

Chapter 5

Effect of Dyes on Water Chemistry, Soil Quality, and Biological Properties of Water

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ABSTRACT

As the textile industries use aqueous method for dyeing processes, the color that is released in the environment is associated with the incomplete absorption of dyes on fibres. So, there is a strong need to reduce the amount of residual dye in textile effluent. Large amounts of liquid wastes are produced from textile industries that contain both organic and inorganic compounds. The degradation of azo dyes is difficult using the conventional processes. These complex azo dyes containing N=N bond have been found to show carcinogenic evidences on reductive cleavage. Azo dyes have capability to alter physical and chemical properties of soil, causing harm to the water bodies. Dyes are toxic in nature, which is lethal for microorganisms present in soil affecting agricultural productivity. The presence of azo dyes in water decreases its water transparency and water gas solubility. This reduces light penetration through water, decreases its photosynthesis activity, causing oxygen deficiency and de-regulating the biological cycles of aquatic system.

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INTRODUCTION

The universal fact for all living or non-living being is; Water is life. But due to enhanced industrialization, this fact has spoiled. The water coming from industries contains lot of contaminants like acids, bases, toxic organic and inorganic dissolved solids, and colors. Among all the waste, most undesirable are colors caused mainly by dyes. The colored water is of no use for domestic or industrial needs. The waste of dyes are predominant complex waste of industrial wastewater. The dye containing waste-water is dark in color and also highly toxic that blocks the sunlight and affect our ecosystem adversely. Of all the dyes present, the contribution of azo dyes for commercial purpose is maximum in textile, plastic, leather, and paper industries as additives. In aquatic environment, the degradation and removal of azo dyes is highly important due to its toxic nature which affects the life of aquatic organisms. Every industry should have an important concern to use clean technology. In this chapter, we will discuss about the processes to decolorise waste water and also the new technologies for textile waste water decolorisation.

EFFECT OF DYES ON WATER CHEMISTRY

Textile wastewater has a major problem due to the presence of colored effluent. Although we can say that all dyes are not as much toxic but they have an adverse aesthetic effect because they are visible pollutants. The colored water reduces the entrance of sunlight into the water bodies affecting the aquatic life. In many cases, if the concentration of dye is present below 1 ppm, that produces an obvious water coloration. The source of major pollution of textile wastewater comes from the dyeing and finishing processes. The major pollutants include highly suspended solids (SS), biochemical oxygen demand (BOD), chemical oxygen demand (COD), heat, color, acidity, basicity and other inorganic contaminants. The water insoluble dyes or unreactive dyes like disperse and vat dyes, normally exhibit good exhaustion properties, like these types of dyes have fibre binding properties and can be removed by physical processes such as flocculation. On the other hand, if we have water soluble dyes or reactive dyes as effluents, the removal by conventional methods is not that much useful for color removal. The reactive dyes are colored molecules which are used to dye cellulose fibres generally characterized by N=N azo bonds. The azo bond gives color to azo dyes associated with chromophores. The process includes absorption of azo dyes onto the cellulose and further reaction with fibre. The reaction includes covalent bond formation between the dye molecule and the fibre which is much more resistant to unusual conditions. The reactive parts of the dye react with ionised hydroxyl groups on the cellulose substrate. But in alkaline

dyeing condition, the hydroxyl groups are present in the dye bath compete with the hydroxyl groups present on the cellulose fibre that results in the formation of hydrolysed dyes which no longer react with the fibre giving rise to a highly colored effluent. Therefore, it becomes crucial to find an appropriate and effective method of the treatment of wastewater to remove color from textile effluents. Currently, various methods have been used including chemical and physical processes, such as chemical precipitation and separation of pollutants, electrocoagulation, elimination by adsorption on activated carbon etc. But all these methods have a common drawback that they are not destructive instead they transfer the contamination from one phase to another causing a new type of pollution. It becomes necessary to find a new method for further treatment of these effluents (Slokar & Marechal 1998, Galindo et al. 2001, Tunay et al., 1996). Recently, an alternative to conventional methods, is “Advanced Oxidation Processes” (AOPs), which includes the generation of very reactive species such as hydroxyl radicals that has proved very useful for degradation of wide variety of organic pollutants (Kuo & Ho 2001, Legrini et al. 1993). The possible reaction pathways involving the attack of hydroxyl radicals onto organic compounds are: the electrophilic addition of hydroxyl radical to organic compounds (unsaturated or aromatic) that contain a π bond leading to the formation of organic radicals (Equation 1), the hydrogen abstraction by reaction of the hydroxyl radical with a saturated aliphatic compound (Equation 2) and electron transfer with reduction of the hydroxyl radical into a hydroxyl anion by an organic substrate (Bossmann et al., 1998, Tang 2004) (Equation 3).



The hydroxyl radical attack on organic substrates may be influenced by the presence of number of chemical species in water (or originating in the mineralization process), such as carbonate and bicarbonate ions. These ions can react with the hydroxyl radicals (Equations 4 and 5), hence competing with the organic substrates for the hydroxyl radicals.





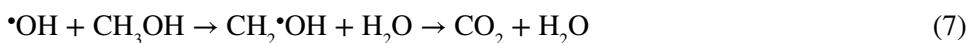
The chemical reactions of the hydroxyl radical in water are of four types-

Addition



The hydroxyl radical reacts with an unsaturated compound and forms a free radical intermediate which undergoes further reaction to form final product.

Hydrogen Abstraction



where an organic free radical and water are formed. Organic free radical undergoes further reaction.

