

Parameters Affecting Anaerobic Color Removal of Textile Wastewaters: An Overview

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Abstract: Release of colored wastewaters represents a major environmental problem worldwide due to the toxicity, mutagenicity and carcinogenicity of the dyes and their breakdown products. Therefore much attention has been focused on the effective treatment of dyes discharged from the dyeing and textile industries. The most widely used dyes in industries are azo dyes which require anaerobic and aerobic phases for their complete biodegradation. Color is removed under anaerobic conditions in which azo dyes act as electron acceptors. Further, aerobic conditions are essential for removal of breakdown products which are known to resist biodegradation under anaerobic conditions. Thus using both anaerobic and aerobic stages represents both decolorization and mineralization of azo dyes. Anaerobic stage is the first and the most important phase for color removal, however; decolorization can be affected by so many parameters such as; organic carbon source added, microorganisms selected, dye structure, cycle time, sludge age, and alternative electron acceptors involved. This review article summarizes the results of several research studies dealing with the factors affecting anaerobic color removal efficiency.

Introduction

Increased population and developments in industrialization have resulted in higher use of textile products leading to release of its huge amount of wastewaters to the environment. Actually the main problem related to the textile wastewaters is colored effluents. There are so many types of dyestuffs used in textile industry to give its color to the fabrics. Dye is the most difficult constituent of the textile wastewater to treat since they are synthetic and typically derived from coal tar and petroleum based intermediates. It is estimated that almost 10^9 kg of dyes are produced annually in the world, of which azo dyes represent about 70% by weight (Dos Santos et al., 2007). Azo dyes are characterized by nitrogen to nitrogen double bonds (N=N). The major problem associated with the dyes and their breakdown products is their toxicity, mutagenicity and carcinogenicity. Their discharge into surface water leads to aesthetic problems and adversely affecting to aquatic life. To overcome this problem, much attention has been focused on the effective treatment of dyes discharged from the dyeing and textile industries. There are many reports on the use of chemical and physical methods for color removal (Cooper, 1993; Hao et al., 2000; Dos Santos et al., 2007). The most commonly used chemical and physical treatment methods for dye-containing textile-processing wastewaters are chemical oxidation, chemical flocculation and settling, adsorption, membrane filtration and ion exchange. By these existing physical and chemical color removal methods, color is generally concentrated in the sludge or colored molecules are partly removed. Moreover, formation of large amounts of sludge and economical limitations presents disadvantages of these methods. Alternatively, biological methods are commonly considered to be the most effective treatment applications since they present lower operating costs and improved applicability (Shaw et al., 2002; Lourenço et al., 2001).

It is known that several microorganisms; such as fungi, bacteria and algae; can decolorize many azo dyes (Pandey et al., 2007). In this review we will focus on the bacterial decolorization. Bacterial decolorization applied for textile effluents are based on anaerobic and aerobic treatment. Under anaerobic conditions, azo dyes are readily cleaved generating aromatic amines. The required electrons are provided by electron donating carbon sources which can be glucose, acetate, volatile fatty acids (VFAs). Hence, azo dye acts as electron acceptor and organic matters act as electron donor under anaerobic conditions. Electrons released from oxidation of electron donor directly accepted by azo dyes which results in azo linkage and color removal. Although these process the

remove color of the wide range of azo dyes, they do not completely mineralize the aromatic amines generated in the anaerobic environment with few exceptions (Brown and Laboureur, 1983). However due to the carcinogenic effects treatment of the aromatic amines is essential. It is known that some of the aromatic amines can be biodegraded under aerobic conditions (Brown and Hamburger 1987; Seshadri et al. 1994; Carliell et al. 1995). Combination of anaerobic and aerobic conditions is therefore the most convenient concept for treating colored wastewaters (Haug et al., 1991; Zaoyan et al., 1992; Seshadri et al., 1994; Kudlich et al., 1996; Hu, 1998).

This review article summarizes the results of several research studies dealing with combined anaerobic-aerobic SBRs. Since anaerobic stage is the first and the most important phase for color removal, parameters affecting color removal should be determined to achieve desirable treatment. Therefore, this review study especially presents the problems dealing with anaerobic color removal. Anaerobic color removal can be affected by so many parameters such as; organic carbon source added, microorganisms selected, dye structure, cycle time, sludge age, and alternative electron acceptors involved. Therefore, factors affecting anaerobic color removal efficiency are briefly discussed in subsequent sections.

