Textile dyeing and textile wastewater treatment

Advances In Textile Dyeing And Textile Wastewater Treatment Using Advanced Oxidation And Membrane Filtration Technologies: A Review

Introduction

The textile industry is a diverse sector in terms of production of raw materials, operating processes, product development, and equipment. The industry is well-characterized for consuming large amounts of water, energy, and discharging high volumes of waste in to public sewage treatment plants (STP). The main sources of pollution in the textile sector are derived from operating processes such as dyeing and finishing mills. These processes use considerable levels of water (ex. 70-150L for 1kg of cotton), chemicals (salts, alkali, wetting agents, etc.), and dyestuffs (e. g. reactive dyes) to achieve the desired properties of the textile product of which contribute to the pollution load in the industry. Major pollutants of environmental concern in textile wastewater include toxic organic compounds, color, suspended solids, and biochemical/chemical oxygen demand (BOD5/COD). The disposal of textile effluent in the municipal STP is an environmental concern because these industrial pollutants may pass through unchanged and enter the receiving rivers or streams potentially harming the welfare of aquatic life. The adverse effect of these pollutants on the aquatic environment include depletion levels in dissolved oxygen, reduction in photosynthetic activity, and increase susceptibility for organisms to acids and bases.

Effluent treatment technologies proposed in literature include activated sludge, coagulation, ozone, electrochemical oxidation and membrane filtration technologies . Conventional treatment methods such as coagulation and activated sludge have been used to manage textile wastewater to governmental standards for discharging in sewage treatment plants however these processes are ineffective for removing color from wastewater. Advanced oxidation processes such as electrochemical oxidation and ozone are alternative applications to effectively remove color and toxic organic compounds however some disadvantages include operating costs and possible production of chlorinated organic by-products in the receiving waters. Membrane filtration processes such as nanofiltration and reverse osmosis are promising technologies for an ecological friendly approach to treating textile effluent for reuse since it consumes less water and energy.

The aim of this review paper is to describe two novel methods for reducing pollution load in textile dyeing of cellulose fabrics. The first method is the use of cationic reagents as a pretreatment for cotton fibers to enhance dye fixation and the second method uses supercritical carbon dioxide (CO2) to replace water as a dye transfer medium. An overview on textile dyes, dye fixation, and dyeing process will be discussed. Furthermore, effluent treatment technologies such as coagulation, advanced oxidation processes (electrochemical oxidation and ozone) and membrane filtration technologies (nanofiltration and reverse osmosis) in which the mechanism and evaluated as promising applications for treating effluent water to be reuse in textile wet processing operations such as dyeing.

Textile Dyes And Dye Fixation

Dyes are described as colored substances with complex chemical structures and high molecular weights. By definition the color arises from the attachment of the auxochrome to the chromophore (light absorbing group) of the dyes that alters both the wavelength and intensity of absorption. Dyes manufactured for clothes makers are designed to have good light stability and chemical resistance to degradation, however due to the high solubility of dyes in water biological treatments are ineffective in removing color from the effluent. Wash fastness is an important factor to weigh into consideration when determining the durability of the product. It is dependent on the covalent bond strength between the fiber and dye against alkaline and acid hydrolysis, and the efficient use of water to remove unreacted dye from the substrate. The degree by which dyes are fixed on to fiber and get discharged into the treatment bath after wash-off is referred to as dye fixation. The influence of dye loss is attributed to several factors such as the type of dye, the depth of shade, application method, and liquid ratio (water/energy consumption).

Cotton and other celullosic fabrics are colored with reactive dyes because these dyes have good light stability and good wash fastness characteristics but poor dye-fixation yields (60-70%). Reactive dyes attach on the fiber via a covalent bond formation between the reactive group of the dye and the nucleophilic group in the fiber. The dye-fiber reaction is facilitated by large amounts of salt and electrolytes that reduce the charge repulsion forces between the negatively charge dye molecules and the negatively charge hydroxyl groups in the fiber as a result of the ionization of cellulose hydroxyl groups in water. However, due to the competitive reaction between the hydroxyl anions (OH-) in the alkaline bath and negatively charge dye molecules for the ionized hydroxyl groups in the cellulose fibers which are the nucleophiles for the dye-fiber reaction; approximately 40% of hydrolyzed (un-fixed) dye remains in the treatment bath at the end of dyeing process.

An extensive demand for wash-off is required to achieve the desired wash fastness characteristics on the product.

