



Hazardous consequences of textile mill effluents on soil and their remediation approaches

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ABSTRACT

Untreated textile mill effluents are major concern as they associate with various hazardous problems for eco-systems and human health. Complex effluent having a number of dyes, metal contaminations and other organic agents used for softening, printing, heat stabilizing can accumulate in natural sources; soil and water if disposed off without treatment or after in complete treatment. Soil is loose material found on the surface of the earth that importantly offers anchorage for plant, hold water and nutrients. Presence of xenobiotics elements in open and partially covered pits left behind by industrial or domestic activities alter chemical and physical properties of arable soil. This article is mainly focusing the effects of textile mill effluents on soil and their remediation approaches. Bioremediation process is a simple which requires almost negligible energy and very less amount of chemical. This process can be efficiently used in rural areas. This paper gives a review of several researches conducted in the past.

1. Introduction

In the current era, with the advent of xenobiotic chemicals several negative consequences are seen on the eco system. They pose danger to the flora-fauna, microorganism and also to the health of the people. Such pollution is typically caused by industrial wastes; pesticides, insecticides, fertilizers, heavy metals, petroleum hydrocarbon, polycyclic aromatic hydrocarbon, solvents and colored effluent disposed of untreated or after incomplete treatment.

Soil plays a vital role in ecosystem. Complex composition of inorganic component (minerals) derived from disintegrated rocks, humus, water etc. Conjointly influence the properties of the soil. The standard American Society for Testing and Materials (ASTM) version of the Unified Soil Classification System has categorized soil on the basis of grain size and texture in clay, gravel, organic clay, organic slit, peat, sand and silt (ASTM, 2017). Clay fraction has high surface area and holds many chemical and physical properties of arable soil. Whereas, sand and silt fractions primarily control the physical character. In contrast to minerals, soil consists mainly of primary (chemically unaltered) and secondary (chemically altered) rocks, silicates and

non-silicates, crystalline and non-crystalline minerals (Schulze, 2002).

Along with this, soils offer anchorage to roots, clench water and nutrients as clichéd “we build on soil as well as with it and in it”. The concentration of the heterogeneous substances vary due to many factors such as metals, chemicals (monomer, solvents, reactive initiator, dyes/pigments) leaching from municipal, chemical industries, accidental spillage and underground leakage that cause soil pollution (Calacea et al., 2005). These problems are of major concern as the contaminated sites are significantly expanding and become appealing. In the United States, more than 40,000 sites were found to be contaminated with the above contaminants, according to a report by the Environmental Protection Agency (EPA) (Sharma and Pandey, 2014). Zhao et al. (2016) studied the status of soil in China based on nationwide survey, they concluded that 16% of soil samples and 19% agricultural soil do not stand over the China’s soil environmental quality limits. Although metals have bio-importance in trace amount but their excessive concentration is of great concern. Nahmani and Lavelle (2002) found that heavy metal enriched soil adversely affects the density of earthworms in grassland of Northern France.

Likewise, dye contamination in water and soil is a visual sign of

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pollution. Dyes are mainly used in the paper, textile, rubber, plastic, drug and cosmetic industries, paints, printing inks, art and craft, leather, food etc. Baocheng et al. (2008) reported huge azo dye contamination in soil and water resources in China. Application of sewage sludge on land and long-term irrigation of agricultural fields from natural streams polluted with textile effluent also account for the movement of organic dyes into agricultural soil. At present, there is more than 1.0×10^5 commercially available dyes globally and further, more than 7.0×10^5 t are produced every year (Markandeya et al., 2018, 2021). A survey carried out by Ecological and Toxicological Association of the Dyestuffs (ETAD) had mentioned that 90% of some 4000 dyes showed LD50 values more than 2 g kg^{-1} (Nair et al., 2014). The excessive concentration of pollutants in soil consequently reduces fertility and quality of soil and ingress in food web. So, it is worth mentioning their direct or indirect effect on human race. Since the soil pollution through effluents and sludge applications is widespread, there is an urgent requirement of simple remediation approaches in developing and under-developed nations.

2. Textile mill effluent composition

In textile mill, fabrics were processed out through various processes such as sizing, desizing, weaving, scouring, bleaching, mercerizing, carbonizing, fulling, dyeing and finishing that merge extreme diversity in raw materials (Correia et al., 1994; Tiwari et al., 2015). Sizing is applied to change the absorptive properties of fabrics by using surface sizing or internal sizing agents such as gelatin, starch, polyvinyl alcohol, polyvinyl acetate, acrylic co-polymers, alkyl succinic anhydride, alkyl ketene dimmer and rosin (Reddy et al., 2014). Bleaching agents such as sodium hypochlorite, sodium chlorite, calcium hypochlorite and hydrogen peroxide are used to remove the unwanted color or deintensifying color. Bleached effluent contains high oxygen content with low biochemical oxygen demand (BOD) due to presence of highly oxidizing agents.