Electron Transfer



where ions of a higher valance state are formed or an atom free radical, if negative ion is oxidized.

Radical Interaction



where two hydroxyl radicals react with each other or the hydroxyl radical react with an unlike radical, to combine or to disproportionate to form a stable product. In applying Fenton's reagent for industrial waste treatment, the conditions of the reaction are adjusted so that first two mechanisms (hydrogen abstraction and oxygen addition) predominate. Typical rates of reaction between the hydroxyl radical and organic materials are $10^9 - 10^{10} \text{ k (M}^{-1} \text{ s}^{-1}\text{)}$. Advanced oxidation processes

(AOPs) have been successful in treating most of the refractory organic compounds present in polluted water. The reason for the use of AOPs is due to the inability of conventional processes to treat highly contaminated toxic water (Movahedyan et al., 2009). Degs et al. (2000) used activated carbon Filtrasorb 400 (F-400) towards three highly used reactive dyes in the textile industry and investigated the removal efficiency of these dyes. The adsorption capacities for the anionic reactive dyes, namely; Remazol Reactive Yellow, Remazol Reactive Black and Remazol Reactive Red were determined by them. The data of calculated adsorption capacity showed high removal ability for these three reactive dyes and a distinguished ability for R. Yellow. F-400 showed a high adsorption capacity which was attributed to net positive surface charge during the process of adsorption. Surface acidity, surface basicity, H^+ and OH^- adsorption capacities for F-400 were also estimated. Daneshvar et al. (2003) found that a commonly used textile dye Acid Red 14 can be degraded photocatalytically by UV-C lamp (30 W) by using TiO_2 suspensions. It was found that when TiO_2 and UV light were used alone they had a negligible effect. A semi-log plot was drawn between concentration of dye versus time was found to be linear which suggests the reaction to be of first order ($K = 1.41 \times 10^{-2} \text{ min}^{-1}$). The other parameters like pH, TiO_2 amount and the concentration of dye before the experiment were also determined. The addition of hydrogen peroxide enhanced the rate of photodegradation of AR14 and the rate was inhibited by ethanol. Accordingly, it could be stated that the complete removal of color, after selecting optimal operational parameters could be achieved in a relatively short time, about 3.5 h. Daneshvar et al. (2004) also degraded acid red 14 (AR14) photocatalytically by ZnO. By using the technique of advanced oxidation processes (AOPs), zinc oxide was found to be more suitable alternative to TiO_2 for wastewater treatment. In the absence of ZnO, the rate of degradation efficiency was small and negligible in the absence of UV light. A linear semi-log plot of dye concentration versus time was resulted suggesting first order reaction ($K=0.0548 \text{ min}^{-1}$). In this also, they examined all the parameters. They found that if hydrogen peroxide is added in proper amount, the rate of dye degradation is enhanced but excess of hydrogen peroxide quenched the formation of hydroxyl radicals ($\cdot OH$).

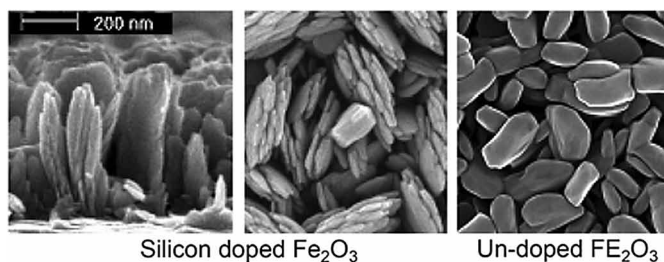
Degs et al. (2008) investigated the adsorption on activated carbon of various dyes namely, C.I. Reactive Blue 2, C.I. Reactive Red 4, and C.I. Reactive Yellow 2 from aqueous solution onto activated carbon keeping in different experimental conditions. The reactive dyes showed high adsorption capacity on activated carbon. The highest adsorption capacity of C.I. Reactive Blue 2, C.I. Reactive Yellow 2 and C.I. Reactive Red 4 dyes at pH 7.0 and 298 K, was found to be 0.27, 0.24, and 0.11 mmol/g, respectively. Giles and Smith classification indicated an L2-type isotherm and also the data showed good correlation with the Langmuir and Ferundlich isotherm models. The adsorption capacity was higher for acidic as compared to basic solutions

