

Azo Dye Decolorization By Chemical, Physical and Biological Techniques

Dr. Mark Moskovitz and Gary Witman, MD

The textile industry utilizes more than 10,000 different dyes and pigments, with the annual worldwide production nearing 2,000,000 tons. The azo class of synthetic dyes is by far the most commonly used dye, representing more than 50% of all dye production. There are more than 2000 structurally different azo dyes in commercial usage. Many different techniques are being used in an attempt to effectively and efficiently remove azo dyes from the wastewater effluents of the textile and other dye stuff industries, among which are the leather, food, cosmetics, color photography, pharmaceutical and paper product industries.

For both environmental and health reasons it is essential to completely remove these azo dyes before they reach the effluent stream going out to the discharge water supply as both the dyes and their intermediate degradation products are mutagenic and may become carcinogenic in anaerobic conditions. Significant amounts of these dyes are lost during the dyeing process. Depending on the class of dye, this loss in waste waters may range from 2% of the original concentration for basic dyes, to as high as 50% for reactive dyes, with an overall average loss of 15%. The azo dye containing effluent discolors the water and increases the biochemical oxygen demand of the contaminated water. (refer to previous technical paper Utilization of Specialized Activated Alumina for Decolorization by Moskovitz and Witman) creating anoxic conditions which may be lethal to aquatic species. The dye mass concentration from most azo containing wastewater discharge is in the range of 10-50 mg/liter of effluent.

Azo dyes are characterized by nitrogen to nitrogen double bonds (-N=N-). They contain at least one and up to four azo groups usually attached to two radicals of which at least one but usually both are aromatic groups. The color of azo dyes is determined by the azo bonds and their associated chromophores and auxochromes. The chromophore is a radical configuration consisting of conjugated double bonds containing delocalized electrons. An auxochrome is a functional group of atoms with nonbonded electrons which when attached to a chromophore alters both the wavelength and intensity of absorption, and as such is able to increase the color of any organic compound. Azo bonds are the most active bonds in azo dye molecules, which may be broken down through oxidation by hydroxyl radicals or reduced by electrons. The breakdown in these azo bonds leads to the subsequent decolorization of dyes.

However, because the goal in coloring is to provide color permanence azo dyes are manufactured to be resistant to biological attack, light, heat and oxidation. As noted above many processes have been investigated to clear up the color in textile wastewater. No one system has yet proven itself on an industrial scale to provide a satisfactory solution. Many physical and chemical methods may be expensive and may not be effective. The physical and chemical methods which have been used for azo dye removal include adsorption, coagulation and membrane processes. Membrane technologies are very effective, but utilize significant amounts of energy. Furthermore, the biological processes so far developed have been relatively ineffective.

Azo dyes are generally resistant to biodegradation due to their complex structures. Many different bacterial and fungal azo dye degrading microorganisms have been tested in an attempt to identify an affordable biological solution for the decoloration of azo dyes which may be accomplished within a time period of minutes to hours. Degradation of azo dyes by bacteria is obtained by bacterial azoreductase enzymes cleaving azo bonds, followed by primarily subsequent anaerobic degradation of resulting aromatic amines. Responsible bacterial DNA fragments have been isolated and azoreductase genes have been cloned. The bottleneck of this sequence is the anaerobic reduction, which is a slow process sped up through the use of catalysts such as quinones as redox mediators. The quinone redox mediators which are currently being utilized are 1,2-naphthoquinone-4-sulfonate (NQS) and anthraquinone-2,6-disulfonate (AQDS). The addition of immobilized quinones increases up to 8 fold the rate of decolorization, with these electron mediators transferring reducing equivalents from an electron co-substrate to the azo linkage.

Another biological approach which is being looked at on a large scale basis is the use of white rot fungi, with the non specific extracellular lignin modifying enzymes (LME) of these fungi capable of degrading many dyes. With fungi, decolorization occurs by aerobic ligninolytic degradation in association with lignin peroxidase. Unfortunately the long growth cycle of fungi and the moderate decolorization rate of fungi limit the usefulness of this technique.

Advanced oxidation processes have been addressed characterized by the production of hydroxyl radicals (OH⁻) as the primary oxidant. The Fenton reagent is an effective oxidizer, but it produces a substantial amount of Fe(OH)₃

precipitate as well as additional water pollution caused by the catalyst which has been added as a salt. Some investigators have attempted to use zero valent iron metal (Fe 0) but with limited success.

A superior system may lie in a two step approach using an initial polishing step with activated carbon, followed by the use of specially activated decolorizing alumina. The use of activated carbon lies in the ability to conduct electrons as well as being a redox mediator containing surface quinonic structures as well as other functional groups including aromatic rings. A high concentration of dye on the carbon surface helps electron transport from the electron donor acetate to the azo linkage since catalysis mostly takes place in the adsorption layer.

As discussed in our earlier paper the use of decolorizing activated alumina were initially designed for the color removal of the taxane compounds harvested from the bark and needles of the Pacific Yew trees. Modifications were made to the pore size, particle distribution and the pH of specially designed alumina. Subsequently it was determined that these modifications made for removal of color from taxane compounds were also appropriate for the removal of azo compounds.

The advantage of using activated alumina to bind and decolorize azo dyes lies in the amphoteric properties of alumina. Both acid and basic dyes are able to bind on to the same particle. This unique property of decolorizing alumina, coupled with the ability to reactivate alumina at temperatures in excess of 400 C and reuse the alumina makes this the most cost efficient method for azo dye extraction.

Additionally, the most effective method for industrial scale azo dye removal may lie in using a tandem reactor in which azo dye waste is removed in a two step physical process. In the first step activated carbon is used as a redox mediator and scrubber. Polishing is then accomplished using specialty activated alumina, with the effluent discharge void of color. This two step physical decolorization process is more cost efficient, safe and reproducible than any other commercially available processing method.

The advantages offered from using adsorption methods implementing activated alumina and activated carbon more than overcome any theoretical advantages which potentially could arise from use of bacterial or fungal based biological systems.