Factors Affecting Anaerobic Color Removal Efficiency

As mentioned before, anaerobic phase is the first stage of decolorization process starting with the formation of intermediary aromatic amines by reductive cleavage of the azo bond (Walker 1970; Wuhrmann et al., 1980; Haug et al., 1991; Blumel et al., 1998). The schematic diagram of enzymatic dye reduction is depicted in Figure 1. The research papers reviewed are proved that color removal is mainly associated with the anaerobic stage of the SBR, however; contribution of aerobic stage is almost none. Therefore, this review study especially presents the problems dealing with anaerobic phase of SBRs. Since most of the azo dyes can be decolorized under anaerobic conditions, anaerobic biodegradation seems to be nonspecific. Nevertheless; decolorization can be affected by so many parameters such as; organic carbon source added, microorganisms selected, dye structure, cycle time, sludge age, and alternative electron acceptors involved. Therefore, factors affecting anaerobic color removal efficiency are briefly discussed in subsequent sections.

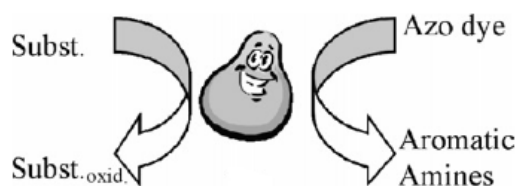


Figure 1. Enzymatic azo dye reduction, adapted from Subst., substrate or primary electron donor; Subst.oxid, products of substrate oxidation (Dos Santos et al., 2007)

Microorganism

In most of the reported processes of azo dye biodegradation, a wide range of organisms are found to reduce azo compounds such as bacteria, algae, and fungi. Azo dyes are generally known to resist aerobic bacterial biodegradation with the exception of bacteria with specialized azo dye reducing enzymes. Bacterial strains which can anaerobically reduce azo dyes, cannot utilize dye as the growth substrate, therefore; require organic carbon sources. There are only a few bacteria that are able to grow on azo dyes as the sole carbon source. Aromatic amines resulting from reductive cleavage of azo bond can be used as a carbon and energy source for bacterial growth. Like carbon source, a nitrogen source is also essential for decolorization process with exception of bacteria that can be used azo dyes as a nitrogen source. As reported before, ammonium chloride is the most suitable among all nitrogen sources for SBR studies, since nitrate is believed that it is a better electron acceptor than azo bond (Wang et al., 2008). Based on the previous publications, azo dye can be reduced by azoreductase-catalyzed reduction under anaerobic conditions. But still there is a speculation whether bacterial flavin reductases are responsible for the azo reductase activity observed with bacterial cell extracts. In a published report, it was reported that flavin reductases are indeed able to act as azo reductases (Russ et al., 2000). Bacteria produce extracellular oxidative enzymes which are relatively non-specific enzymes catalyzing the oxidation of a variety of dyes. It was reported that there are so many diverse groups of bacteria playing role in decolorization. It has been also reported that mixed microbial community could reduce various azo dyes and members of the *γ-proteobacteria* and sulfate reducing bacteria (SRB) were found to prominent members of mixed bacterial population by using molecular methods to determine the microbial population dynamics (Pandey et al., 2007).

Dye Structure

It appears that almost every azo compound that has been tested is biologically reduced under anaerobic conditions, nevertheless; though similar conditions were provided, different color removal efficiencies were achieved. This indicates that, dye structure is important when investigating biological color removal by SBRs. It was reported that metal-ion containing dyes can have adverse effect on decolorization efficiency (Chung et al., 1978; Brown and De Vito 1993). It has been also reported that azo compounds with methyl, methoxy, sulpho or nitro groups being less likely to biodegrade than the others with a hydroxyl or amino group (Zimmermann et al., 1982; Claus et al., 2002). Azo dyes with a limited membrane permeability such as; sulfonated azo dyes, cannot be reduced by intracellularly (Stolz, 2001).

