PREFACE

Environmental issues associated with residual colour in dye house effluents are not new. Over the past few decades manufacturers and users of synthetic colorants have faced increasingly stringent regulations promulgated by agencies established to safeguard human health and environment. This has meant that much of the emerging technology in these two areas arose as a need to comply with regulation. A significant proportion of this technology has been directed specifically to analyze for and remove colour and priority pollutants from effluents to circumvent pollution problems by eliminating their source.

The global consumption of textiles is currently around 30 million tones, with expected growth at 3% per annum. The coloration of this total needs approximately 800,000 tones of dye, promoting an industry of 2500 million pound per annum (Glover and Pierce, 1992). In the dye stuff market the textile industry shares a whooping 2/3 of the total synthetic organic dyestuff production; making it the largest consumer of synthetic coloring material (Kulkarni et al., 1985). The huge quantities of water employed in the dyeing and finishing operation associated with the dye house processes provides the textile industry with another dubious distinction of being one of the largest water consuming industry. According to an estimate made by the internal technical report, 1994, 100 L of water is consumed for every tonne of cloth processed. This calls for a serious
approach to environmental issues associated with residual colour in the
dye house effluents.

The long-standing dyers goal has been to evenly achieve and consistently produce specific color at low costs in a safe, timely and efficient manner. Thus, if it were possible to achieve quantitatively 100% dye bath exhaustion with no wash off the problem of residual colour would not have gained prominence.

Despite efforts to improve the fixation of dyes on specific substrates, enhance biodegradability by affecting changes through modification in the chemical structure of dyes and achieve better control over dye manufacturing and dye consumption, the reactions than bind dyes on to a substrate don not always run to completion. An equilibrium will be established between the dye bath and the fabric after which no further binding of the dye to the fabric can occur. Residual dyes, auxiliaries and chemicals are often left in the process water and discharged with the wastewater. Therefore the wash off from the dye house invariably contains large amount of residual dye. Estimates indicate that approximately 12% of the synthetic textile dyes used each year are lost to waste streams during manufacturing and processing operations and that 20% of these losses would enter the environment through effluents from waster water treatment plants (Brown, et al., 1981). According to another estimate over 7 x10^5 tonnes and approximately 10,000 dyes are produced annually worldwide, of which about 10% is lost in the industrial effluents (Vaidya et al., 1982). The three major chromophores of various commercial dyes are Azo,
Antraquinone and Indigo (Ratte, 1995). These effluents are discharged to sewers from where they enter into the Municipal wastewater treatment plants.

In the dye-manufacturing units there is considerable debate on the level of environmental hazard produced by colored effluents. Many of them have stated that there are no tenable arguments for the classification of dyestuffs as dangerous substances in the effluent. They go even further to say that dye stuffs should not be regarded as water pollutants since their harmful effects are negligible. Nonetheless, although the problem of color could be argued as only aesthetic, it is accepted that the problem has to be rectified. Thus, the mounting pressure on the industry to treat the dye house effluents have led to a host of new and old technologies competing to provide cost effective solution to the problem of residual color imparted by dyes.

Dyes are highly structured polymers required to exhibit a high degree of chemical, photolytic and microbiological stability in order to fulfill the fastness requirements. Consequently, the dyes are so structured that they do not degrade under typical usage conditions. Constant product changes and batch dyeing operations could cause considerable swings in the wastewater characteristics thereby presenting difficulty in acclimating the microorganisms to the substrate. Synthetic dyes are therefore not uniformly susceptible to degradation in conventional biological wastewater treatment processes because of their resistance to microbial attack. Attempts to develop aerobic bacterial strains for dye degradation often
resulted in a very specific organism, which showed strict degradation ability on individual dyes (Kulla., 1981). Hence, these dyes pass through the treatment systems virtually undegraded. These synthetic colorants although impart only a small fraction of the total organic load, the high degree of color that they impart is very detectable. To make matters worse the human eye can detect dyes at concentrations as low as 0.005 mg/L in clear river water.

