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SEQUENTIAL ANAEROBIC-AEROBIC TREATMENT OF AZO DYE WASTEWATER

The content of this book is part of the thesis submitted in partial fulfilment for the award of the degree of Ph.D. of the Indian Institute of Technology Bombay

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ACRONYMS

ADMI	American dye manufacturing institute
AOP	Advanced oxidation processes
AQS	Anthraquinone -2-sulfonate
AQDS	Anthraquinone-2,6-disulfonte
COD	Chemical oxygen demand
CSTR	Completely stirred tank reactor
d	day(s)
DO	Dissolved oxygen
FAD	Flavinadeninenucleotide
FMN	Flavinmononucleotide
g	Gram(s)
GAC	Granular activated carbon
GDP	Gross development product
h	hours(s)
HRT	Hydraulic retention time
min	minute(s)
mL	milli liters
mV	milli volts
M	Molar
MLSS	Mixed liquor suspended solids
MLVSS	Mixed liquor volatile suspended solids
MMR	Maximum rate ratio
NAD	Nicotinamide adenine dinucleotide
NADPH	Nicotinamide adenine dinucleotide phosphate
nm	nanometer(s)
OLR	Organic loading rate
ORP	Oxidation-reduction potential
PAC	Powdered activated carbon
PVA	Polyvinyl alcohol
SBR	Sequencing batch reactor
SLR	Sludge loading rate
SRT	Sludge retention time
t	Time
TOC	Total organic carbon
TDS	Total dissolved solids
TMA	Total methanogenic activity
TS	Total solids
UASB	Upflow anaerobic sludge blanket
VSS	Volatile suspended solids

Chapter 1

Introduction

1.1 Background and motivation

Textile industry is the single largest foreign exchange earner for India. Currently it accounts for about 8 % of gross development product (GDP), 20 % of the industrial production and over 30 % of export earnings of India. About 38 million people are gainfully employed with the industry making it the second largest employment providing sector after agriculture (http://www.icmfindia.com/industry/india/index.asp).

Textile industry is classified into 3 main categories viz. cotton, polyester and manmade textile manufacturing. Among all the textile fibers cotton is widely used. There are more than 1000 textile mills mainly centered in Mumbai, Surat, Ahmedabad, Coimbatore, Delhi and Kanpur. The rivers such as Kulu near Mumbai, Ganga at Kanpur, Kali at Meerut (Uttar Pradesh), Hoogly near Calcutta, Cauvery (Tamil Nadu) and many more fresh water streams are seriously polluted by these textile industrial effluents which include wastes like metals (Cu, Zn, Pb, Hg, Cr, Co) and other organic and microbial impurities The main reason for this serious problem is that all these industries use the older conventional treatment technology consisting of chemical coagulation followed by activated sludge process, which makes them difficult to cope up with the change in the scenario of stringent new regulations on disposable limits which are improvised by the pollution control boards. Over the last five years several mills have closed or are on the verge of closure due to noncompliance with the state pollution control (Shailaja, 2005).

India has the largest cotton acreage in the world, and cotton is the dominant fibre in the Indian industry. Approximately 12.3 millions of 480 lb. bales of cotton were produced in India in the year 2000 and were around 14.1% of the total world production of cotton (http://www.icmfindia.com/industry/india/index.asp). Azo dyes are extensively used for dyeing of cotton. They comprise about 60-70% of the total dyes produced, i.e. around 26,000 in number and hence the largest group of synthetic colorants known (Mohan *et al.*, 2002).They are characterized by their typical nitrogen to nitrogen (–N=N-) bonds, which is highly electron deficient in nature. Due to the poor exhaustion properties of azo dyes as much as 40% of the initial dye applied remains unfixed and end up in effluents (Shah, 1998). As a consequence, they are the most common group of synthetic colorants released into the environment. They are synthetic in nature, have complex chemical structures, alien to the natural biotic environment and hence persist in nature. Azo dyes, on reductive cleavage of one or more azo groups form aromatic amine, which are generally, acknowledged being an animal carcinogen. Various experiments conducted on animals revealed the potential of azo compounds to cause cancer and reported to be carcinogens for human beings also. Among all types of dyes investigated, the toxicity of azo dyes on the *Bacillus cereus* and *Escherichia coli* cultures was found to be prominent.

Several countries due to its potential toxic nature have banned the use of azo dyes. Rao and Reddy (1996) have reported that dye had altered considerable physical and engineering properties of the soil. About 1000 mg/l of dye is present in a typical dyebath (Ince and Tezcanli, 1999). About 40-65 liters of wastewater is generated per kg of cloth produced. Dyeing, desizing and scouring processes are the major sources of water pollution in a textile industry. Apart from the aesthetic deterioration of the natural water bodies, they also cause harm to the flora and fauna in the natural environment. Rao *et al.* (1993) observed that the toxic nature of dye effluents cause death of soil microorganisms which may effect agricultural productivity. Some of the rare species of flora and fauna in the catchment area where dye effluents are discharged in Rajasthan state (India) was eliminated and also the vegetative cover of the catchment area is considerably reduced (Mohan *et al.*, 2002). Hence, it becomes imperative that dye is to be removed from the effluents before it is disposed off.

Wastewaters from a textile industry are complex waste products containing dyes, sizing agents, and dyeing aids that are characterised by their deep colour and high concentrations of environmental pollutants. Generally effluent is characterized by pH: 9.8-11, COD: 1300-2000 mg/l, TS: 4900-7000 mg/l and colour: 1500-4500 ADMI units (Neelima and Dilip, 1998). Colour and COD are the two parameters of importance and are to be taken care of in case of textile wastewaters. COD is mainly due to the usage of sizing agents like starch, polyvinyl alcohol etc. Colour is due to the use of dyes, pigments and pastes in dyeing and printing of yarns and fabrics.

Various physicochemical, advanced oxidation processes, biological processes and usually a combination of aforementioned treatment technologies are adopted to treat textile wastewaters to achieve the discharge limits and disposed off. In the past mainly chemical coagulation followed by Activated sludge process was adopted to treat the textile wastewaters. However azo dyes due to their hydrophilic nature and present in hydrolyzed conditions in wastewaters could not be removed by this technique. In general physicochemical methods and advanced oxidation processes are costly. Biological processes are cheaper than the others in investment and operation costs. Investment costs for biological processes range from 5 to 20 times less than chemical ones such as ozone or hydrogen peroxide. Meanwhile treatment costs range from 3 to 10 times less (Mario *et al.*, 1997).

Colour removal using pure cultures (algal, fungal and bacterial) is impractical, because to maintain them in the pure form on a large scale and actual field conditions is quite difficult. Due to the electron withdrawing nature of the azo dyes/ bonds they are not susceptible to oxidative catabolism (Knackmuss, 1996). However under anaerobic conditions, decolourisation of azo dyes and reactive dyes can be easily achieved (Carliell *et al.*, 1995). During anaerobic metabolism, in the presence of a labile carbon source, the azo bond is gratuitously broken, thus rendering the dye colourless, with the formation of corresponding aromatic amines. The aromatic amines thus formed are toxic to the anaerobic biomass, but