Cycle Time

Though cycle time plays an important role in the SBR for the decolorization process, not so many reports are found in literature. The long retention times are often applied in the anaerobic phase of the reactor studies such as 18h, 21h. In several studies, it was reported that there is a positive correlation between the anaerobic cycle time and color removal (Kapdan et al., 2003; Albuquerque et al., 2005). Indeed, in combined anaerobic-aerobic SBRs, since bacteria shifted from aerobic to anaerobic conditions, or vice versa; anaerobic azo reductase enzyme can be adversely affected from aerobic conditions which are essential for aromatic amine removal, thereby resulting in insufficient color removal rate. To investigate the effect of cycle time on biodegradation of azo dyes, Çinar et al. (2008) operated SBR in three different total cycle times (48-h, 24-h and 12-h), fed with a synthetic textile wastewater. The results indicated that decrease in anaerobic cycle time, the system performance on color removal is not adversely affected; on the contrary, both color removal efficiency and COD removal efficiency are slightly improved.

Sludge Age

The sludge retention time (SRT) is known as very important operational parameter for color removal in SBR system. To obtain efficient color removal rate, adequate microbial population is desired. It was reported that 10 days sludge retention time remained insufficient to obtain adequate population, and to ensure the color removal, sludge retention time was increased to 15 day (Lourenço et al., 2001).

Redox Mediators

Since long retention times are often applied in the anaerobic phase of the SBR, it can be concluded that reduction of many azo dyes is a relatively slow process. Reactor studies indicate that however; by using redox mediators; which are compounds that accelerate electron transfer from a primary electron donor (co-substrate) to a terminal electron acceptor (azo dye), azo dye reduction can be increased (Keck et al., 2002; Kudlich et al., 1997). By this way, higher decolorization rates can be achieved in SBRs operated with a low hydraulic retention time (HRT) (Cervantes et al., 2001; Dos Santos et al., 2003). Flavin enzyme cofactors, such as flavin adenide dinucleotide (FAD), flavin adenide mononucleotide (FMN) and riboflavin as well as several quinone compounds such as AQS, AQDS and lawsone have been found as redox mediators (Semde et al., 1998; Cervantes et al., 2000; Rau et al., 2002a; Rau et al., 2002b). Though accelerating effect of redox mediators is proved, differences in electro-chemical factors between mediator and azo dye is limiting factor for this application. It was reported that redox mediator applied for biological azo dye reduction must have redox potential between the half reactions of the azo dye and the primary electron donor (van der Zee et al., 2003). The standard redox potential for different azo dyes is screened generally between -430 and -180 mV (Dubin and Wright 1975).

Alternative Electron Acceptors

Decolorization of azo dyes starts by reductive cleavage of azo bond. Electrons releasing from oxidation of organic compounds in the wastewaters goes through the azo dye and cleaves the azo bond. As anaerobic color removal occurs by the way of reduction of the azo dye which acts a final electron acceptor in the microbial electron transport chain, existing different electron acceptors in anaerobic zone can be assessed as limiting factor for the dye removal. Alternative electron acceptors such as oxygen, nitrate, sulfate and ferric ion; may compete with the azo dye for reducing equivalents, and resulting in insufficient color removals under anaerobic conditions. Electron flow preference as a function of the different electron couples is depicted in Figure 2. Among the electron acceptors involved in electron transport chain, oxygen is the most effective electron acceptor. Anaerobic reactors in full-scale treatment systems are designed as open to the atmosphere. The effect of oxygen entering anaerobic reactors through the surface is generally assumed to be negligible since surface area is small relative to

