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## Impact of Dyes on the Chemistry of Water and its Implications: A Review

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**ABSTRACT:** The textile dye industry is widespread and is fundamental and essential as these provide employment to large population. On the other hand, the mixing of dyes in water may changes the chemistry of water and may cause other impacts to the consumers directly and indirectly. It is very difficult to separate dyes from water by using conventional techniques. An attempt has been made to review the impact of dyes and its impacts on the society with the help of existing literature.

**Keywords:** water, dyes, impacts, chemistry, dye industry

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### INTRODUCTION

The textile industry is one of the rapidly growing sectors of Jaipur's economy. It has the capacity to reduce unemployment and labour demands. Its processes are based on chemical reactions in liquid medium, thereby generating large volume of toxic wastewater. Some of the major processes include: Sizing- saturation of mainly hydrophobic wraps by high viscosity macromolecular solution using sizes like starch and desizing- removal of sizes from fabric using strong chemicals such as acids, bases or oxidizing agents (Babu *et al.*, 2007). Other important processes include bleaching-treatment of cotton and polyester to achieve a white absorbent fabric that is suitable for dyeing, printing and finishing (Babu *et al.*, 2007). The bleaching process uses oxidizing agents like chlorine and hydrogen peroxides. Dyeing and printing are achieved by the use of various types and colour of dye such as azo dyes and sulphur dyes.

Historically, the interiors of a home furnished in rich, deep colors indicate a great amount of affluence and high standing. Today, as in the past, warm hues lend a feeling of comfort and warmth to a home. The task of making clothing and home furnishings fell to the lady of a house, or on her servants, until the mid 1800s.

Fabric remains dating back to over 1000 B.C. have been identified as dyed using madder and cochineal (Wouters *et al.*, 1990) and colonists in America used plants such as indigo to color their garments (Edgar, 1998).

The ready-to-wear apparel industry is only about 180 years old. Records date clothing factories back only to 182 (Stamper *et al.*, 1988). As the responsibility for the making of clothing and textiles moved from within the home to factories, the stigmas and importance of color began to slacken. This is not to say, however, that colors do not have importance in society today. Recent studies have shown certain colors to give advantages to sports teams. For example, a study by Durham University found that, when other factors are equal, competitors wearing red had a considerable advantage in sporting events (Rincon, 2005). Also, certain hues denote feelings and power. Blue generally symbolizes peace and tranquility, while many men consider their red ties a "power tie".

#### *Techniques used to identify dyes in water*

In 1991 (Yinon and Saar 1991) used HPLC technique to analyze series of disperse dyes extracted from polyester and cellulose fibers, a basic dye from orlon fiber and a vat dye from denim.

Molecular characterization of each dye was obtained from the extract of a single fiber, 5-10 mm long. This was achieved by HPLC separation followed by mass spectrometry identification of the separated dyes. Davila-Jimenez *et al* (2002) exposed individually several textile dyes to electrochemical treatment. Chromaticity variation and the formation of degradation products were followed using UV spectrophotometer and HPLC techniques. The dyes studied belong to the azo, methine, indigo, and natural and arylmethane classes. Rafols and Barcelo (1997) developed new method for determination of the disulphonated azo dyes (Acid Red 1, Mordant Red 9, Acid Red 13, Acid Red 14, Acid Red 73, Acid Yellow 28, Direct Yellow 28, and Acid Blue 113) and of the monosulphonated azo dyes (Mordant Yellow 8, Mordant Black 11 and Mordant Black 17). The method is based on using liquid chromatography- atmospheric pressure chemical ionization (APCI), mass spectrometry (MS) with positive ion (PI) and negative ion (NI) modes of operation and liquid chromatography- high flow pneumatically assisted electrospray (ES) mass spectrometry with negative mode.

High fragmentation was observed when using APCI with losses of one or two  $\text{SO}_3\text{Na}$  groups, either attached to one ring or two different rings. Losses of Na and 2Na are common to all techniques used high flow ES was the most sensitive technique for all the dyes studied, except for Mordant Red 9 with a linear range varying from 1-3 to 700-800 ppb. APCI using negative ion mode was one order of magnitude less sensitive than ES, with a linear range varying from 50-70 to 2000-3000 ppb, whereas, positive ion mode APCI-MS showed the poorest linear range and sensitivity. The estimation of Direct Yellow 28 and Acid Blue 113 in water samples was also reported by pre-concentrating 500ml of water with solid-phase extraction followed by LC-high flow pneumatically assisted ES-MS.