Zhang et al. (2012) studied the toxic effects of dye components coexisting with oxidants present in textile wastewater in zebra fish and interpreted the reduction in quantity of enzymes superoxide dismutase and glutathione-S transferase activities and further emphasized on the cytotoxicity and genotoxicity due to production of reactive oxygen species. Thereby, processed wastewater has increased levels of BOD, chemical oxygen demand (COD) and total solid sediments due to variety of operational conditions. The drain wastewater is responsible for blocking of the soil pores, which results in loss of soil productivity (Kant, 2012). Dyes alone are not hazardous to environment and human health, the supplementary substances in dyeing process such as chlorinated solvents; trichloro-ethane, used to remove oils, gums, lubricants, dust, dirt and other impurities in scouring process, are highly prone to causing damage to the central nervous system of human. A range of heavy metals are also used in textile dyes. Antimony (Sb) can be naturally present in cotton, synthetic fibers and leather. Some dye fixatives such as chromium (Cr) are also used to introduce color fastness and form coordination with dye to attach to fabrics. Cadmium (Cd) is applied to natural, synthetic fibers and leather that are considered as carcinogens including lead (Pb) and Cr (VI). Nonylphenol ethoxylates are industrial detergents applied as emulsifiers, dye-dispersing agents for dyes and prints that degrade into nonylphenol, can impair human fertility and can even be fatal. Nonylphenol has been subjected to an EU-wide ban since 2005. In mercerizing, cotton is treated in NaOH bath and finally neutralized with acid, which affects the pH of generated wastewater. Fulling wastes are largest sources of BOD arising from soap, detergents and lubricants. In contrast to fabrics; dyeing polyester and polyester blend dyeing carrier such as chlorobenzene are also applied as degreasers and insecticides. Chlorobenzenes are highly toxic to hepatic, thyroid and central nervous system and are restricted under EU law and cannot be used in the production of apparel above the concentration of $1.0 \times 10^{-3} \text{ g kg}^{-1}$. Phthalates used in printing and softening process can impair

reproduction and fertility. Organotin compounds are applied in apparel to prevent body odor. They also act as heat stabilizer and biocides. These organotin can affect immune system and reproductive system. Formaldehyde is used as a finishing agent in textile resins which facilitates easy care but harms the mucous membranes and respiratory tract. Table 1 summarizes the chemical agents used in different operations conducted in textile mill.

2.1. Dyes: definition and classification

Dyes are mainly conjugated aromatic structures comprising of two key components: chromophore group and auxiliary functional group to hold fibers. A chromophore is a radical configuration which consists of conjugated double bonds having delocalized electrons. Some examples of common chromophoric configurations include azo (-N=N-), carbonyl (=C=O), carbon (=C=C=), carbon-nitrogen (<C=NH or -CH=N-), nitroso (-NO or N-OH), nitro (-NO_2 or =NO-OH) and sulfur (C=S). The chromogens are aromatic structures which normally contain benzene, naphthalene and anthracene rings, comprising of chromogen-chromophore structure accompanied by an auxochrome. Due to the presence of ionizing groups known as auxochrome, there is a much stronger change in the maximum absorption of the compound and provides bonding affinity. Some of the common auxochrome groups include; ammonia group (-NH_3), carboxyl group (-COOH), sulfonyl group (-HSO_3), hydroxyl group (-OH). Currently, thousands of textile dyes are used, classified into various groups and marketed under diverse commercial names. Dyes may be classified in innumerable ways on the basis of their chemical nature and trade names. On the basis of chemical nature, dyes can be classified into water soluble acidic and basic dyes, complex disperse, azo and anthraquinone based dyes together with metal complex dyes (Hunger, 2007). Metallic dyes derive their color from "metallic salts." They are commonly used in coloring of hair and its products designed for men. This gradual quality makes these products appealing to men who do not want an obvious, instant color change.

Water soluble dyes such as reactive dyes; cationic in nature, used in dyeing cellulose, protein and polyamide fibers. They are found in liquid, power and print paste form. During dyeing the reactive group of this dye forms covalent bond with polymer fiber and becomes an integral part of the fiber. It is water soluble, light fastness properties, anionic in nature, better wash and form strong covalent bond with the cellulosic fiber. On the other hand, water insoluble dye such as vat dye is indigo and the anthraquinone derivatives, which are used particularly on cellulosic fibers. The dye is applied in a soluble, reduced form to impregnate the fiber and then oxidized in the fiber back to its original insoluble form.

Acid dyes, basic and direct dyes consist of water soluble constituents but disperse dyes are less soluble, and suitable for dyeing of polyester fibers [16]. Azo compound (-N=N-) accounts for 60–70% of all synthetic dyes which are applied in a number of industries due to their fast,

Table 1
Chemical agents used in different operations conducted in textile mill.