and also with the increase in ionic solution the removal of dye was increased. The thermodynamic study was done which indicated that the adsorption of dyes was an endothermic process. Ip et al. (2009) studied the adsorption of Reactive Black 5 dye, in a two stage activation process onto two bamboo based active carbons by using phosphoric acid and three conventional adsorbents, carbon F400, bone char and peat. Langmuir isotherm was used to determine the monolayer saturation adsorption capacities for this dye and was found to be: 176, 157, 7, 447 and 545 mg dye/g adsorbent for active carbon F400, bone char, peat, bamboo carbon (2123 m²/g) and bamboo carbon (1400 m²/g), respectively. A sodium phosphate salt was added to study its effect on the adsorption capacities which was found to increase for both bamboo carbons to over 900 mg/g. Habibi et al. (2005) investigated the photocatalytic degradation using TiO₂ in aqueous solution for these textile dyes namely C.I. Direct 80, 3BL, C.I. Direct Blue 160, RL and C.I. Reactive Yellow 2, and X6G. Optimized results were obtained by studying different parameters like oxygen effect, temperature, catalyst loading, UV-light irradiation time, solution pH and inorganic ions such as SO₄²⁻, Cl⁻ and NO₃⁻. The results of above investigation showed that by use of an efficient photocatalyst and using appropriate parameters leads to complete decolorization and decrease in chemical oxygen demand (COD) of dye solutions. Tang et al. (1995) also studied photocatalytic oxidation using TiO₂/UV slurry reactor for five dyes, namely Acid Blue 40, Basic Yellow 15, Direct Blue 87, Direct Blue 160, and Reactive Red 120. It was found that at all pH values Direct Blue 160 and Reactive Red 120 follows the Langmuir-Hinshelwood kinetic model, on the other hand, Acid Blue 40 fits the model at pH 3, Basic Yellow at pH 3, 5, and 11, and Direct Blue 87 at pH 7 and 9 only. When the dye solutions were studied at neutral pH 7, the rate of oxidation follow the order: Direct Blue 87 > Reactive Red 120 > Basic Yellow 15 > Acid Blue 40 > Direct Blue 160. They also studied the effect of Fe²⁺ and H₂O₂ on the reaction kinetics. Bi et al. (2011) in recent years reported that Ag₃PO₄ has an excellent photooxidative capability for dye degradation and O₂ evolution from water by using UV-visible light. They developed an easy route for fabrication of single-crystalline Ag₃PO₄ rhombic dodecahedrons with only {110} facets exposed and cubes bounded entirely by {100} facets in high-yield. When their photocatalytic study was done it was concluded that rhombic dodecahedrons exhibit much higher activities than cubes for the degradation of organic contaminants, the reason may be due to their higher surface energy of {110} facets (1.31 J/m²) than of {100} facets (1.12 J/m²).

Bokare et al. (2007) used Fe–Ni bimetallic nanoparticles for the degradation of Orange G, a monoazo dye. A nanocatalyst loading of 3 g/L showed complete dye degradation (150 mg/L) after 10 min of reaction time. In the degraded products HPLC-MS analysis showed that the synthesized nanoparticles reductively cleaved the azo linkage to produce aniline as the major degradation product. When the

study was done for 1-year-stored nanoparticles, an oxidative degradation of Orange G was observed. Surface chemistry plays an important role in directing the mode of degradation. The reductive dye degradation was proceeded by hydride transfer from nickel, whereas formation of a Fe^{2+} -Ni(0) galvanic cell in stored nanoparticles generated hydroxyl radicals from water in a non-Fenton type reaction. The latter were responsible for the generation of radical centers on the dye molecule, which led to a coupling-mediated oxidative degradation of Orange G. The generation of hydroxyl radicals is further substantiated with radical quenching experiments using ascorbic acid indicating that stored nanoparticles degrade Orange G through a predominantly oxidative mechanism. Zhang et al. (2013) studied the photocatalytic degradation of organic dyes using Graphene oxide/ZnO composites under UV radiations. They prepared composites of reduced graphene oxide/ZnO (RGO/ZnO) with different particles size of ZnO by solvothermal reaction of graphene oxide (GO) and ZnO in an ethanol-water solvent. It was observed that as compare to bare ZnO-S1 sample, the RGO/ZnO-S1 composite with ZnO particle size of 20–100 nm exhibits the enhanced photoactivity toward degradation of organic dyes and reduction of heavy metal ions Cr (VI) in water. However, when the particle size of ZnO is 50–500 nm in the composite RGO/ZnO-S2, it showed decreased photoactivity as compared to bare ZnO-S2. BY studying various characterization techniques, it was concluded that RGO/ZnO-S1 exhibits smaller particle size as compared to RGO/ZnO-S2 which leads to a more interfacial contact and a chemical bonding between RGO and ZnO-S1, and hence it increases the photoactivity. The hybridization of RGO with ZnO in an appropriate manner is able to significantly inhibit the well-known photocorrosion of semiconductor ZnO. This work can found applications of RGO/semiconductor photocatalysts in environment purification. Cesar et al. (2006) deposited thin, silicon-doped nanocrystalline $\alpha\text{-Fe}_2\text{O}_3$ films on F-doped SnO_2 substrates by ultrasonic spray pyrolysis and chemical vapor deposition at atmospheric pressure (Figure 1). At pH 13.6 the photocatalytic activity of these films were measred with regard to photoelectrochemical water oxidation. It was observed that silicon doping influences the morphology of the $\alpha\text{-Fe}_2\text{O}_3$ which in turn decreases the feature size

Figure 1. SEM images of silicon doped and undoped Fe_2O_3



of the mesoscopic film. The silicon-doped α -Fe₂O₃ nano-leaflets show a preferred orientation with the (001) basal plane normal to the substrate. The best performing photoanode would yield a solar-to-chemical conversion efficiency of 2.1% in a tandem device using two dye-sensitized solar cells in series.

