of modern dyes, conventional biological (activated sludge) treatment methods for industrial wastewater are ineffective, resulting in an intensively coloured discharge from the treatment facilities. Thus, there is a need for developing treatment methods that are more effective in eliminating dyes from waste stream at its source.

In the present work we review existing processes as well as promising new technologies for textile wastewater decolourisation. Particular emphasis is given to biotechnological and advanced oxidative processes. Results using the latter methodology are presented as such processes are highly efficient and simple to operate.

1. INTRODUCTION

Dyeing of textile request water and generates a substantial quantity of effluents containing mineral salts and dyes at high concentrations. Out of the different classes of dyes used, reactive dyes are by far the most commonly used. An estimated 700000 tons of dyes are produced annually world wide of which 60-70% are azo dyes. Reactive dyes make up about 38% of the total amount produced. By the year 2004, the use of reactive dyes is forecasted to increase to about 50%. As a result of the chemical reactions involved in the fixing of reactive dyes to fabrics, as much as 20 to 50 % of reactive dyes can be released into waterways depending upon dyestuff type, the application route and depth of shade required.

2. CURRENT PROCESSES FOR DYE COLOUR REMOVAL

Several industrial-scale wastewater treatment systems are now available. However, these are largely ineffective for colour removal and do not address water recycling. The systems used at the industrial level fall into 3 main categories.

2.1 Biological Activated Sludge Ponds

These are the most common type of treatment system used where COD removal is 30-40%. Because the waters do not contain sufficient nutrients, and the BOD to COD ratio is usually less than 0.3, only hardy anaerobic bacteria can survive. Up to 50% of the colour is removed. This is done in part by anaerobic bacteria by converting reactive azo dyes to mutagenic amines. Apart from the formation of toxic amines, additional problems are odour problems and accumulation of sludge. Wastewater sent to activated sludge ponds is never recycled. In strictly anaerobic systems near total COD and colour removal is achieved but in practice these conditions are difficult to achieve.

2.2 Physico-Chemical Techniques

Adsorption supports such as activated charcoal can be use as o adsorbents for hydrophobic compounds, including dye molecules. The technology is simple and activated charcoal (from wastes such as wood, etc) can be obtained at a low cost. However, the desorption process is problematic and not cost-effective. Therefore bound substances, including dyes, need to be disposed.
Coagulation used together with either flocculation or sedimentation is often used in the textile industry. Coagulation is promoted by addition of an inorganic polyelectrolyte eg. polyaluminum chloride. These particles are then separated by flotation or sedimentation. Some features of this technology are: 1) it responds quickly to operational factors and therefore automation is simple; 2) the equipment requires less space than the biological lagoon but equipment is more expensive; 3) removal of 90% of suspended solids and about 10 to 50% COD can be achieved; 4) overdoses of polyelectrolyte lead to residual concentrations of polyelectrolyte in the effluent, which has a detrimental effect on the nitrification process; 5) the main problem of the dye colour in the solid phase remains, although removal from the aqueous phase may be up to 90%; and 6) sludge produced is dependent on the nature of the flocculant used.

2.3 Membrane Technologies

These comprise three categories, namely, ultrafiltration, nanofiltration and reverse osmosis. The major drawbacks are high capital costs combined with high energy costs. The membranes are prone to clogging and need to be regenerated at regular intervals. These are therefore costly both in terms of labour and cost of membrane replacement. In any case, the colour-forming dye molecules are not degraded. Instead, these are concentrated and subsequently need to be disposed.

3. BIOTECHNICAL REMOVAL OF DYES

Biological processes are designed to take advantage of the biochemical reactions that are carried out in living cells. Such processes make use of the natural metabolism of cells to accomplish the transformation or production of chemical species. Synthetic dyes or their analogues are not found in nature and may therefore not be readily biodegradable. However, bioprocess, whether they are made up of whole microorganisms or enzymes derived from these, are sufficiently versatile to be tailored according to the target application.

3.1. Aerobic Bacterial Systems

Actinomycetes, particularly *Streptomyces* species, are known to produce extracellular peroxidases. These have been shown to catalyse hydroxylation, oxidation, and dealkylation reactions against various xenobiotic compounds. With the notable exception of the actinomycetes, the isolation of bacteria capable of the aerobic decolourisation and mineralization of dyes, especially sulfonated dyes, has proven difficult. Most dye-decolourising bacteria studied are able to mineralize industrially relevant azo dyes only to a limited extent and little is known about the mechanisms involved. The role that cytoplasmic enzymes, such as azoreductases have *in vivo* is not certain. Keck et al. (1997) have shown that that these enzymes do not have as important a role as previously thought.

This is analogous to the situation with anaerobic degradation of dye molecules which is discussed below.

The BIOCOL process is a recent example of a pilot scale process using whole *Shewanella putrefaciens* cells, which were grown and immobilized on an activated carbon support (Conlon et al. 2002). Both the carbon and the biocatalyst are contained in adsorption cartridges, through which the water is pumped for colour removal. The carbon adsorbs the dyes, providing a large surface area on which bioreduction of the dyes by the cells can take place.