Textile Dyeing

Before the fabric enters the dyeing process it must be properly treated to remove all natural impurities and chemical residues applied during operating processes such as fiber production, and fabric weaving and knitting. The pretreatment process includes desizing, bleaching, and mercerization of which contribute nearly fifty percent of waste pollution generated by the industry. Conventional dyeing processes use large amounts of water nearly 100L of water per 1kg of textile. Water is a “ poor” medium for transferring dyes on to the fabric from an environmental point of view because of the increasing shortage of water available. Salts and alkali are added when dyeing cotton with reactive dyes in order facilitate the affinity for the dye molecules on the fiber. The treatment bath at the end of dyeing process is heavily polluted with toxic organic compounds, electrolytes, and residual of dyes of which can be expensive to recover and purify. Effluent disposal is the primary option since treated water to be reuse in the industry needs to have no color, no suspended solids, low COD, and low conductivity levels. Therefore, the development of environmentally safe production methods is challenging since both the wastewater quality and quantity depend to a considerable degree on the technique used for a certain substrate (fiber).

Influence Of Cationization For Dyeing Cellulose Fibers With Reactive Dyes

The influence of cationization for dyeing cotton with reactive dyes enables an environmentally friendly approach to increase dye utilization, lower water and energy consumption, and reduce effluent disposal/treatment.

Cationization of cotton is generally performed by introducing amino groups in the cellulose fiber through the reaction of the hydroxyl groups in the cellulose fiber and the reactive group (e. g. epoxy and 4-vinylpyridine) of the quarternary cationic agents. The pretreatment of cellulose fibers with reactive cationic agents will increase dye adsorption as a result of the columbic attraction between anionic dye molecules and nucleophiles on the substrate. The dye-fiber reaction can occur under neutral or mild acidic conditions without the use of electrolytes and therefore severe wash-off procedures can be eliminated since hydrolysis of dyes generally occurs in alkaline conditions.

EPTMAC, 2, 3-epoxypropyltrimethylammonium chloride, is an example of a quarternary cationic agent used in research studies to investigate the use of cationization for improving dye adsorption of cellulose with reactive dyes. Under alkaline conditions EPTMAC will react with alcohols to form ethers and thus produce a cationized fiber when it reacts with the methyl hydroxyl groups at the C6 position of the cellulose polymer. A combination of electrostatic interactions such as ion-ion or ion-dipole forces, intramolecular and intermolecular hydrogen bonds, and van der waal forces may influence the adsorption of the cationic group of the pretreatment agent to the anionic carboxylic groups in the cellulose fiber. The reaction between the reactive group of dye molecules and the amino-functional nucleophiles of the cationized fiber has been proposed by Blackburn and Burkinshaw (2003) to occur via a nucleophilic substitution mechanism or a Michael addition to a double bond.

Factors that appear to influence the cationic process of dyeing fabrics include cationic reagent concentration, dye concentration, and temperature. Kanik and Hauser (2004) demonstrated that increasing the cationic reagent concentration in the pretreatment solution caused a decrease in dye penetration of the substrate suggesting that an increase in surface coloration occurred as result of the strong ionic attraction of dye molecules for the cationic charges on the fiber. Montazer et al. (2007) reported that the color strength (K/S) values for dyeing with treated cotton with cationic process were often 2-4 times better than that of dyeing via conventional methods (K/S values range from 1-4). The effect of temperature influenced the percent of total dye utilization by increasing the absorption of cationic reagent for the substrate.

Subramanian et al. (2006) demonstrated that better color strength values (K/S value 12. 987) and maximum total dye utilization (T value 95. 1%) were obtained when 20% concentration of cationic reagent (CIBAFIX WFF), 10g/L of soda ash, and an optimal temperature of 70ºC was used as the cationization parameters. A substantial reduction in industrial pollutants such as BOD5, COD, and total dissolved solids were determined using cationic reagent CIBAFIX WFF compared to dyeing untreated fabric by conventional methods. Blackburn and Burkinshaw (2003) reported the pretreatment of fabric via cationization reduced the level of water consumption to nearly half of that applied during the normal dyeing process (<100L per 1kg of cotton fabric) of which generally is applied to remove un-reacted dyes from the fiber.

Textile Dyeing In SuperCritical Carbon Dioxide

Supercritical fluid technology is a promising application for the development of a water-free dyeing process in that it can be environmental friendly, energy saving, increase productivity, and eliminate effluent treatment and disposal. The beneficial properties of dyeing textiles in supercritical carbon dioxide (SC-CO2) are that it is expensive, non-toxic, non-flammable, CO2 can be recycled, and control in dye application rate. SC-CO2 exhibits densities and solvating powers similar to liquid solvents adding to its advantages in textile processing, since its low viscosity and rapid diffusion properties allow the dye to diffuse faster into the textile fibers.