Of the dyes commercially available, approximately 50% are azo compounds (Kulkarni et al., 1985). These compounds are characterized by aromatic moieties linked together with azo group (N=N). These azo dyes can be divided into monoazo, diazo and triazo classes and are round in six application categories acid, basic, direct, disperse, azoic and pigments. These azo dyes are wide spread class of environmental pollutants that find wide applications in textile, cosmetic, food colorants, printing and pharmaceutical industries (Ryan et al.,). These synthetic compounds have been identified as the most problematic compounds in the textile effluents due to their high water solubility and low exhaustion rate leading to elevated dye concentrations in the spent dye bath. The strong electron withdrawing character of the azo group generates electron deficiency, thus stabilizing these aromatic pollutants against conversion by oxygenases (Kulla et al., 1983). As a consequence these compounds are less susceptible to oxidative catabolism and many of them tend to persist under aerobic environmental conditions. This statement is supported through the studies conducted by Shaul and coworkers (1987) in which more than a
hundred azo dyes were tested in aerobic activated sludge systems of which only a few were actually biodegraded. A literature review indicated that adsorption to the sludge is the primary removal mechanism for dyes in a biological wastewater treatment and that factors inhibiting permeation of the dye through the microbial cell membrane like increased water solubility and increased molecular weight reduce the effectiveness of biological degradation (M.Dohanyos, V. Medera, H.R.Hitz, W.Huber and R.H. Reed, W.C.Tincher, K.Wuhrmann, K.Mechener (1978) and T.Kappeler ( 1980)). The results from such studies reveal that the dyes were removed from wastewater via physical and physico-chemical processes such as diffusion, adsorption and chemical reaction. The dyes that adsorbed to the sludge had fewer sulfonic acid groups and were of higher molecular weight both of which are features that tend to reduce water solubility. Further more, the coupling components that go into the synthesis of azo dyes like naphthalene-sulfonic acids as well as aromatic amino derivatives represent an extensive non-biodegradable class of compounds (Krull, R and Hempel, D.C. (1994). Due to their recalcitrance in aerobic environment’s they pass through the aerobic treatment systems virtually undegraded and eventually end up in anaerobic sediments, shallow aquifers and ground waters (Braughmann et al.,). All these findings substantiate the view that the conventional aerobic treatment systems such as the activated sludge process are grossly inadequate in meeting the present standards for acceptable effluent making the dye related industries incapable of responding to stringent legislation.
In the recent years concern over the environmental fate of these azo dyes have grown. This can be partly attributed to the intense coloration, which they impart to the natural water bodies on discharge, and largely to the fact that these dye partition strongly to the bottom sediments where under anaerobic conditions they undergo reductive cleavage via a four electron reduction at the azo linkage generating aromatic amines (Brown et al., 1983). Unfortunately, as suspect mutagens and carcinogens, these aromatic amines cannot be regarded as environmentally safe end products (Chung, K.T., (1992) and Ames, B.N., (1975)).

Research by Huang (1991) and Field, J.A., (1995) report that these aromatic amines are more amenable to treatment under aerobic conditions provided the co-substrate and the oxygen are in balance. Literature reviews indicate that the aromatic amines generated as a result of reduction of the N=N bond are in most cases benzene or naphthalene derivatives, which can be rapidly oxidized by aerobic microorganisms in oxic environs. This study throws up a new option of utilizing integrated and sequential anaerobic – aerobic system to achieve complete biodegradation of azo dyes. Microbial anaerobic processes capable of producing and maintaining low oxidation reduction potential cleaves the chromophore N=N generating stoichiometric amounts of amines to be further metabolized by the aerobes under oxic environs. Some studies also reveal that some nitro-aromatic compounds and azo dyes could be completely mineralized and serve as a carbon, energy and nitrogen source for anaerobic bacteria in contrast to the common assumption that they are only
biotransformed to mutagenic and carcinogenic aromatic amines. Although the use of microbial consortium does provide a very interesting treatment option towards achieving biodegradation of dyes; isolation of specific microorganism that degrade one or more dyes and application of this technology to a textile dye wastewater that contains many dyes and varies in composition may pose practical difficulties. Moreover, such systems require an acclimatized microbial consortium, which could be time consuming under the event of constant product changes and batch dyeing operations prevalent in the dye house. Eliaz et al., (1997) reports complete biodegradation of the azo dye azodisalicylate under anaerobic conditions taking up to 50 days. Thus it is accepted that the azo dyes are non-specifically reduced under anaerobic conditions, but the slow rates at which many dyes react may present a serious problem for the application of anaerobic technology as a first stage in the complete biodegradation of these compounds. Therefore, it is significant to explore an alternative cost effective treatment option to achieve a faster and more efficient abiotic cleavage of azo linkages. Towards this direction, the second part of this study explores the possibility of utilizing the reduction chemistry provided by Zero Valent Iron (ZVI) in decolorizing azo dyes.

The first part of this study brings to light a host of various treatment options (both old and new) competing with one another to provide cost effective solutions for the dye-house towards effective colour removal. The number of different wastewater treatment methods that have emerged in the recent past is clearly indicative of magnitude of the problem and the
diversity of types of wastewater encountered. However, one major factor that offsets many of their applications is their associated costs for installation and maintenance.

Historically the Fenton’s reagent has been of interest mostly from a synthetic or a mechanistic perspective, for their relevance to enzyme reactions or free radical damage to cells. However, it is only recently that the potential of this seemingly simple reagent that generates highly reactive hydroxyl radicals at low temperature has attracted the attention of several researchers towards destruction of refractory organics. The second chapter of this study investigates the performance of Fenton’s reagent towards the oxidation of selected dyes that find wide application in the textile and carpet dyeing units (particularly in the Alapuzha District, Kerala).