Dong et al. (2007) investigated the use of inorganic salts for photocatalytic decoloration of three azo dyes, namely Mordant Black PV, Reactive Blue MS and Direct Sky Blue 5B, the salts used were sodium chloride, sodium sulphate, sodium nitrate and potassium chloride in water based on Fe(III)–oxalate complexes/H₂O₂ system in a specially designed photoreactor by UV–vis spectrum and TOC measurements. It was found that the degradation is limited in the presence of salts. As the concentration of inorganic salts increases in water it gives reduced decoloration efficiency and kinetic reaction constants of the dyes. The photocatalytic decoloration and degradation was inhibited by Sodium chloride and potassium chloride than sodium sulphate and sodium nitrate under the same reaction condition. Oladoja et al. (2008) investigated the importance of castor seed shell (CSS) for water remediation contaminated with Methylene Blue (MB). The castor seeds were thoroughly washed to remove any water extractable constituents, then re-grounded, sieved and used in series of agitated batch adsorption experiments. Freundlich and Langmuir isotherm models were used to study the equilibrium sorption. They observed that the sorption process of MB was done on heterogeneous surface of the CSS which comes out to be 158 mg/g obeying the pseudo-second-order kinetic model more than the pseudo-first order. This observation made them for further analysis using this kinetic model. The role of chemisorptions in the mechanism of sorption was established by an empirical relationship between the pseudo-second-order rate constant, K, and the initial MB concentration. The results of this relationship showed that pseudo-second-order chemisorptions are important in the sorption process. Namasivayam and Kavitha (2002) studied the adsorption of Congo Red by coir pith carbon using various parameters such as agitation time, dye concentration, adsorbent dose, pH and temperature. Both Langmuir and Freundlich isotherms were followed by equilibrium adsorption data following second-order rate kinetics. The adsorption capacity was found to be 6.7 mg dye per gram of the adsorbent. It was also observed that a range of acidic pH favoured the adsorption of Congo Red. According to the desorption studies done, it was found that chemisorption might be the major mode of adsorption. Chakraborty et al. (2011) studied the equilibrium, kinetics and thermodynamics of Crystal Violet (CV) adsorption onto NaOH-modified rice husk (NMRH). All the parameters were used like contact time, pH (2–10), adsorbent dose (0.5–5 g) and temperature (293, 303 and 313 K). It was found that the adsorption was favoured at higher pHs and lower temperatures and the data were well described by the Freundlich model that follows pseudo-second order kinetic model. The study of thermodynamic

parameters suggests that the adsorption is a typical chemical process, spontaneous and exothermic in nature.

Sun et al. (2011) prepared a magnetite/reduced graphene oxide (MRGO) nanocomposites using a simple one step solvothermal strategy by the use of cost effective and non-toxic precursors for the removal of dye pollutants. Graphene and magnetic nanoparticles when combined together have an advantageous efficiency in the treatment of wastewater. It was found that the efficiency of MRGO composites depends strongly on Fe_3O_4 loading and pH value. They had also used these nanocomposites in the treatment of industrial waste water and lake water. The results give a gist that the MRGO composites are effective adsorbents for removal of dye pollutants and thus could provide a new platform for dye decontamination. Expanding the application of high-strength hydrogels has attracted tremendous attention in the fields of biomedical engineering, agriculture and wastewater treatment owing to their versatility and outstanding deformation resistance. Cui et al. (2015) constructed a new class of graphene oxide (GO)/hydrophobically associated polyacrylamide composite hydrogels (GHA gels) by using one-pot method. Without using any cross linker, the GHA gels gets cross-linked by GO sheets and hydrophobically associated domains giving high mechanical strength, high toughness and have self healing ability and fatigue resistance. With the addition of GO sheets, this gel has improved adsorption capacity for removing dye from waste water. When heated with ethanol, the dyes removed from GHA gels rapidly and get dissolved in ethanol that can be used in next water purification cycle. Graphene oxide (GO) sheets possess highest adsorption capacity for removing organic dye contaminants from water bodies. Taking this as advantage, Guo et al. (2015) prepared GO/polyethylenimine (PEI) hydrogels as efficient dye adsorbents by facile method. The hydrogels were obtained by hydrogen bonding and electrostatic interactions between amine-rich PEI and GO sheets. The removal rates for dyes methylene blue and rhodamine B exhibit within about 4 h following the pseudo-second-order model. The adsorption of dye is mainly because of GO sheets whereas the PEI was added to improve the gelation process of GO sheets. The most important thing is that the dye-adsorbed hydrogels can be easily separated from an aqueous environment which suggests large-scale applications of the GO-based hydrogels for organic dye removal and wastewater treatment.

EFFECT OF DYES ON SOIL CHEMISTRY

The polluted waste water from industrial effluents adversely affects soil fertility and growth of plants. The substances dissolved in industrial effluents changes the physical, chemical and biological properties of water affecting their growth,

productivity, making them susceptible to various pathogen and destroy the food chain quality. Among all the polluted sources, the textile wastewater is said to be the most polluted source in both quantity and composition. This wastewater has been found to be toxic to several crop plants.