SC-CO2 has been successfully employed as a solvent system in the dyeing and finishing processes for synthetic fibers such as polyesters. In polyester dyeing, SC-CO2 penetrates inside the fibers causing them to swell thereby making the fibers accessible to the dye molecules. As the pressure is lowered the dye molecules are trapped inside the shrinking polyester fibers and no waste is generated since the dye molecules cannot be hydrolyzed and no additional energy is required to dry the fabric after dyeing [18]. Since non-polar dyes are primarily used in supercritical CO2 dyeing further development is required to enhance the dyeing of natural fibers with ionic dyes such as acid dyes or reactive dyes because the affinity of natural textiles with dyes occurs by chemical (covalent bonds) interactions or fixed by physical (van der waals) forces. 20-21 Kraan et al. (2003) reported four factors that influence the role of supercritical CO2 dyeing for natural fibers "(1) dye solubility at operating pressure and temperature, (2) fiber accessibility to allow diffusion of dye molecules on substrate pores, (3) dye-fiber substantivity, and (4) the reactivity of dye with the textile."

Sawada et al. (2004) investigated the action of co-surfactant on the phase boundaries of the pentaethylene glycol n-octyl ether C8H5 reverse micelle using various kinds of alcohols and discussed he solubility of ionic dyes in the C8H5 reverse micellar system when co-surfactant density of CO2 and temperature are varied. The research strategy was to dissolve the ionic dye in a SC-CO2/reverse micellar system that involves dispersing a small quantity of water in SC-CO2 and co-surfactant suitable dye bath that contained conventional ionic dyes in SC-CO2. Alcohol, particularly 1-pentanol seems is a suitable co-surfactant to accelerate the solubilization of water in SC-CO2; it assists the formation of stable reverse micelles. Pentaethylene glycol n-octyl ether C8H5 as a surfactant is soluble in liquid and SC-CO2; the complex C8H5/CO2 system has a potential to enhance the solubility of water by an addition of co-surfactant in comparison with a typical reverse micellar system in organic media.

Beltrame et al (1998) investigated the effect of polyethylene glycol as a pre-treatment of cotton fabrics in SC-CO2 and the results showed that the dye uptake was strongly increased if cotton was pretreated with PEG. PEG is able to form hydrogen bonds with cellulose chains this prevents the complete deswelling of the fibers during the SC-CO2 treatment thus maintaining to cotton the more accessible to dyeing. At the end of the treatment however when the CO2 is evacuated the dyes migrate out of the polymer in the undissolved state through the polymer pores and washing fastness is consequently very low. In order to avoid these undesired effects benzamide which is soluble in SC-CO2 is a good solvent for disperse dyes as a synergistic agent; it is able to form hydrogen bonds with cotton and PEG thus favoring dye entrapment through the partial occlusion of cellulose pores. The results yield good dye uptake, light and wet-washing fastness are good increasing the durability of the product. Fernandez Cid et al (2005) prior to dyeing the cotton it was presoaked in a solution of methanol to swell the fibers. The methanol replaces the water in the cotton and will attach the cotton hydrogen bonds. The hydrophobic part of the methanol will make diffusion of hydrophobic non-polar reactive dyes into the cotton possible.

Application In Wastewater Treatments

The treatment of textile wastewater for reuse in textile operations represents an ecological and economical challenge since textile effluents vary in composition due to the different chemicals or physical processes used on fabrics and machinery. Textile pollutants of environmental concern include residual dyes, color, BOD, COD, heavy metals, pH, high suspended solids, and toxic organic compounds. 2 Typical effluents characterized in the textile industry and their measurements are presented in Table 1 [23].

Table 1. Effluent Characteristics of Textile Wastewater [derived from Kdasi et al., 2004]

Parameters	Values
pH	7. 0- 9. 0

Biochemical Oxygen Demand (mg/L)	80-6,000
Chemical Oxygen Demand (mg/L)	150-12,000
Total suspended solids (mg/L)	15-8,000
Total dissolved solids (mg/L)	2,900-3,100
Chloride (mg/L)	70-80
Total Kjeldahl Nitrogen	70-80

(mg/L)	
Color (Pt-Co)	50-2500

The removal of COD and BOD are important from an environmental point view since high levels can deplete the level of dissolved oxygen in receiving rivers causing an increased amount of non-biodegradable organic matter. 23 Some advantages and disadvantages for the various chemical-physical treatment processes applied for cleaning wastewater is listed in table 3 (edited from babu et al).

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