the reactor volume. Oxygen can get into the anaerobic reactors of waste water treatment plants with the mixed liquor recirculated from the aerobic zone and mixing. The impact of oxygen on anaerobic color removal efficiency becomes progressively larger when it is thought that oxygen is the most effective electron acceptor on the electron transport chain. Researchers have reported that decolorization is significantly affected from the, high-redox-potential electron acceptor, dissolved oxygen. This is because; released electrons by oxidation of organic compounds are preferentially used to reduce oxygen rather than the azo dye. Oxygen has an adverse effect on decolorization under anaerobic conditions, therefore; facultative or obligate anaerobes are necessary for azo dye reduction (Chang and Kuo, 2000). Inhibition of azo reductase activity by oxygen was also reported for *Pseudomonas luteola* (Chung and Stevens, 1993; Blumel et al., 1998). Indeed, NADH leads to bacterial biodegradation of azo dyes by acting electron donor. In the case of the fact that oxygen is the electron acceptor, the consumption of NADH by oxidative phosphorylation can adversely affect the enzymatic decolorization of azo dye. In a recent study results also suggested that the presence of oxygen inhibits azo decolorization when the dissolved oxygen concentration in the medium was higher than 0.5 mg/L (Xu et al, 2007). This is mainly due to the adverse effect of the molecular oxygen on anaerobic azo reductase enzyme.

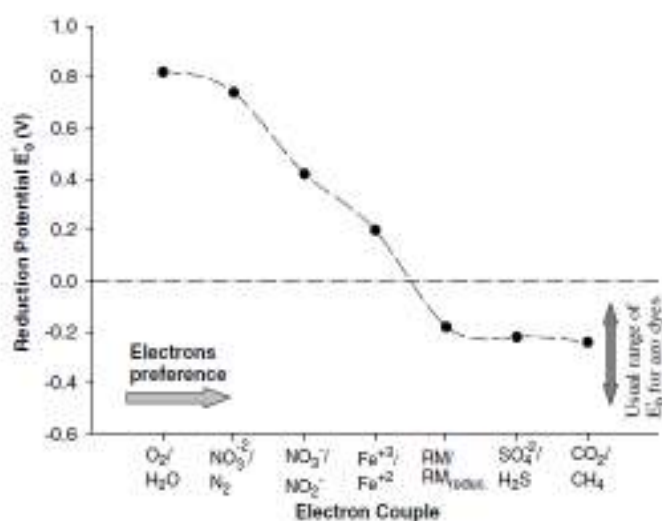


Figure 2. Electron flow preference as a function of the different electron couples, RM and RMred are the oxidized and the reduced form of the redox mediator, respectively (Dos Santos et al., 2007)

Among the electron acceptors involved in electron transport chain, nitrate is the second effective electron acceptor. Nitrate is normally found in textile processing wastewaters and generally coming from the salts such as, sodium nitrate which is included in dye baths for the improvement of dye fixation to the textile fibers. Nitrate concentrations used during textile processing can reach 40–100 g/l (Carliell et al., 1998). The importance of nitrate in anaerobic phase of SBR is that nitrate can compete with the azo dye for the reducing equivalents formed and resulting in decreasing decolorization (Carliell et al., 1995; Carliell et al., 1998, Lourenço et al., 2001; Panswad et al., 2000; Wuhrmann et al., 1980). Wuhrmann et al (1980) was reported that azo dye cannot be decolorized until denitrification ends up. Like nitrate, sulfate is also a constitute of textile processing wastewaters. Sulfate is generally added to the dye baths for ionic strength adjustment or it may be formed by the oxidation of sulfur species used in dyeing processes, such as sulfide, hydrosulfide, and dithionite (van der Zee et al., 2003). There are so many reports highlighting different effects of sulfate on azo dye degradation. It seems that in the presence of sulfate, decolorization may be rather stimulated than competitively suppressed (Carliell et al., 1995; Carliell et al., 1998; Panswad and Luangdilok, 2000; van der zee, 2003; Albuquerque et al., 2005). It was reported that when inhibiting sulfate-reducing activity of microbial population in SBR by the addition of molybdate, anaerobic azo dye removal efficiency is decreased. Indeed, since sulfate acts as an electron acceptor under anaerobic conditions, may compete with the dyes for the electrons available, thus causing an adverse effect on the decolorizing process. However; microbial population and sulfate concentration is also important for the reactions taking place during anaerobic phase. High sulfate concentrations are found to adversely affect decolorization unless sufficient amount of substrate is supplied to overcome the negative effects of elevated concentrations of sulfate (Cervantes et al., 2007). Furthermore; when sulfate is reduced under these conditions by sulfate reducing bacteria (SRB); sulfide, which is known as bulk reductant, is generated and can in turn serve as an electron donor. Sulfide generation is found to also contribute to the reduction of azo dyes. It is also reported that cofactors involved during microbial reduction of sulfate such as; cytochrome C3 (-205 mV) and NADH (-324 mV); have appropriate redox potential. Therefore, can channel the electrons to azo dyes.