Ahmad et al. (2012) studied the industrial effluent that was used directly for irrigation at Bhairavgarh area, Ujjain city. The samples were collected from both contaminated and uncontaminated areas at 0-25cm depth for analysis. From ten different locations three sites were selected for collection of soil samples. For selected parameters, the wastewater was analyzed before irrigation which showed that the water was alkaline in nature. The results of soil samples indicated its neutral to slight alkaline nature. The concentration of cation and anion, organic carbon and organic matter were also shows a wide variation in contaminated soil samples as compared to uncontaminated samples. The investigation showed that continue use of waste water deteriorate soil quality in the area. Hardie et al. (2011) studied the effect of soil moisture on preferential flow in a texture-contrast soil by applying 25 mm Brilliant Blue dye tracer to soil profiles at high and low antecedent soil moisture. In the wet treatment, the dye tracer infiltrated to depths between 0.24 and 0.40 m, at an average rate of 120 mm h⁻¹. Whilst in the dry treatment, the same volume of dye tracer infiltrated to between 0.85 and 1.19 m depth at an average rate of 1160 mm h⁻¹. As a result of water repellency, in dry antecedent conditions, finger flow developed in the A1 horizon. In the wet treatment, the wetting front developed permutations but did not break into fingers. The flow rate in A2 was slower than A1 despite of similar particle size distributions due to the absence of macropores. In the dry treatment, the dye tracer ponded on the upper surface of the B21 horizon, which then spilled down the sides of the large clay columns as rivulets, at rates of between 2000 and 3000 mm h⁻¹. The dye tracer accumulated at the base of the columns resulting in backfilling of the inter column shrinkage cracks, at an estimated rate of 750 mm h⁻¹. In the subsoil, water movement occurred via shrinkage cracks which resulted in flow by-passing 99% of the soil matrix in the B21 horizon and 94% of the soil matrix in the B22 horizon. This knowledge could be used to: (i) improve irrigation and fertilizer efficiency (ii) explain variations in crop yield (iii) reduce salinity through improved leaching practices, (iv) reduce the risk of agrochemicals contaminating shallow groundwater. Heins and Flury (2000) studied that brilliant Blue FCF can be used as a dye tracer to stain flow pathways in porous media. In the solid phase the dye interacts in somewhat complicated manner as it is an ionic organic molecule. They investigated the suitability of Brilliant Blue FCF as a dye tracer in vadose zone hydrology. The main aim was to test the chemistry of aqueous solution on dye absorption spectra and also to analyse the effect of ionic strength and type of cations on dye sorption to soils. Langmuir model was confirmed by sorption isotherms. The soil sample having lowest pH and highest clay content found to have

substantial sorption. As the ionic strength increases it leads to sorption of Brilliant Blue FCF. The absorption spectrum of the dye is not sensitive to pH nor ionic strength. Flury et al. (1994) also studied that flow pathways of water and solutes in soils form distinct patterns, which are not a priori predictable. The primary cause is a macropore structure, but other factors like initial or boundary conditions can also influence a soil by producing bypassing of infiltrating water. The study was done to assess the flow pathways of water in different soils and to investigate the effect of initial water content on the flow pattern. They carried dye-tracing experiments in 14 different field sites which represent good portion of soils used for agricultural crop production in Switzerland. The site consisted of two 1.4 by 1.4 m plots, out of which for 2 months before the experiment, one was covered with a plastic roof to achieve different initial water contents. Then the Brilliant Blue FCF (C.I. Food Blue 2) dye was applied within 8 hours onto the plots with a sprinkling apparatus. The plots were excavated one day after irrigation and then the pattern of stained was examined on a vertical 1 by 1 m soil profile. It was found that the flow pattern showed spatial structure with remarkable differences. Like in most of soils, water was bypassed in the soil matrix. While in some soils, dye penetrated beyond 1 m depth whereas in others it remained in the top 50 cm. The bypass flow was more prone in structured soils, deep dye penetration and pulse splitting than nonstructured soils. Initially, the water content had less pronounced effect in some soils and no effect in others.

As it is clearly understood that water coming out from industries is major source of water pollution that generates a maximum quantity of chemicals including dyes. Direct discharge of this wastewater causes undesirable changes in the environment. The protection of environment is a major concern so researchers are trying to find out a novel method that can slow down the damage caused to the environment. Verma et al. (2012) investigated some novel pre-hydrolysed coagulants that helps in decolourisation of textile wastewater such as Polyaluminium chloride (PACl), Polyaluminium ferric chloride (PAFCl), Polyferrous sulphate (PFS) and Polyferric chloride (PFCl). Kasteel et al. (2002) studied that the food dye Brilliant Blue FCF is generally used as dye tracer in field studies to observe the flow pathways of water in soils. The other researchers found out that non-linear sorption is important for Brilliant Blue especially at small concentrations. Also, the rate of retardation increases with decreasing concentrations as well as with increasing ionic strength of solutions. They compared the movement of Brilliant Blue with that of bromide in field soil. It was assumed that Brilliant Blue does not follow the same flow paths as bromide. Valentine et al. (2006) screened single strains of nine white-rot fungal species for their ability to degrade polycyclic aromatic hydrocarbons (PAHs) in forest and salt marsh soils. Out of all, *Bjerkandera adusta*, *Irpex lacteus* and *Lentinus tigrinus* were proved to be excellent PAH degraders in both saline