Novotna *et al.*, (1999) developed a reversed-phase HPLC technique for identification and quantization of nine natural quinone dyes applied to historical textile fibers. A porous RP18e column was used with a convex gradient of methanol in a mobile phase of 0.1M aqueous citrate buffer (pH 2.5) and diode-array detection at 270 nm. For identification of alizarin, purpurin and xanthopurpurin, occurring together in the madder plant, an isocratic method was used with a methanol- 0.2M acetate buffer (pH 4.3) (75: 25) as the mobile phase. After an acid extraction of textile fibers and the analysis of the extracts, alizarin and

purpurin were identified and quantitated in three fibers. The limits of detection obtained are similar, ranging from 0.6 ppb (xanthopurpurin – isocratic separation at 254 nm) to 12 ppb (carminic acid – gradient separation at 270 nm). The repeatability is satisfactory, as typical RSDs (n=6) amount to 3.3% for the isocratic and 6.6% for the gradient elution separation. Perez-Urquiza, Prat and Beltran (2000) presented an ion-interaction high-performance liquid chromatographic method for quick separation and determination of the sulphonated dye Acid Yellow 1, and the sulphonated azo dyes Acid Orange 7, Acid Orange 12, Acid Orange 52, Acid Red 2, Acid Red 26, Acid Red 27, and Acid Red 88. RP-ODS stationary phase is used, and the mobile phase contains an acetonitrile-phosphate buffer (27: 73) mixture at pH 6.7, containing 2.4mM butylamine as ion interaction reagent. Good separations were obtained using isocratic elution and spectrophotometric detection at 460 nm. The detection limits for the eight dyes ranged from 7 - 28ppb for an injection volume of 100 $\mu\text{l}$ . This method allows the quantification of the studied dyes in spiked tap water samples in conjunction with solid-phase extraction. It allows the analysis of water samples containing between 0.3 and 1.2ppb of the studied dyes.

Fisher *et al.*, (1990) investigated the separation and identification of complex mixtures of natural and synthetic textile dyes using HPLC with diode array detection. Separation was carried out on a reversed phase column with acetonitrile-phosphoric acid gradient elution. The results showed that the anthraquinones from madder root and the insect dye cocheneal present in ancient red dyes can easily be distinguished from azo – dyes present in later textile fibers.

Tayem (2002) developed a simple HPLC method for quantitative determination of three dyes (Blue R Special, Red RB 198 and Yellow RNL 107). The HPLC method is based on using a mobile phase consisting of acetonitrile: water (60:40, v/v) containing 0.45M N-Cetyl-N,N,N-trimethylammonium bromide (CTAB) and buffered to pH=7.92, RP-C18 column was used with a flow rate of 0.6mL/min. The retention times for Blue R Special, Red RB 198 and Yellow RNL 107 were found to be 5.4 min, 7.8 min and 2.3 min with a range of a linear of 0.10-5.00ppm, 0.10-1.20ppm and 0.05-1.50ppm for the three mentioned dyes, respectively. The relative standard deviations were found to be (5.21%, 4.75% and 3.10%) for these dyes, respectively (n=3).

Zubi (2003) investigated the HPLC method for the determination of three dyes (Acid Orange 7, Acid Orange 10 and Acid Orange 12) and their retention times were found to be 2.8 min, 4.8 min and 3.1 min, respectively. Calibration graphs for the determination of the studied dyes were linear in the range 0.05-4.0ppm, 0.10-4.0ppm and 0.10-4.0ppm with relative standard deviation of 3.8%, 4.1% and 4.2% (n=3) and detection limit of 0.03, 0.05 and 0.05ppm, respectively. Bae *et al.*, (14) investigated the adsorption of three anionic dyes (Reactive Red 120, a monochlorotriazinyl red dye and Direct Blue 1) on cellulose from a neutral dye bath at 80°C over a wide concentration range of sodium sulfate using UV-Spectrophotometric technique. Harbin *et al.*, (1990) developed a novel spectro-photometric method to estimate the total amounts of textile dyes on air monitoring filters in industrial hygiene applications. The method was developed in response to the complexity of the samples and the low levels of dyes which were anticipated to be present. By measuring the total sample absorbance over the wavelength interval, an estimate of the quantity of dyes present can be determined from a Beer's law calculation using the average spectral absorptivity constant. Feasibility of the method was demonstrated on dye mixture solutions containing both 10 and 20 dyes, with as many as five different dye classes being present simultaneously. Dye recovery experiments established that the air filter extraction procedure produced recoveries in the 78-101% range for 40 to 160 µg total amounts. Simulated textile plant air filters were prepared which contained 18 dyes from three dye classes at levels ranging from 40 to 180 µg total amounts. After correcting for dye recovery, the total dye estimates were observed to have relative errors ranging from 0 to 24%. The primary factors affecting the accuracy of the total dye estimation method are the number of dyes in the mixture, the standard deviation, the spectral absorptivity constants, and the levels of dyes present on the air filter.