Chemical agents	Operations
Acrylates	Sizing
Hydrogen peroxide (H_2O_2), sodium chlorate(I) (NaClO), sodium chlorate (III) (NaClO_2), Peracetic acid	Bleaching
Alcohol sulphates, Anionic surfactants, and Cyclohexanol	Mercerizing
Urea	Hydrotropic agent
Ammonia	In pigment printing pastes
Sulphates and sulphites	Reducing agents by-products
Non-ionic surfactants, chelating agent	Scouring
Dyes and Pigments	Dyeing
Cr compounds	Mordant
Organotin, Dichlorophenyl (ester), Triclosane, Isothiazolinones	Heat stabilizer and biocides
Paraffin and polyethylene	Softening agents

bright and intensive coloring properties and less production cost as a consequence of π -bond delocalization. Tables 2 and 3 show the dye classification based on solubility and chemical nature respectively. As a result of high degree of chemical and photolytic stability, dyes are less responsive to biodegradation and pass through activated sludge facilities with negligible color reduction. Azo dyes are organic compounds having the functional group $R-N=N-R'$, in which R and R' are usually aryl. These dyes are commercially important family of azo compounds, i. e. compounds containing the linkage $C-N=N-C$. Azo dyes are widely used to treat leather articles, textiles, and some foods. Azo dye reduction releases aromatic amines to create bio toxicities in relation to mutagenicity, carcinogenicity or genotoxicity. On the other hand, sulfur dyes are used mainly for dyeing textile cellulosic materials or blends of cellulosic fibers with synthetic fibers such as polyamides (nylons), acrylic fibers and polyesters. They are used for silk and paper in limited quantities for specific applications.

Nonionic dyes are the disperse dyes since they do not ionize in aqueous medium and are recommended for polyester and acetate fibers. These are composed of azobenzene or anthraquinone backbone along axillary auxochrome; nitro, amine and hydroxyl groups. Baughman and Perenich (1988) demonstrated the capability of some disperse dyes to bioaccumulate.

The basic dyes are used for dyeing acrylic fibers. Aromatic amine benzidine is important precursor for synthesis of dyes. In 2014, EPA classified nine benzidine based dyes under the toxic substances control act (TSCA) due to their potential metabolism into carcinogenic amines. On the other hand, anthraquinone-based dyes such as alizarin are not readily degradable due to their fused aromatic ring structure. Fig. 1 shows chemical variation of different classified dyes. The dye Acid red 2 having color index 13,020, Acid red 27 having color index 16,184, Rhodamine B having color index 45,170:1, Crystal violet having color index 42,555, Methyl orange having color index 13,025, Mordant red 3 having color index 58,005.

3. Impacts of dye pollution

The complex colored textile mill effluents have considerable influence on soil feature. In worldwide scenario, about 15% of all the produced dyes are lost during the process of dyeing and finishing and released in the textile effluents that possess a strong color, fluctuating pH, high COD and bio-toxicity. To demonstrate the metal distribution in effluent and soil, Manzoor et al. (2006) studied textile mill located in Pakistan, and found textile effluents principally effected soil wherein, Cr and Pb occurred in major proportion 5.96 mg kg⁻¹ and 4.46 mg kg⁻¹. Dindar et al. (2009) analyzed the effect of organic dye Reactive black 5

Table 2
Dye classification based on solubility.

Types of dye	Solubility	Application	Examples
Acid dyes (anionic)	Soluble in water	Silk, wool, nylon, modified acrylic fibers	Nigrosine, picric acid, eosin, acid fuschin, India Ink
Basic dyes (cationic)	Soluble in water	Acrylic fibers	Methylene blue, Safranin, Crystal violet
Direct	Soluble in water	Cotton, paper, leather, wool, silk, nylon	Direct orange 39, direct blue 86
Vat dyes	Insoluble in water	Cotton, wool	Indigo
Reactive dyes	Soluble in water	Cotton, cellulose fibers	
Disperse dyes	Insoluble in water	Cellulose acetate, polyester	Disperse orange, Disperse blue
Sulfursyes	Soluble in water	Cotton	Sulfur black 1
Azoic dyes	Insoluble in water		Para red, methyl orange, congo red, bismarch brown

Table 3
Dye classification based on chemical structure and their toxicity effects (Ding et al., 2012).

Group	Name of dyes	Effects
Azo	Disperse orange1, Methyl red, Methyl orange, Amaranth, Reactive black 5	Aryl azo compounds are stable, azo reduction form aromatic amines, bladder cancer, mutagenic
Anthraquinone	C.I Acid Blue 43, C.I. Vat Violet 1, Acid Blue 25, Alizarin, Anthrapurpurin, Carminic acid, Morindone	Mutagenic, carcinogenic
Indigoid dye	Indigo carmine, acid blue 74	Skin irritation, eye itching
Triphenyl methane dye	Methyl violet, Fuchsine dyes, phenol dye, Malachite green dye, Victoria blue dyes	Zootoxicity, Phytotoxicity
Xanthene dye	Rhodamine B, Fluorescein, Eosin	Inhibition enzyme activity, observed mortality in <i>Daphnia pulex</i>

(RB5) and Sulfonated azo dye (SA) in soil and found arginine ammonification rate, nitrification potential and number of ammonium oxidizing bacteria significantly decreased by 10–20% and 28–70% in presence of RB5 (>20 mg kg⁻¹ dry soil) and SA (>8 mg kg⁻¹ dry soil) respectively. Further, they concluded that organic dye pollution also restricts the nitrogen-use-efficiency of plants and thereby reduce the productivity of terrestrial ecosystems.