and non-saline conditions. The three strains were tested to find out the salinity level and PAH concentration having negative effects on the ligninolytic activity of the fungi as measured by the anthraquinone dye Poly R-487. It was also observed that salinity characteristic of sea water have minimum effect on ligninolytic activity of *I. lacteus* and *L. tigrinus* as compared to *B. adusta* by salinity levels of 32‰. The statistical analyses confirmed that the decolorization rate varied with salinity and PAH concentration, and between fungi. Topac et al. (2009) studied that the involvement of organic dyes in soil via wastewater and sludge has been of increasing concern in developing or under-developed countries where the methods to remove this contaminants are very rare. Hence, they did an incubation study to investigate the sulfonated azo dye impact, Reactive Black 5 and sulfanilic acid, a typical representative of aromatic sulfonated amines, on soil nitrogen transformation processes. The result of this study indicated that nitrogen related processes in soil can be used as bioindicators of anthropogenic stress caused by organic dyes. It was found that urease activity, arginine ammonification rate, nitrification potential and ammonium oxidising bacteria numbers decreased in the presence of these dyes. It was concluded that the organic dye pollution restrict the nitrogen-use-efficiency of plants, thus further reducing the productivity of terrestrial ecosystems. Kolekar et al. (2008) isolated dye degrading bacterial strain identified as *Bacillus fusiformis* KMK 5 from the textile dyes contaminated soil of Ichalkaranji, Maharashtra, India based on the biochemical and morphological characterization as well as 16S rDNA sequencing. It was observed that KMK 5 tolerate and degrade azo dyes, Disperse Blue 79 (DB79) and Acid Orange 10 (AO10) under anoxic conditions. The complete mineralization of DB79 and AO10 was observed within 48 h. The degradation potential increases the applicability of this microorganism for dye removal. Licudine et al. (1997) investigated the use of extraction of xanthene dyes, phloxine B and uranine from soil by the use of supercritical fluid (SF) carbon dioxide (CO₂) modified by organic solvents and inorganic salts or chelating reagents Methanol (MeOH), n-butylamine (n-BA), and a chelating agent, ethylenediaminetetraacetic acid tetrasodium salt (Na₄EDTA), were found to be the most effective modifiers of SF CO₂ for quantitative recoveries of phloxine B and uranine in soils. At these supercritical fluid extraction (SFE) conditions, recoveries of related xanthene dyes (i.e., 2',7'-dichlorofluorescein, 4,5,6,7-tetrachlorofluorescein, eosin Y lactone, erythrosin B, and rose bengal) fortified at 25 µg/g in Hawaiian soils ranged from 65 to 93%. These mixture of dyes were separated by HPLC. A mixture of MeOH, n-BA, and sodium hexametaphosphate [(NaPO₃)₆] was effective for conventional solvent extraction of phloxine B and uranine from fortified soils. However, SFE was more selective and gave cleaner extracts. Recoveries were comparable to those by solvent extraction.

EFFECT OF DYES WASTE ON BIOLOGICAL PROPERTIES OF WATER

In textile waste water, dyes are considered as important pollutants. Globally, environmental problems associated with the textile industry are those associated with water pollution caused by the direct discharge of untreated effluent and release of toxic chemicals into the aquatic environment. It drastically decreases oxygen concentration in water body due to the presence of hydrosulfides and blocks the passage of light through water body which is detrimental to the water ecosystem. About 40% of globally used colorants contain organically bound chlorine which is a carcinogen. Heavy metals, present in textile industry effluent, are not biodegradable, hence, they accumulate in primary organs in the body and over time begin to fester, leading to various symptoms of diseases. Untreated or incompletely treated textile effluent can be harmful to both aquatic and terrestrial life by adversely affecting the natural ecosystem and causing long-term health effects (2017). Textile dyes have xenobiotic nature having aromatic structure and are non-biodegradable. These dyes are poisonous to flora and fauna because they reduce the penetration of light and create an obstacle in the process of photosynthesis. The textile industry uses mostly synthetic dyes derived mainly from intermediates of coal tar and petroleum. The dyes are available commercially in the form of powders, granules, pastes or liquid dispersions which are developed regularly for fulfilling the demands of latest technology, new fabrics, detergents, new dyeing machineries causing serious environmental concerns posed by some existing dyes. The dyes used by industry must be risen up to meet all these new and specific technical requirements and hence the consumption of these dyes is increasing through rapid changes. Having attached to toxic effects, these dyes can cause mutagenesis, chromosomal fractures, carcinogenesis, and respiratory toxicity. Hence, a focus should be made to bring specific techniques for the removal of these dyes from different kinds of wastewater streams.

Daneshvara et al. (2007) investigated the potential of *Cosmarium* species that belongs to green algae as a feasible biomaterial for treatment of triphenylmethane dye and Malachite Green (MG). The results of this study revealed the ability of this algal species in dye removal. The effect of other parameters like temperature, pH, dye concentration and algal concentration were also examined on decolorization process. The algal efficiency and stability was also examined in long term repetitive examinations. The correlation between decolorization rate and the dye concentration was also described using Michaelis–Menten kinetics. Hong et al. (2011) conducted a study on global pollution problem caused by textile industries creating impact on quality of water resources. As estimated by World Bank 17 to 20% of water pollution from industries comes from textile dyeing and treatment. Now a days, metal oxide semiconductors have been used in advanced oxidation process (AOP)

for the treatment of dye wastewater as it possess good degradation efficiency, low toxicity and physical and chemical properties. Hong et al. in their study discussed metal oxide semiconductors in which the semiconductors are generally divided into three categories: (i) titanium dioxide; (ii) zinc oxide; and (iii) other metal oxides (such as vanadium oxide, tungsten oxide, molybdenum oxide, indium oxide and cerium oxide). The synthetic wastewater treatment containing azo dyes was carried out by anaerobic biological method and chemical oxidation. Turgaya et al. (2011) conducted a study whose main target was to compare different treatment methods and to evaluate the effect of different parameters on effectiveness of treatment. Firstly in the microbial process, the results showed that with the increase in residence time, the yeast extraction amount and microorganisms addition that were growing originally on forest residues had positive effects on the dye removal. Secondly, in the catalytically wet peroxide oxidation process, CWPO, the condition of reaction were optimized at 0.5 g/L activated carbon loading with 2 mL H_2O_2 /300 mL solution at pH = 3. It was found that at optimum conditions approx. 93% of dye was removed. This CWPO process was originally tested with textile wastewater at these optimized conditions. The percentage of dye removal with this wastewater was 50%. An investigation on adsorption effect of the activated carbon was also done. The removal efficiency was found to be 15% at pH = 7 by just adsorption. At pH=3 i.e. in acidic conditions and at higher temperature the adsorption effect of activated carbon increased. The adsorption and oxidation efficiency were found to be compatible at 80 °C and at lower temperature, adsorption was found to be more effective than the oxidation. The study concluded that, the decolorization was found to be 60% by adsorption and 40% by oxidation.