Govertet *al.*, (1999) reported a linear sweep and cyclic voltammetric studies of indigo, indanthrene dye and sodium dithionite in alkaline solutions. The results were applied to develop amperometric determination methods for these Vat dyes and reducing agent. On different electrode materials (Au, glassy carbon, Pd, Pt) the reduced dyes give an anodic voltammetric signal. Zanoni *et al.*, (17) determined two anthraquinone based chlorotriazine reactive dyes, Protion Blue

Mx-R (PB) and Cibacorn Blue 3GA (CB) at nanomolar level using cathodic stripping voltametry. When the differential pulse Voltammetric stripping mode is used no peak is obtained for the reduction of the anthraquinone moiety in these dyes, although the signal is present when the linear sweep mode is used. The absence of this peak in the differential pulse mode is believed to occur because, when this group is reduced in the adsorbed state on application of the potential pulse, it is reduced so rapidly that reduction is complete before the current is monitored at the end of the pulse. Siren and Sulkava, (1997) developed a capillary zone electrophoresis (CZE) method for routine screening of black reactive dyes and black acid dyes isolated from cotton and wool materials; detection was based on UV absorption. The electrolyte solution was 3-[Cyclohexylamino]-1-propane sulphonic acid buffer (pH 10.8), which was chosen to maintain the current at a low level under high voltages. Pretreatment of the cotton and wool samples involved extraction with NaOH or NH<sub>3</sub>. With the CZE technique the dyes were detected at very low concentration levels. The dye components were identified using a newly developed marker technique. The marker components for the calculations were UV-absorbing phenylacetic acid, benzoic acid and meso-2, 3-diphenylsuccinic acid.

Perez-Urquiz (2000) developed a method based on capillary electrophoresis coupled with photodiode-array detection to determine several sulfonated dyes including a sulfonated dye (acid yellow 1), and the sulfanated azo dyes acid orange 7, acid orange 12, acid orange 52, acid red 26, acid red 27 and acid red 88. A CElect- FS75 CE column is used. The electrophoresis buffer contains a 1:5 dilution of 10 mM phosphoric acid and tetrabutylammonium hydroxide buffer (pH 11.5), and 25 mM of diethylamine, the final pH being 11.5. The detection limits for the seven dyes ranged from 0.1 - 4.53 µg/ml.

Preisset *al.*, (2000) developed techniques using LC/NMR and LC/MS to characterize the organic constituents of industrial waste water with emphasis on polar, nonvolatile compounds. In the effluent of textile company, various compounds such as anthraquinone dyes and their by-products a fluorescent brightener, a by-product from polyester production and auxiliaries such as anionic and nonionic surfactants and their degradation products were identified.

### *Physico-chemical studies and implications*

Kavitha *et al.*, (2012) determined the behavior of various parameters of the pharmaceutical wastewater. The company produces bulk drugs, antibiotics, pain killers, food additives, personal care products and others. It is important for the industry to develop its own wastewater treatment system before discharging the effluent in order to meet the Karnataka State Pollution control Board (KSPCB) standards.

Soniet *et al.*, (2006) made a comparative toxicological studies of textile dye wastewater (untreated and treated) on a freshwater fish, *Gambusia affinis*, the study revealed a marked reduction in mortality and cytotoxic effects on RBCs, measured as reduction in their counts and percent changes in their shape (poikilocytosis) and variation in their size (anisocytosis), after subjecting them to both physicochemical and biological treatments. On comparing the data of mortality and the cytotoxic effects on RBCs, they found poikilocytosis is a better indicator for toxicity measurement of both untreated and treated wastewater, especially at their lowest concentrations where percent mortality was found to be either nil or lower than the percentage of poikilocytic RBCs.