4. Environmental impacts

The overall environmental impacts due to release of textile effluents can be broadly classified into three levels as first, second and third based on sequence of their manifestation or occurrence after disposal. At level first, undesirable coloration of surface due to the common practice of disposal of colored water is into the streams or nearby water bodies, consequently influences the ecosystem, which pushes into secondary level impacts. Further, whole movement leads to degradation in quality due to chemical and biological transformation in the ecosystem conditions at third level.

4.1. First level impacts

The first and foremost impact of dyes is contributing aesthetically repelling colors to surface with which it comes into contact. The disposal can be done either on land or into a surface water body that adversely influences soil and ground water quality causing strong coloration and exposure to toxic chemicals. This leads to a development of repulsive tendency in usage of water by human beings and higher animals.

4.2. Second level impacts

Dye accumulation affects the lives of aquatic organisms as a whole and overall productivity of the ecosystem is reduced. Color has shown strong interference with the natural process of photosynthesis in cyanobacteria and other photosynthesizing aquatic plants due to reduced light penetration. Thus, it may lead to reduction in output of producers and consequently, may affect the whole aquatic food-chain. Prominent changes also take place in prey-predator relationship due to extinction of some species and leading to unbalanced growth in proportion of the surviving species.

4.3. Third level impacts

Third level impacts include subsequent chemical and biological transformations in ecosystem. Textile mill effluents contain wide variety of chemicals including acids, bases, salts, wetting agents, retardants, accelerators, detergents, oxidizing agents, developers, stripping agents

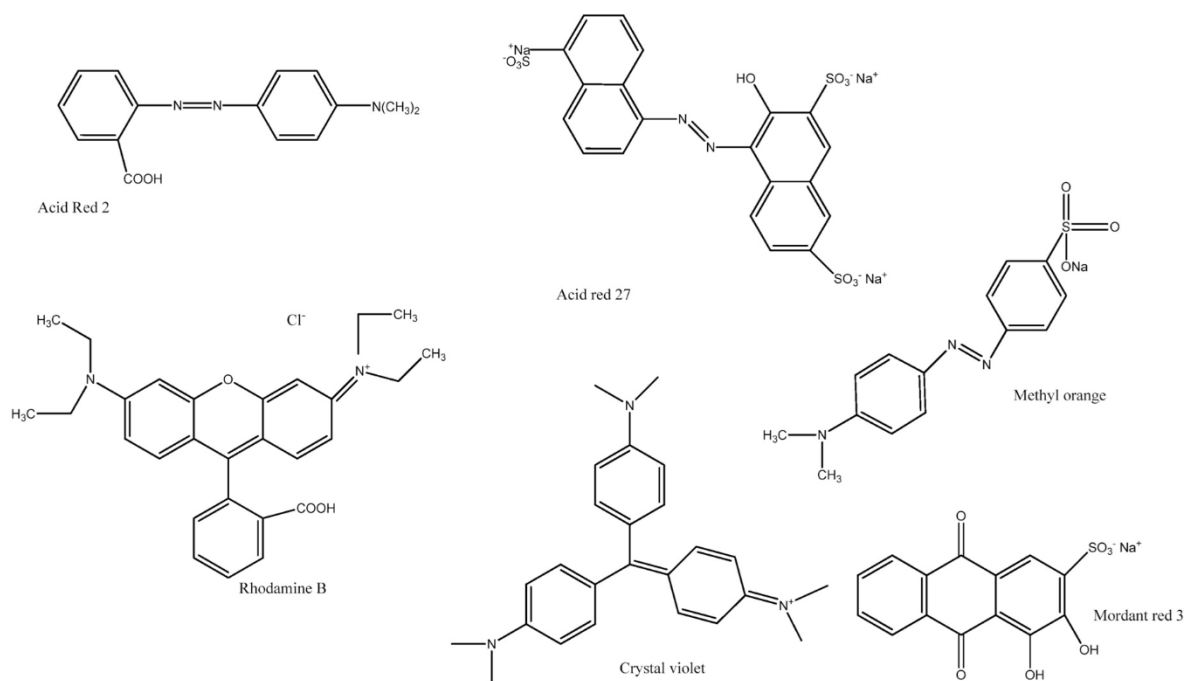


Fig. 1. Chemical structure of dyes.

and finishing agents used to carry out wet processing operations. As previously mentioned, the untreated effluents are many times known to contain extremes of pH and temperature, high BOD, high COD and high concentrations of suspended solids (Tiwari et al., 2015).

Even at very low concentration in industrial effluents, dyes have potential to cause critical damage to ecosystem, leading to death of fish and other macro and micro-organisms; subsequently biodegradation of these dead organisms reduces the dissolved oxygen (DO) content in water. With time, depletion of the DO may lead to development of anaerobic conditions in ecosystem, production of hydrogen sulfide along with organic acids and thus decreases pH of the aquatic environment. Reduction in pH amplifies or initiates the death of organisms and cycle continues further as explained above, making the water unfit for the survival of aerobic life-forms.