Meanwhile, the redox potentials with more positive of the dye reduction than the redox potential of biological sulfate reduction (-220 mV) can be accelerated by sulfate. It was also reported articles that ferric iron can act as an electron acceptor under anaerobic conditions in which azo dye reduction occurs. Like sulfate, it was found that addition of ferric iron to the reactor stimulates the azo dye reduction. Indeed, the reactions are dealing with the redox couple Fe (III)/Fe (II) which can act as an electron shuttle for transferring electrons from electron donor to the electron accepting azo dye. Meanwhile, reactions of both reduction of Fe (III) to Fe (II) and oxidation of Fe (II) to Fe (III) facilitate the electron transport from the substrate to azo dye, thus acting as an extracellular redox mediator (Albuquerque et al., 2005).

Primary Electron Donor Type

Since anaerobic azo dye reduction is an oxidation-reduction reaction, a liable electron donor is essential to achieve effective color removal rates. It is known that most of the bond reductions are occurred during active bacterial growth (Nigam et al., 1996). Therefore, anaerobic azo dye reduction is extremely depended on the type of primary electron donor. It was reported that ethanol, glucose, H₂/CO₂ and formate are effective electron donors, contrarily; acetate and other volatile fatty acids are normally known as poor electron donors (Dos Santos et al., 2003; Tan et al., 1999; Pearce et al., 2006). So far, because of the substrate itself or microorganisms involved, with some primary substrates better color removal rates have been obtained but with others no effective decolorization have been observed. Electron donor concentration is also important to achieve higher color removal rates. Since there are so many reactions involved in bioreactor, competition for reducing equivalents by other reactions may increase the required amount of primary substrate. Though in theory the amount of electron donor per mmol monoazo dye azo is 32 mg COD, it was reported in a study that even if 60-300 times higher of the stoichiometric amount is used, more electron donor source is needed (O'Neill et al., 2000).

Dye concentration

In several studies, large variations in dye concentrations have been applied in the reactor studies and it was reported that dye concentration may play a role in the decolorization process. In the case of exceeding the reactor's biological azo dye reduction capacity, high dye concentration may adversely affect the dye removal efficiency and COD removal efficiency. Kapdan and Öztürk (2005) reported that increasing initial dyestuff concentration adversely affect the COD removal performance of SBR. Nevertheless; dye removal rate may be increased by increasing dye concentrations (Cruz and Buitron, 2001). Some of the reactor studies have been proved the possibility of azo dye toxicity to microorganisms involved in biodegradation. Though toxicity is related to dye concentration, dye type applied is also important (Luangdilok and Panswad 2000). Metal-complex dyes and reactive dyes are known to have toxicity effect on decolorization process from the literature (Libra et al., 2004).

Conclusion

Azo dye containing wastewaters seems one of the most polluted wastewaters which require efficient decolorization and subsequent aromatic amine metabolism. Based on the available literature, it can be concluded that anaerobic- aerobic SBR operations are quite convenient for the complete biodegradation of both azo dyes and their breakdown products. Nevertheless, like the other methods used for biological treatment, SBRs treating colored wastewaters have some limitations. Presence of forceful alternative electron acceptors such as nitrate and oxygen, availability of an electron donor, microorganisms, and cycle times of anaerobic and aerobic reaction phases can be evaluated as quite significant. Though treatment of azo dye containing wastewaters needs combined anaerobic-aerobic phases, microorganisms are subjected to continually alternating anaerobic and aerobic conditions. Thus, it is presumable that anaerobic enzymes involved in the azo dye reduction may be adversely affected from aerobic conditions, as well as aerobic enzymes involved in the aromatic amine mineralization may be adversely affected from anaerobic conditions. Since little is known about the regulations of the enzymes involved in complete biodegradation of colored wastewaters, this approach seems to need advanced investigation to improve color removal and aromatic amine mineralization.

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