Joshi and Kumar (2011) analyzed physico-chemical properties of soil of agricultural region and the water used for irrigation in Sanganer area of Jaipur. A wide variation in the physico-chemical properties of soil of agricultural region and the water in Sanganer area were found. The physico-chemical characteristics of the effluent water and soil samples adjoining the textile effluent, of agricultural region of Sanganer were found to have great variation in the physico-chemical properties. The pH of the effluents ranged from 7.6-7.9 and electrical conductivity from 3.5 - 4.55 mmhos/cm and temperature 25.0-29.0°C. Cations ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^{+}$  and  $\text{K}^{+}$ ) and anions ( $\text{HCO}_3^-$ ,  $\text{CO}_3^-$  and  $\text{Cl}^-$ ) concentration of the water also shows a wide variation. The pH of the soil samples ranged from 7.6 - 9.2 and EC from 0.83 - 1.20 mmhos/cm. organic carbon and organic matter of the soil samples were ranged from 0.18 - 0.42 and 0.31 - 0.72%, respectively. Values of nitrogen, phosphate and potash concentration in the soil samples were found to have great variability.

Prasad and Rao (2011) carried out physicochemical characterization of the textile industry effluent collected from Coimbatore in Tamil Nadu, India and Effects of physicochemical

parameters (pH, Temperature, Carbon and Nitrogen sources) on the Acid Red 128 decolorization by the selected bacterium were studied. Decolorization was effective at pH 8, 35°C with starch and peptone as carbon and nitrogen sources and in static conditions. This decolorization potential increased the applicability of this microorganism for the dye removal.

Simeonov *et al.*, (2003) studied the quality of surface water within a region is governed by both natural processes and anthropogenic effects like urbanization, industrialization, agricultural activities and human exploitation of water resource. The input of waste into surface water bodies has a negative impact not only on the aquatic life but also affects the self purification property of the water body. The effluents from industries have a great deal of influence on pollution of water body by altering the physical, chemical and biological nature of receiving water body. This further results in vast degradation of the surface waters and makes worse their use for agricultural, drinking, industrial, recreation and other purposes. Indiscriminate use of synthetic chemical dyes should be restricted or the workers while handling these dyes should at least take proper precautions.

The majority of dyes pose a potential health hazard to all forms of life. These dyes may cause allergic responses, skin dermatoses, eczema (Su and Horton: 1998, and may affect the liver (Jaskot and Costa, 1994), the lungs, the vasco-circulatory system, the immune system and the reproductive system (Nikulina *et al.*, 1995) of experimental animals as well as humans. Textile dyes have found to be toxic, genotoxic and mutagenic in various test systems.

Harbin *et al.*, (1990) developed a novel spectrophotometric method to estimate the total amounts of textile dyes on air monitoring filters in industrial hygiene applications. The method was developed in response to the complexity of the samples and the low levels of dyes which were anticipated to be present. By measuring the total sample absorbance over the wavelength interval, an estimate of the quantity of dyes present can be determined from a Beer's law calculation using the average spectral absorptivity constant. Feasibility of the method was demonstrated on dye mixture solutions containing both 10 and 20 dyes, with as many as five different dye classes being present simultaneously.

Pala *et al.*, (2003) investigated the decolorization of prepared aqueous solutions of three reactive azo dyes used in textile processing by adsorption on different types of powdered activated carbon (PAC). The color removal efficiencies and equilibrium adsorption isotherms for these three dyes (Remazol Gelb 3RS (yellow), Remazol Rb133 (red), Remazol Schwarz B133 (blue)) were investigated using five commercial powdered activated carbons and two other activated carbons prepared by physical activation of olive wooden stone (OWS), and solvent extracted olive pulp (OWSR). The equilibrium is practically achieved in 60 minutes while most of adsorption took place within the first 20 minutes. The color removal efficiency was found as high as 100% for the commercial activated carbons while 80% efficiency was obtained using the OWS and OWSR. Since OWS and OWSR are waste materials, their use in the synthesis of activated carbon production process will reduce solid waste pollution and raw materials costs.