In general, microorganisms are highly sensitive to changes in their environment (eg. pH, salinity, temperature, and the presence of toxic or inhibitory compounds). Therefore, such processes may be difficult to control over the long term, and may be subject to frequent operational problems. They also require a supply of macro- and micronutrients for sustaining the microbial growth. Furthermore, large quantities of biomass are formed and these must ultimately be disposed. Moreover, while biological systems are commonly used to remove the bulk organic load in wastewaters, these systems often have difficulty in removing toxic pollutants to consistently low levels. Therefore conventional biological processes using whole cells need to be optimized before water quality can be improved sufficiently to meet wastewater discharge legislative criteria.

3.2. Anaerobic Bacterial Decolourisation of Dyes

Under anaerobic conditions many bacteria have been reported to readily decolourise azo dyes. Initially, the bacteria bring about the reductive cleavage of the azo linkage, which results in dye decolourisation and the production of colourless aromatic amines. It has been demonstrated that in anoxic sediment environments, uncharged azo dyes readily undergo biologically-mediated reduction to the corresponding amine. The potential toxicity, mutagenicity and carcinogenicity of such compounds is well documented (Chung et al. 1992).

The initial step in bacterial azo dye metabolism under anaerobic conditions involves the reductive cleavage of the highly electrophilic azo bond in the dye molecule. This process was thought to be catalysed by a variety of soluble cytoplasmic enzymes with low substrate specificity which are known as azoreductases. The role of azoreductases was critically re-evaluated following the classical work of Keck et al. (1997). As most azo dyes have sulphonated substituent groups and a high molecular weight, they are unlikely to pass through cell membranes. It has been shown that certain quinone-based compounds generated during metabolism of specific substrates can act as mediators shuttling redox equivalents to azo dye molecules from the bacterial membrane. These mediator compounds are either formed during the metabolism of certain substrates or they may be added externally. Addition of synthetic redox mediators such as anthraquinone sulphonates, even at very low concentrations, will facilitate the non-enzymatic reduction of the azo dyes in the extracellular environment (Stolz 2001). The search for novel, cost-effective mediators that can be used to accelerate the decolourization process will require more research.

Although the anaerobic reduction of azo dyes is relatively easy to achieve under laboratory conditions, complete mineralisation of the molecule is difficult. In a study by Donlon et al. (1997) the partial mineralisation of the azo dye Mordant Organge 1 by methanogenic granular sludge in a continuous-upflow anaerobic sludge blanket was

described. However, complete mineralisation did not take place. To overcome the problem of the recalcitrance of azo dye breakdown products under anaerobic conditions, a number of groups have used a two-stage treatment process (Lourenço et al. 2000). In the first anaerobic stage, the azo dye is readily reduced to the corresponding colourless amine. These are then metabolized relatively easily under aerobic conditions. For detailed reviews on the anaerobic treatment of textile effluents. In summary, combined anaerobic-aerobic systems have been shown to be feasible at the laboratory scale using different reactor configurations. However, the challenges for implementing such a system at the industrial scale are many.

3.3. Enzymatic Processes for Colour Removal

In an attempt to overcome some of the problems associated with whole biological systems, recent research has focused on the application of enzymes, purified to the necessary extent (Soares et al. 2001a; 2002). Indeed, the potential for using enzymatic systems for colour removal has been recognized for some time. The reasons for this interest are many: (1) the rate of introduction of recalcitrant pollutants into the environment is increasing, and it is becoming increasingly difficult to achieve an acceptable degree of removal of these pollutants using conventional chemical and biological processes; (2) there is a need to develop alternative methods that are faster, cheaper, more reliable, and simple to implement; (3) there is a growing recognition that enzymes can be used to target specific pollutants for treatment; (4) recent biotechnical advances make it possible to produce enzymes more cheaply and with characteristics that are in tune with the targeted application; and (5) enzymatic processes are amenable to process control.

The key to the successful application of enzymes for wastewater decolourisation is the selection of an appropriate cocktail (Soares et al. 2001b). Although there is a wealth of information available in the scientific literature obtained using model systems employing single dyes, this data cannot be extrapolated to the industrial scenario. It is well known that textile effluent is a complex mixture of numerous dyes, as well as many auxiliary compounds. This is further complicated by variations in the dye composition as a result of seasonal and fashion-dictated variations. Hence, any solution aimed at removing colour from wastewater will have to contemplate these and any other variables in the production cycle.

Many authors have recognized the potential for enzymatic treatment systems. However, the development of these processes from an industrial perspective has lagged behind. The main reason for this appears to be the cost of enzymes that have traditionally been very expensive to produce in the quantities that are required at an industrial scale. Enzymes are expensive because of the cost of their isolation, purification and production. Apart from the cost, the effect of each of the operational parameters on the colour removal process must be investigated using real textile effluent. In any case, the introduction of novel fermentation technologies together with new host systems for enzyme overproduction

means that some of the major barriers that have limited the applicability of enzyme technology can be overcome.