5. Health impacts

5.1. Carcinogenicity

Available studies have indicated that some benzidine-based dyes are main cause of cancer in experimental animals and are converted into benzidine by metabolic processes after entering into animals. From the accumulated evidence, it could be concluded that benzidine-based dyes are probable human carcinogens. Dyes that are based on o-toulidine contain o-toulidine (3, 3-dimethyl benzidine) attached to other constituents by diazo linkages. Dyes based on o-dianisidine (3, 3-dimethoxy benzidine) consist of o-dianisidine attached to other constituents by diazo linkages (Prival et al., 1984). Based on animal studies, o-toulidine and o-dianisidine dyes are considered as carcinogenic (Sani et al., 2018). Benzidine-based dyes may consist of residual amounts of other substances such as 4-aminobiphenyl, which is carcinogenic. Therefore, it may be an outcome of possible contamination with carcinogenic materials in addition to concern for the metabolic conversion of such dyes to cancer-causing substances (Singh et al., 2019). Dye used in textile sectors, significantly compromise the aesthetic quality of water bodies, increase chemical and biochemical oxygen demand, impair photosynthesis, inhibit plant growth, enter the food chain, provide recalcitrance and bioaccumulation, and may promote toxicity, mutagenicity and

carcinogenicity. The carcinogenicity of azo dyes (food and textile) (LD50) values are between 250–2000 mg kg⁻¹ body weight, indicating that for a lethal dose many grams of azo dyes have to be consumed in a single dose. The Lethal concentration dose (LC50) shows blue dye having the least value. The blue and red dyes were found to be more toxic than the yellow dye, the LC50 values being as follows: 392 µg mL⁻¹ (Yellow dye); 370 µg mL⁻¹ (Red dye) and 361 µg mL⁻¹ (Blue dye). This could be due to the concentration of heavy metals in the dye [24]. Red dye had the value of LC50 (21.5 µg mL⁻¹, with a percentage mortality of 60%), Yellow dye (0.95 µg mL⁻¹, with a mean percentage mortality of 90%), Orange dye (343.1 µg mL⁻¹, with a percentage mortality of 47%). Majority of textile dyes have LD50 values between 250–2000 mg kg⁻¹ body weights, indicating that for a lethal dose many grams of azo dyes have to be consumed in a single dose.

5.2. Mutagenicity

Abdou et al. (1987) investigated the impact of styryl and azo analogues of cyanine dyes on breaking the dormancy period and on induction of chromosome damage. Both the compounds were found to be strong mutagenic agents, the azo analogue more efficient than the styryl. The mutual factors were found to be effective in breaking dormancy in garlic at a fixed concentration.

5.3. Teratogenicity

Teratogenicity effects were observed with 2-nitro-p-phenylenediamine, 4-nitro-o-phenylenediamine and 2, 5-toluenediamine sulfate dyes by subcutaneous injection on days 6–15 of gestation to pregnant outbred albino mice. These dyes resulted in a significance increase in the average of malformed fetuses. A substantial reduction in average weight during pregnancy was also observed at these dosage levels. Similarly, significant average fetal weight loss was also found, which defines embryo toxicity at significant dosages (Marks et al., 1981).

5.4. Allergic effects

Azo dyes are largely non-toxic, but some of their degradation

products like aromatic amines may be allergic in nature. Particularly, disperse azo dyes may cause allergic reactions (Malinauskiene et al., 2013). Sontag (1981) experimented with rats and mice and observed that female mice were more vulnerable to the carcinogenic effects of the substituted-benzenediamines than the rats. It was also observed that rats showed a greater range of target-organ susceptibility. Chemical Handing Guide of p-phenylenediamine specifies that occupational exposure might be responsible for total loss of eye sight.

6. Remediation

The contaminated soil has multiple impacts on the ecosystem. Remediation has grown and evolved, to recover public health, environment quality and the economy. Primarily, soil analysis is essential to determine the risk factor. Nutrient contents and mineralization potential of soil provides the activity of soil microorganism that is related to functional or structural components (Cambardella and Elliott, 1993). Brown et al. (2006) showed the utility of visible and near-infrared diffuse infrared reflectance to air-dry soil secondary forecasters including sand content or pH. After the characterization of soil, noxious elements have to be eliminated to improve quality.

Lebeau (2011) classified soil remediation in three ways, in-situ, where treatment was carried without digging the soil (chemical oxidation, enhanced bioremediation, metals stabilization), on site includes excavation of soil, and return to the actual location after treatment and ex situ, contaminated soil is hollowed out and relocated after treatment. Lebeau (2011) also classified disinfection technology into four groups based on the remediation process on contaminants. (1) Removal: Contaminants are physically treated without separating from the host medium, (2) Separation: Several kinds of ex-situ processes such as gravity separation, sieving/physical separation and magnetic separation have been applied successively after desorption, solvent extraction, soil washing and soil vapor extraction for extraction and separation of contaminants from soil, (3) Destruction: It can be applied to in-situ as well as ex-situ in order to neutralize toxicants into less toxic derivatives, (4) Finally, containment leads to attachment of toxicant onto surface and subsurface (Lebeau, 2011).