Janosa et al. (2009) used spruce wood shavings from *Picea abies* for an adsorptive removal of both basic as well as acid dyes from waters. The properties of sorption were changed by modifying the sorbents with HCl, Na_2CO_3 and Na_2HPO_4 . The sorption ability was increased for the wood sorbents treated with alkaline carbonate solution as well as with phosphate solution for the basic Methylene Blue dye whereas when treated with mineral acid sorption ability was decreased for Methylene Blue to some extent. The opposite is observed for the sorption of the acid dye – Egacid Orange. At low pH it was observed that the sorption of basic dye was decreased in accordance to ion-exchange mechanism of the sorption. On the other hand, on increasing pH, the sorption rate of acid dye increases. Only minor effects were seen in the presence of inorganic salts as well as surfactants. Deniz (2013) investigated the capability of *Prunus amygdalus L.* (almond) shell for removal of dye methyl orange from aqueous solutions. The effects of pH, ionic strength, adsorbent concentration and mesh size, dye concentration, contact time, and temperature were evaluated for the removal of dye. It followed pseudo-second-order kinetic model. The thermodynamic analysis favoured the reaction to be spontaneous, favorable, and exothermic. Form the study,

a conclusion was made that almond shell is a low-cost adsorbent for removal of methyl orange from aqueous media. Yang et al. (2010) synthesized a novel dumbbell-shaped ZnO photocatalyst by microwave heating. The synthesized photocatalyst was analysed by using different techniques like X-ray diffraction (XRD), scanning electron microscopy (SEM) and UV–Vis absorption spectrum (UV–Vis) which indicated the photocatalyst to possess united dumbbell shape with 2 μm diameter and 5 μm length. Methylene blue dye was used to evaluate the degradation capability of this catalyst showing approx. 99.6% of decolorization at optimum condition. Also, the results showed that the degradation follows pseudo-first-order kinetics and the Langmuir–Hinshelwood model. Gupta et al. (2011) developed a mesoporous carbon from waste of rubber tyre for the removal and recovery of toxic azo dye, Acid Blue 113. They also determined the surface area, porosity, and density. At different parameters like pH, adsorbate concentration, sieve size, adsorbent dosage, contact time and temperature conditions, the adsorption of the dye over the prepared adsorbent and a commercial activated carbon was achieved. Thermodynamic parameters were calculated by applying Langmuir and Freundlich adsorption isotherm models. The kinetic studies followed first order kinetics for adsorption process and recovery of dye was done by eluting 0.1 M NaOH through the column.

Wang and Zhu (2005) investigated that NaOH modified fly ash samples were tested against methylene blue basic dye for adsorption in aqueous solution. The results indicated that the adsorption capacity was increased on sonochemical treatment of fly ash that depends on concentration of NaOH and treatment time. The adsorption tests showed that pH of solution and temperature of adsorption influence the adsorption behaviour. Salehia et al. (2010) prepared and characterize a novel biocompatible composite (Chitosan–zinc oxide nanoparticle) (CS/n-ZnO). They immobilized zinc oxide nanoparticles onto Chitosan. The textile dyes, Direct Blue 78 (DB78) and Acid Black 26 (AB26) were used as model compounds. They also studied the isotherm and kinetics of dye adsorption that followed pseudo-second order kinetics. It was concluded that the CS/n-ZnO is a biocompatible, eco-friendly and low-cost adsorbent and it might be a suitable alternative for dye removal from colored aqueous solutions. Bradder et al. (2011) prepared Graphite oxide (GO) by a modified Hummers–Offeman method and was tested as an adsorbent for the removal of dyes in aqueous solution. The GO structure was characterized by N_2 adsorption, X-ray diffraction (XRD), and Fourier transform infrared (FT-IR) spectroscopy. The GO structure does not showed any significant changes in surface area, on the other hand the layered graphene structure was expanded, and several surface oxygen functional groups were formed playing a significant role in adsorption. It was found that the dye amount adsorped on GO was much higher than that on graphite. The mechanism of adsorption was proposed as electrostatic attraction. Mittal et al. (2008) used bottom Ash and De-Oiled Soya as adsorbents for the removal of a hazardous

azo dye—Metanil Yellow from its aqueous solutions. By using Batch adsorption, kinetic studies and column operations extraction of lethal dye from wastewaters can be enabled. The data of adsorption equilibrium confirms both Langmuir and Freundlich isotherm models and also a monolayer coverage of dye over adsorbents. The saturation factors were found to be 99.15 and 99.38% for Bottom Ash and De-Oiled Soya columns, respectively. They also made attempts to regenerate the dye from the exhausted columns using aqueous sodium hydroxide as eluent. Kasgoz and Durmus (2008) prepared Acrylamide (AAm)-2-acrylamide-2-methylpropanesulfonic acid sodium salt (AMPSNa) hydrogel and AAm-AMPSNa/clay hydrogel nanocomposite having 10 w% clay by in situ copolymerization in aqueous solution in the presence of a crosslinking agent (N,N'-methylenebisacrylamide (NMBA)). Safranin-T (ST) and Brilliant Cresyl Blue (BCB) dyes were used to study the swelling properties and kinetics of the hydrogel. They also calculated the swelling and diffusion parameters in water and dye solutions. The study showed that the AAm-AMPSNa/clay hydrogel nanocomposite possess improved swelling capacity as compared to the AAm-AMPSNa hydrogel. It was also found that the diffusion mechanisms show non-Fickian character. Incorporating Clay into the hydrogel structure not only increases the adsorption capacity but also the adsorption rate. It was found that the adsorption of dyes by the hydrogel nanocomposite completed in 10 min while the AAm-AMPSNa hydrogel adsorbed dyes approximately in 90 min. It was found that the adsorption kinetics of hydrogel nanocomposite followed a pseudo-second-order model also the Langmuir model fits the adsorption data better than the Freundlich model.