Feng, Hu and Yue, (2013) developed a novel nanocomposite of iron oxide and silicate, prepared through a reaction between a solution of iron salt and a dispersion of a laponite clay for the photoassisted Fenton degradation of azo-dye Orange . It has been found that the H<sub>2</sub>O<sub>2</sub> concentration in solution, solution pH, UV light wavelength and power, and catalyst loading are the main factors that have strong influences on the photoassisted Fenton degradation of Orange .

Padmavathy *et al.*, (2003) attempted to degrade some reactive dyes aerobically. The organisms which were efficient in degrading the azo dyes Red RB, Remazol Red, Remazol Blue, Remazol Violet, Remazol Yellow, Golden Yellow, Remazol Orange, Remazol Black, were isolated from three different sources and were mixed to get consortia. The efficiency of azo dye degradation by consortia was analyzed in presence of various cosubstrates, such as glucose, starch, lactose, sewage and whey water, and their effects on dye decolorization have been studied. Bell and Buckley, (2003) investigated the decolorization of the dye CI Reactive Red 141 in a laboratory-scale anaerobic baffled reactor (ABR). The results of the physical decolorization tests suggested significant decolorisation due to adsorption to the biomass; however, it is possible that the dye chromophores were reduced due to the low redox potential environment within the test bottles. No dye breakthrough, due to adsorption saturation was observed during operation of the reactor.

Chemical oxygen demand (COD) reduction was consistently >90%. Color reductions averaged 86%. The biomass showed acclimation to the dye, with increased methanogenic activity with each increase in dye concentration. The reactor operation was stable, even with increases in the dye concentration. This investigation has shown that successful treatment of a highly colored wastewater is possible in the ABR.

Koyuncu, (2003) investigated the direct filtration of reactive dye house wastewaters by nanofiltration membranes based on permeate flux, and sodium chloride and colour removal. Experiments were performed using both synthetic and industrial dye bath wastewaters with the fluxes of the industrial dye bath wastewaters lower than those of the synthetic solutions. The effects of operating conditions such as pressure and pH were assessed.

The water quality of the Bandi river is under the stress of severe pollution due to discharge of effluents from more than 800 textile dyeing and printing industries located at Pali city. The river carries exclusively industrial effluents throughout the year except in monsoon period. The study revealed that the chemical parameters – COD (993 mg/L), suspended solids (800 mg/L), chloride (1702 mg/L), sulphate (943 mg/L), sodium (2163 mg/L) and Cr +6 (0.15 mg/L) have exceeded the maximum discharge limits laid down by Bureau of Indian Standards. A decrease in concentration of various pollutants downstream Pali during monsoon season was observed due to dilution of industrial waste waters by the flow of fresh water upstream of Pali city (Rathore 2011). However, excessive and indiscriminate use of dyestuffs has become increasingly a subject of environmental concern. These dyes can enter the environment through the industrial effluents of dye manufacturing plants and from textile dyeing and printing operations, as wastewater effluents. Assessment of genotoxicity of dyes is therefore of utmost importance. Short-term genetic bioassays have proved to be an important tool in such studies because of their simplicity, sensitivity to genetic damage, speed, low cost of experimentation and small amount of sample required. A total of 7 dyes were tested for their mutagenicity, by Ames assay, using strain TA 100 of *Salmonella typhimurium*. Only 1 dye, Violet showed absence of mutagenic activity. The remaining 6 dyes were all positively mutagenic.

Choudhary and Ohja (2011) argued that waste water from textile industries has a high PH, high temperature and a high concentration of organic materials. Removing Colour and organics from waste water is more important because the presence of small amounts of dyes is clearly visible and detrimentally affects into the water quality. In primary treatment process of textile based effluent, simple chemicals such as lime (10% sol.), iron salts (5% sol.), polyelectrolyte (0.1% sol.) gave good result and removed Colour, COD, BOD, TSS faster than physical processes. The analysis results according to Jar-test were depicted in the stage-wise performance of inlet and outlet effluent quality in ETP.

## CONCLUSIONS

The textile dyes are not threat to only the environment but a possible danger for the people that may use this water for drinking purposes. It may also cause negative impacts to the people who are directly and indirectly associated with this profession. Most of the studies indicated that there is appreciable change in the physical and chemical properties of water by different types of dyes. Hence, it is argued that dye effluent should not be discharged into the water bodies without proper treatment. He best option is to use the water for other purposes after proper treatment instead of discharging the dye effluent in water bodies.

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