6.1. Biosurfactants

Biosurfactants are amphiphilic substances produced on microbial cell surfaces, or excreted extracellularly, having hydrophobic and hydrophilic moieties that help in reduction of surface tension and interfacial stress between individual molecules at the surface and interface, respectively. A biosurfactant must retain structurally hydroxylated and cross-linked fatty acids (mycolic acid), glycolipids (rhamnolipids, trehalolipids and sophorolipids), polysaccharide-lipid complex, lipoprotein or lipopeptide (Surfactin), phosphor lipid, or cell surface itself (Kumar et al., 2020, 2022). These have shown several advantages over synthesized surfactants including their biodegradability, biocompatibility, digestibility, ability to put up with a wide deviation of temperature, pH, and salt concentration along with antimicrobial activity and easy availability of raw material (Ding et al., 2012). Amphiphilic moiety can form host-guest complexes with the hydrophobic impurities of water and soil by a method which encapsulates the hydrophobes into the self-assembled aggregates (micelles) of surfactants. Fig. 2 illustrates chemical structure of bio surfactants and mode of action to decontaminate the soil. Surfactants can be categorized according to their Hydrophile-Lipophile Balance (HLB) that influences their physico-chemical properties. The HLB classification can be used to decide the aptness of use of surfactants. In general, surfactants with low HLB are lipophilic, however, high HLB refers to better solubility of water. Table 4 summarizes some biosurfactants derived from bacteria and fungi (Ongena

Table 4
Biosurfactants derived from microorganisms and fungi.

Organism	Type of surfactant	References
<i>Torulopsisbombicola</i>	Glycolipid (sophorose lipid)	Ongena et al. (2007)
<i>Pseudomonas aeruginosa</i>	Glycolipid (rhamnose lipid)	Mulligan (2005)
<i>Bacillus subtilis</i>	Lipoprotein (surfactin)	Ongena et al. (2007)
<i>Pseudomonas sp. DMS 2847</i>	Glycolipid (rhamnose lipid)	Mulligan (2005)
<i>Acinetobacter calcoaceticus</i> 2CAC	Whole cells (lipopeptide)	Ongena et al. (2007)
<i>Candida bombicola</i>	Sophorolipids	Mulligan (2005)

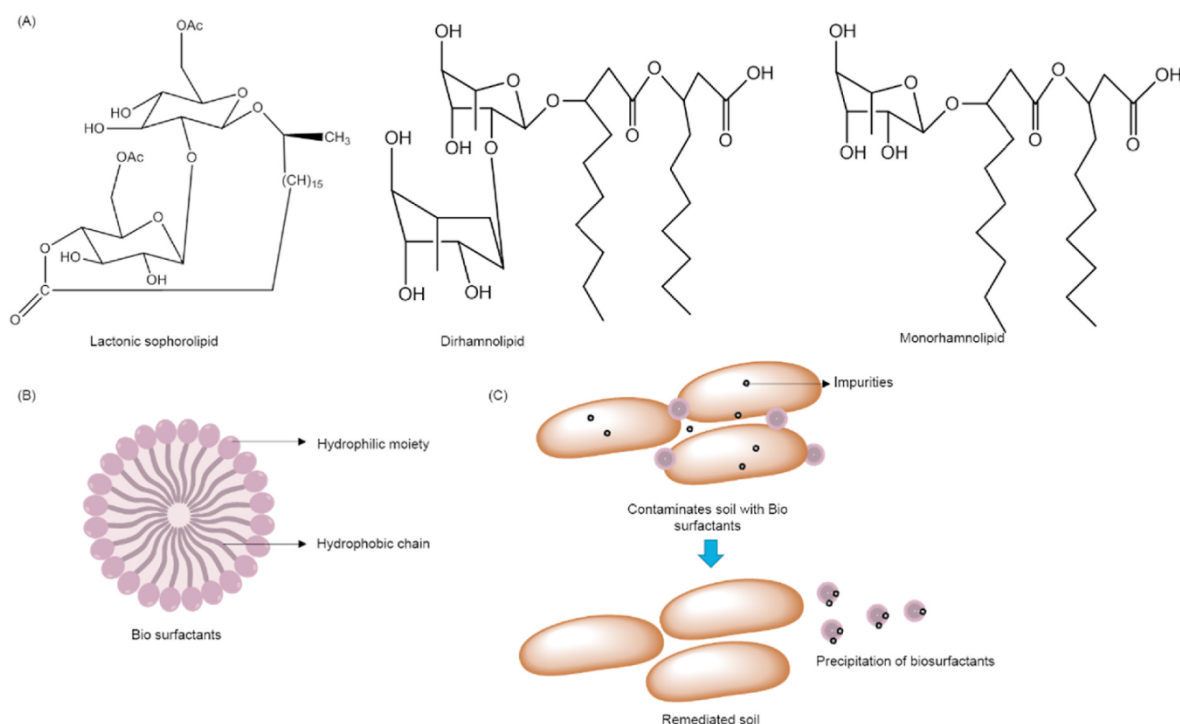


Fig. 2. A: types of biosurfactants, B: Micelles and C: mode of action of decontamination of soil by biosurfactants.

et al., 2007).