Das et al. (2010) investigated bioaccumulation of synthetic dyes viz. Acid Blue 93, Direct Red 28 and Basic Violet 3 by growing cells of yeast, *Pichia fermentans* MTCC 189 in growth media prepared from sugarcane bagasse extract. At pH 5.0 they found maximum dye bioaccumulation. They used two kinetic models viz. Noncompetitive and Uncompetitive models for the determination of toxic effects of dyes on the growth rate of *P. fermentans* MTCC 189. Basic Violet 3 was found to be more toxic than the other two dyes. The optimum conditions predicted that *P. fermentans* MTCC 189 have the capability of bioaccumulating Basic Violet 3 dye upto 69.8%. Gamra and Ahmed (2015) presented a simple and successful route to synthesize titania nanoparticles by controlled sol-gel progress. To increase the surface area chitosan as bio-template was involved in the progress of preparation and manipulated the defined particle and pore structure. XRD and TEM were used to study the crystalline behavior and the nanostructure nanoparticles. The crystalline results indicated the existence of anatase phase revealing the role of chitosan in stabilizing titania nanoparticles and stop the growth of these particles into rutile phase. It is obvious to notice that a change in sample crystallography from anatase to completely amorphous nanoparticles upon adsorption of malachite green dye

indicates a strong adsorption of this dye that destroys the crystalline feature of titania sample. The enthalpy change (ΔH°) value for malachite green dye indicated the removal process to be endothermic and follows pseudo-second order rate equation and the negative values of standard free energy (ΔG°) suggest that the adsorption process to be spontaneous.

REMEDIATION OF TEXTILE DYES WITH BIOLOGICAL AGENTS

Faraco et al. (2009) evaluated the effect of *Phanerochaete chrysosporium* and *Pleurotus ostreatus* whole cells and their ligninolytic enzymes on models of colored industrial wastewaters. They defined the models of acid, direct and reactive dye wastewaters from textile industry. It was found that *Phanerochaete chrysosporium* has provided an effective decolorization of about 45% in one day of treatment and within 7 days the decolorization rate was reached upto 90%. On the other hand *P. ostreatus* decolorizes and detoxified acid dye wastewater model upto 40% in only 1 day and 60% in 7 days. Alvarez et al. (2013) proposed a novel remediation strategy that consists of sequential biological and physical process for the removal of textile polluted effluent. They proved the decolorization ability of *Anoxybacillus flavithermus* in an aqueous effluent containing Reactive Black 5 and Acid Black 48. In less than 12 h, the decolorization efficiency was reached almost 60% which points out the suitability of the selected microorganism.

Azo dyes are considered as major chemical in textile industrial wastewater and its remediation before it reached to agricultural land is important for the safety of surrounding environment. Darwesh et al. (2014) focused on the isolation, screening and azo dye removal by bacteria which was isolated from dumping site of textile wastewater. They teste total 14 isolates in their study. Out of 14, one was most efficient in decolourization of RB dye which was identified by 16s DNA sequences to *Pseudomonas aeruginosa* strain. Mullan et al (2001) also investigated the bioremediation to degrade textile dyes by using microorganisms such as white-rot fungi and anaerobic bacterial consortia. Wafaa and Rahim (2006) worked on the removal of direct and reactive dyes using biotic and abiotic agents. They investigated the removal of dyes using sugarcane bagasse, sawdust, rice straw, charcoal and fungal biomass as dye removing agents. They used seven fungal strains for the removal of textile dyes. It was found that after 2h of incubation *Penicillium commune*, *P. freii*, and *P. allii* removed 96, 64 and 65%, respectively, of direct violet dye. Rice straw was also found to be more efficient in dye removal, than was bagasse or sawdust. Rice straw was effective in removing 72% of direct violet dye within 24 hours.

CONCLUSION

The water from textile industries which is discharging directly into the natural water bodies is a serious threat not only to the environment but also to the human life for the people who may use this wastewater for drinking purpose. This wastewater also leaves a negative impact on the people who are directly and indirectly associated with this profession. The study by far has proved that the chemicals present in wastewater containing dyes causes appreciable changes in the physical and chemical properties of water. Hence, it is a matter of great concern that the industrial effluents should not be discharged directly into the water bodies without proper treatment.

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KEY TERMS AND DEFINITIONS

Advanced Oxidation Process (AOPs): Advanced oxidation processes (AOPs) are a set of chemical treatment procedures designed to remove organic or sometimes inorganic materials in water and wastewater by oxidation through reactions with hydroxyl radicals (OH).

Azo Dyes: Azo dyes are organic compounds, which contain the colouring azo function (N=N) which is often bound to an aromatic ring.

Biological Oxygen Demand (BOD): Biological Oxygen Demand (BOD) is the amount of dissolved oxygen needed by aerobic biological organisms to break down organic material present in a given water sample at certain temperature over a specific time period.

Chemical Oxygen Demand (COD): Chemical oxygen demand (COD) is a measure of the capacity of water to consume oxygen during the decomposition of organic matter and the oxidation of inorganic chemicals.