In a recent pilot-scale trial Soares and co-workers showed that a suitably selected enzymatic cocktail could be used to remove colour from real industrial process waters. In this trial, colour removal was measured at the three wavelengths specified by EU legislation, and followed over a 3 month period. This approach appears to be promising as the textiles tested after being processed with the recycled waters showed satisfactory properties in terms of colour difference and washing fastness. Nevertheless, these trials carried out at the textile company require further validation.

4. ADVANCED OXIDATION PROCESSES

There is an increasing interest in utilization of advanced oxidation processes for destruction of recalcitrant compounds with and without heterogeneous catalysis. These systems are based on the production of hydroxyl radicals as powerful oxidizing agents (Bali et al., 2004). The combination of UV irradiation with catalysts such as TiO_2 is one of such methods which has attracted a lot of attention in recent years, due to its effectiveness in mineralization of organic compounds (Legrini et al. 1993), including contaminant dyes (Gonçalves et al. 1999) in textile residual waters. A vast amount of research work on this subject was published (see Arslan-Alaton et al. 2003). Interest in this photocatalytic process is mainly due to the low cost of the catalyst (TiO_2) and to the fact that it can be powered by sunlight, thus reducing significantly the electric power requirements and therefore the operating costs (Zhang et al. 1998).

It is well known now that when an aqueous TiO_2 suspension is irradiated with light energy greater than the band gap energy of the semiconductor ($h\nu > Eg = 3.2$ eV) conduction band electrons (e^-) and valence band holes (h^+) are formed. The photogenerated electrons react with the adsorbed molecular O_2, reducing it to superoxide radical anion $O_2^{\cdot -}$, and the photogenerated holes can oxidize either the organic molecules directly or the OH^- ions and the H_2O molecules adsorbed at the TiO_2 surfaces to $OH^{\cdot}$ radicals (Hoffmann 1999). These will act as strong oxidizing agents and can easily attack the adsorbed organic molecules or those located close to the surface of the catalyst, thus leading finally to their complete mineralization

Experimental observations indicate almost complete oxidation of most of the organic compounds to CO_2 *via* photocatalytic processes. The quantitative formation of carbon dioxide is of great significance in water treatment, because it provides unequivocal evidence for the total destruction of organic pollutants present in water. It should be noted that with visible light the photodegradation proceeds by different routes, such as electron transfer from the excited state of the dye molecules adsorbed on the TiO_2 surface into the conduction band of TiO_2, a process less efficient in comparison to the photocatalytic one.

4.1. UV- Photochemical Process for Dye Transformation

In some recent studies decolourisation of dyes using a UV-photochemical process was carried out without the use of a semiconductor. A decolourisation profile, similar to the

one shown in Figure 1, was obtained for all dyes studied. Optimal levels of decolourisation were achieved using only 30 mg L^{-1} of hydrogen peroxide.

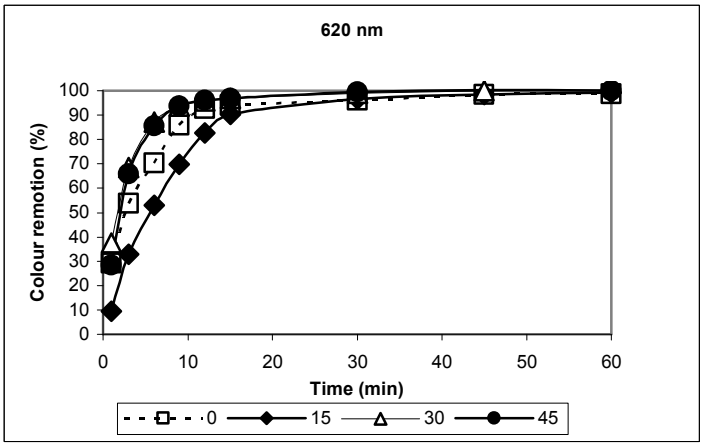

Figure 1- Photocatalytic decolorisation of black dye, RBB, with different concentration of hydrogen peroxide (0, 15, 30 and 45 mgL^{-1})

Interestingly when simple mixtures of dyes were used, the red LBR was the most recalcitrant. This contrasts sharply with the decolourisation of real process waters where the yellow LBY, was invariable the dye that was the most recalcitrant. This highlights the discrepancy between using model dye mixtures and real wastewater which contains numerous additives. Photochemical treatment without any semiconductor was very effective in dye decolourisation and also provides a clear advantages from the ecological point of view. The presence of hydrogen peroxide was a key factor to improve the effectiveness of the decolourisation process as it reduced the reaction time for total decolourisation by half.

5. CONCLUSIONS

In both the enzymatic as well as the photocatalytic process, the yellow LBY dye was by far the most recalcitrant when real effluent is used. This contrasted with the results obtained using model dye mixtures. Clearly, care is needed in extrapolating results from simplified systems.

The two novel processes described will need to be used in tandem with traditional methods in order to remove the additional pollutants present in effluent. This should provide a complete and environmentally friendly processes for remediating textile effluent.

Finally, operational costs will need to assessed by taking into account all of the expenses involved in implementing an industrial treatment facility.

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