The recalcitrant aromatic nature of dye/pigments and their chlorinated derivatives are difficult to biodegrade and are prone to create health hazards. To attempt soil remediation, microbes are allowed to grow either by addition of nutrition (nitrogen, phosphorus and carbon compounds) or ex-situ microbial population production and their addition along with essential nutrients, to the contaminated soil. The applicability of described strategy depends upon the type of the pollutant, soil conditions and availability of the adapted culture (Mulligan, 2005). Lin (1999) studied the efficiency of rhamnolipids (bio-surfactants) used in electrokinetic remediation of mica soil contaminated with phenanthrene and found complete removal in 14 d bench-scale study. They showed *Pseudomonas aeruginosa* bacteria could produce rhamnolipids under the electric field. Phenanthrene is a tricyclic aromatic hydrocarbon, isomeric with anthracene used in synthesis of dyes.

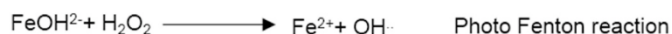
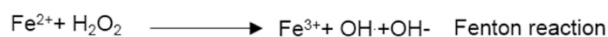
6.2. Oxidation-reduction

The oxidation process is generally used method of removal of dye by aromatic ring cleavage which diminishes the conjugation. Chromophore groups in dyes are usually organic compounds with conjugated double bonds that can be fragmented into smaller molecules. Peroxidases and/or phenoloxidases can act on particular recalcitrant contaminants by precipitation or converting to other non-toxic compounds and allowing final treatment of the waste (Durain and Esposito, 2000). Peroxidases are hemoproteins, usually produced by several micro-organisms and plant sources, which carry out reactions in the presence of hydrogen peroxide. Horseradish peroxidase (HRP) can aid in the oxidation of phenols, biphenols, anilines, benzidines and similar heteroaromatic compounds. HRP is appropriate for treatment of wastewater because it maintains its activity over a wide range of pH and temperature. HRP, lignin peroxidase and manganese peroxidase mineralize a variety of recalcitrant aromatic compounds (Durain and Esposito, 2000). In former, productive step cell-transformation of xenobiotic substances by ecto and extra cellular enzymes include a huge number of oxidoreductases and hydrolases. Both these enzymes play a degradative role and convert xenobiotic substances into partially degraded or oxidized products which can be easily taken up by the cells (Gil-Díaz et al., 2016).

Numerous dyes are not subjected to biological degradation because of their complex structures and toxicity. In-situ and on-site chemical remediation methods have a benefit over biological treatment on such dyes. Fentons reagent (H_2O_2 -Fe(II)), electrolytic Fenton chemistry, ozonation, and photochemical are responsible for generation of peroxide species. Especially, Fenton' reagent has been effectively applied to treat soils contaminated with harmful chemicals as shown in Scheme 1. But, the high sludge production and short life of ozone are main drawbacks of bulk application.

6.3. Electrokinetic separation and electrochemical oxidation

Electrokinetic (EK) remediation is a greener technology based on low intensity direct current through the soil between ceramic electrodes. Cationic impurities such as metal and ammonium ions are separated towards the cathode while anions are segregated at the anode (Bonilla



Scheme 1. Generation of free radical in Fenton reaction and Photo Fenton reaction.

et al., 2000). Elicker et al. (2014) treated metal containing sludge sample by EK. Boron doped diamond anode and NaCl solution have been used to enhance the oxidation. Lee et al. (2009) performed electrokinetic separation and electrochemical degradation in Acid Blue 25 contaminated kaolin soil and successfully 89% disinfection was achieved at 30 mA for 7 d. A bench scale experiment was done by Annamalai et al. (2016) for in-situ degradation of organic molecule and electro migration of metal impurities in presence of 2 V cm^{-1} voltage gradient. The EK remediation comprises of two main processes, electro migration (EM) and electro osmosis (EO). The EM deals with transport of charged species toward the opposite electrodes. The rate of migration of ions fairly depends on ionic movement and the electrical gradient. Whereas, effluents entrapped into pores of soil migrate towards the cathode (rarely towards the anode) by the process of electroosmosis.

The applicability of EK has been achieved by in-situ treatment or after the extraction of dye from soil. Annamalai et al. (2016) employed the EK for treatment of indigo textile dye bearing soil and liquid media. They also demonstrated the role of electro active species to reduce treatment time.

6.4. Phytoremediation

Phytoremediation makes use of plants to remove contaminants from the environment. It uses wild or transgenic plants to remove a wide variety of heavy metals and organic pollutants from the soil (Peuke and Rennenberg, 2005). Phytoremediation comprises of extraction, degradation, stabilization and volatilization. Phytoextraction refers to the removal of metals or organics from soils by collecting them in the biomass of plants. Phytodegradation or phytotransformation is the application of plants for uptake, storage and degradation of organic pollutants; rhizofiltration includes the elimination of chemicals from aqueous sources through plant roots. Phytostabilization helps in the reduction of bioavailability of the contaminants by immobilizing or binding them to the matrix of soil, and phytovolatilization utilizes plants to take up contaminants from the growth matrix, alter them and release them back into the atmosphere. The detoxification process can be accomplished by uptake and translocation, sequestration into the vacuole. Finally metabolization takes place through oxidation, reduction or hydrolysis and conjugation with glucose, GSH or amino acids. Phytoremediation is also considered as a possibly profitable technology since the resulting biomass can be used for economic enhancement with no additional CO_2 production. A single major drawback of phytoremediation is its relatively slow speed. The accumulative toxicants can disrupt the enzymatic activity or generate high amount of reactive oxygen species. Kabra et al. (2011) used *Glandularia pulchella* (Sweet) for phytoremediation of a sulphonated azo dye Green HE4B. Whereas, Khandare et al. (2011) degraded highly sulphonated diazo reactive dye by using in vitro cultures of *Zinnia angustifolia*.

6.5. Nanoremediation

Nano remediation deals with use of nanoparticles to diminish contaminants by oxidation or reduction process. It also acts as catalyst and facilitates the rate of reaction. Nanomaterials are materials with a dimension of 100 nm or less with high surface area and high surface reactivity (Fajardo et al., 2015). Many researchers have reported mono/bimetallic nanoparticles and composite to degrade organic pollutant (Dhiman et al., 2017; Haq et al., 2018).

Zero valence iron oxide (nZVI) is highly reactive agent used to remove both organic and inorganic contaminates. It can also be used to recover/remove dissolved metals from solution. Fajardo et al. (2015) assessed the residual toxicity and influence of old nZVI after an experiment on leaching of soils polluted with heavy metals for better understanding of the toxicological effects of nanomaterials on environmental biota, soil condition and functionality and no negative effects on physico-chemical soil properties was found. In another study, Gil-Díaz

et al. (2016) examined the efficiency of nZVI in decreasing the availability of Cd, Cr or Zn in contaminated soils. The effects of nano remediation on the growth of barley plants as well as its effect on properties of soil and stability of metal immobilization were also assessed in a greenhouse experiment set up. Immobilization of Cr was steady over the time period and doses of Cr were toxic to the barley plants. In contrast, the decrease of Cr availability after the nZVI treatment made a decrease in soil phytotoxicity and helped in development of the plants allowing them to grow completely. Taking these outcomes into account, it can be concluded that the application of nZVI is a promising remediation approach, and its efficacy would be conditioned to the soil properties and bioavailable concentration of the metal.

6.6. Biodegradation

The elimination of contaminants from soil depends on complex interaction of the physical, chemical and biological factors within the environment. Bioremediation technology is a cost-effective method, which utilizes organisms to neutralize the pollutants (Baocheng et al., 2008). Bioremediation process of dye treatment of from contaminated soil is very effective and can say sustainable approach. It is economical and very effective treatment process. The consumption of the energy during treatment of dye containing soil is very less. Treatment of carcinogenic dye may also be very beneficiary by using microbes as microbes digested the level of carcinogenicity of dye. Yadav et al. (2021) showed that laccase is the responsible to reduce the level of dye carcinogenicity. Authors used *Allium cepa* to check the toxicity and found that laccase reduced the toxicity of dye.

Microbial degradation of hydrophobic compounds occurs due to their structure, availability of microorganisms and the physico-chemical conditions which affect the metabolic competence of the microorganisms. It includes various significant parameters such as pH, water, aeration status (redox potential), presence of oxygen, nutrients and temperature. Biodegradation of organic contaminants can be achieved accurately, but according to some authors, microorganisms and their ecology needs be understood fully. Holden et al. (1997) suggested a need to determine the elements regulating the preferred metabolic pathway; the distribution of degrading microbial communities relative to pollutants.

7. Conclusions

In this review, we attempted to show the hazardous problems of textile mill effluent on soil and remediation process of dyes from soil. Textile mill effluents are complex in nature due to the presence of varied dyes, metal contaminations and other organic agents, in different operational conditions, that can be accumulated in natural sources; soil and water after untreated disposal which are potentially toxic for ecosystem and human life and presence of xenobiotics elements in open and partially covered pits left behind by industrial or domestic activities alter chemical and physical properties of arable soil. Several green methods (bioremediation, bio surfactants and phytoremediation) encourage decontamination of soil in safe manner whereas; chemical and nano-based treatments are emerging technologies that facilitate remediation of soil in less time. The chemistry involved in bioremediation and engineering aspects of the process still remains unexplored. Better understanding and knowledge about the process is expected to assist the researches in improving the method and overcome the problem of dye contamination.

Availability of data and materials

There is no such dataset.

Competing interests

The authors declare that they have no competing interests in this section.

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Authors' contributions

The main investigator was Markandeya, who designed the manuscript. The technical drafting of the manuscript was done by SPS, while DM helped in writing the manuscript.

Conflict of interest form

There is no conflict of interest.

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