Treatment, Recycling, and Reuse of Wastewater from Tannery Industry: Recent Trends, Challenges, and Opportunities

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Abstract

Leather industry is one of the greatest economic sectors known as well as one of the highly polluting industries as it generates intolerable solid and liquid wastes. Major pollutants in tannery effluents are sulfides, sulfates, chlorides, tannins, and heavy metals. Hence, tannery effluents are very toxic and have an adverse effect on agricultural lands and water sources. In order to minimize the toxicity, use of microbes to treat industrial effluents has always been an eco-compatible and cheaper method. There are many conventional physio-chemical treatment methods to bring down the influence of discharged effluent on the living but its high operational cost and execution setup are the major drawbacks. In addition to toxic chemicals, several heavy metals are also present in tannery effluents, and are not easily digested by conventional techniques. The present chapter focusses on the use of microbes with potential to degrade noxious compounds contaminating groundwater and soil. The potential microorganisms having degrading property could be isolated and mass multiplied under lab conditions. Potential microbes will selected from effluent affected sites and may further use for the suistanable agricultural practices. Bioremediation and phytoremediation are proven to be effective and is considered as a novel, cost-effective method for the complete removal of toxic chemicals, heavy metals, and dyes originating from tanneries. The treated wastewater can be recycled for irrigation and in industries.

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14.1 Introduction

Tanneries are one of the most pollution-emitting industries that are cause for the emergence of effluents with organic as well as inorganic dissolved and suspended solids content. These industries are often responsible for the discharge of toxic elements along with the wastewater into the ecosystem beyond the permissible limit. This increase of toxicity in the effluent is directly discharged into the running water bodies that affects living beings and the environment. Therefore, it has become important for minimizing the major impact of discharged wastewater that affects the lives of living creatures in the environment. As the population is increasing, urbanization is also showing its growth. To achieve the demand of population, industrialization is also at its peak which ultimately gives rise to the detrimental effect on our environment. The leather industry fulfils the demand for footwear, musical instruments, leather items, employment generation, etc. and is one of the leading industries of the world (Durai and Rajasimman 2011). Tanneries consume a large amount of water and in return release the same amount in the form of wastewater after processing. Thus, it is one of the leading contributors to environmental pollution and is a global concern for biodiversity (Kundu et al. 2014; Kumar and Thakur 2020). Because of the inappropriate treatment of the discharged effluent, it is beyond the permissible limit. Tanning is a leather manufacturing process by the treatment of various chemicals on animal skin and hides. During this transformation, a highly coloured, cloudy, and stinky effluent is generated (Dargo and Adhena 2014). The dumped effluent affects the area in their vicinities such as water bodies, adjacent land, and groundwater, and is unfit for irrigation as well as for drinking purposes, imposes adverse effects on the consumers of each trophic level (Ramachandran et al. 2013). The discharged effluent consists of chromium salts, sulphides, inorganic salts, organic salts, chlorides, tannins, heavy metals, dissolved solids, suspended solids, nitrogenous compounds, pentachlorophenol, and gaseous wastes as well (Masood and Malik 2011). Tanneries use tanning agents such as basic chromium sulphate [Cr (III)] in the "chrome liquor" for making leather soft, lightweight, and heat/water-resistant. But chromium (Cr) is a harmful pollutant. Among several forms of Cr, trivalent and hexavalent forms are biologically stable and hexavalent Cr is more soluble hence more harmful than trivalent. Another pollutant that is used for the preservation and treating of leather is pentachlorophenol (PCP), an aromatic compound. It is used as a biocide and also recalcitrant to biological degradation if accumulated in food chains can be the cause of human health issues (Verma et al. 2019).

That is why it is very important to clean tannery wastewater before discarding it into receiving water bodies and land as it can be the cause of pollution. An intensive attempt has been made to treat the effluent discharged. To meet the challenges, tanneries use conventional techniques to treat the effluent before discarding it to the surrounding environment. Conventional treatment methods require humongous operational cost; require a large area, energy, chemicals, and labour; and also cause further environmental damage by producing a large amount of sludge. So tannery effluents should be treated more precisely before it affects flora and fauna otherwise it will enter the food chain. Therefore, an alternative that is eco-friendly and cost-effective wastewater treatment techniques would be significant. Bioremediation is an emanating technique for the cleaning of noxious pollutants present in the effluent. A holistic approach should be needed to reuse and recycle wastewater for the sustainable development of ecosystem. A multidisciplinary approach not only reduces the scarcity of water but also same time minimize the unfavourable effect of noxious pollutants on the environment and on health. The present chapter focusses on the characteristics of tannery effluents, their detrimental effect, and also its effective remediation methods before its release into the environment.

14.2 Characteristics of Tannery Wastewater

Tanning is a chemical process of leather manufacturing that involves the use of different chemicals on animal skin and hides. There are four main steps for the production of leather: (a) beam house, (b) tanyard, (c) post tanning, and (d) finishing operations (Durai and Rajasimman 2011). The process of leather manufacturing and features of wastewater produced is shown in Fig. 14.1. The quality of tannery discharge depends upon the chemicals used, industry size, tanning operations, and amount of water used in the different processes in tanning. The pollution parameters of tannery effluents can be characterized by biochemical oxygen demand (BOD), chemical oxygen demand (COD), suspended solids (SS), dissolved solids, heavy metals like chromium, mercury, iron, zinc, copper, cadmium, lead, sulphates, sulphides, and nitrates (Buljan et al. 2011). The pH of the effluent generally ranges from 7.5 to 10 as carbonate, bicarbonate, and hydroxides salts present in tannery effluents give it an alkaline nature and eventually affect the water ecosystem (Kongjao et al. 2008). Moreover, during the production process, effluents contain lime, toxic chemicals, halides, sulphates, ammonia, heavy metals, suspended solids, dissolved salts, oil, grease, and wastewater sludge. This also leads to increasing eutrophication in water bodies. These pollutants are toxic and also carcinogenic to humans as well (Tamburlini et al. 2002; WHO 2002). Because of high contamination, this water is not safe for drinking purposes. The dark-coloured water is itself a pollution indicator and the expulsion of coloured effluents can severely damage the water ecosystem by obstructing light penetration. Further, the addition of salt as preservatives on the skin and organic matter in effluents increase the TDS value with the increase in BOD and COD levels, which decreases the value of dissolved oxygen (DO). Along with the wastewater, solid waste is also generated during leather processing as well as sludge generated during effluent treatment. In leather processing, approximately 85% of mass is generated as solid waste. These solid

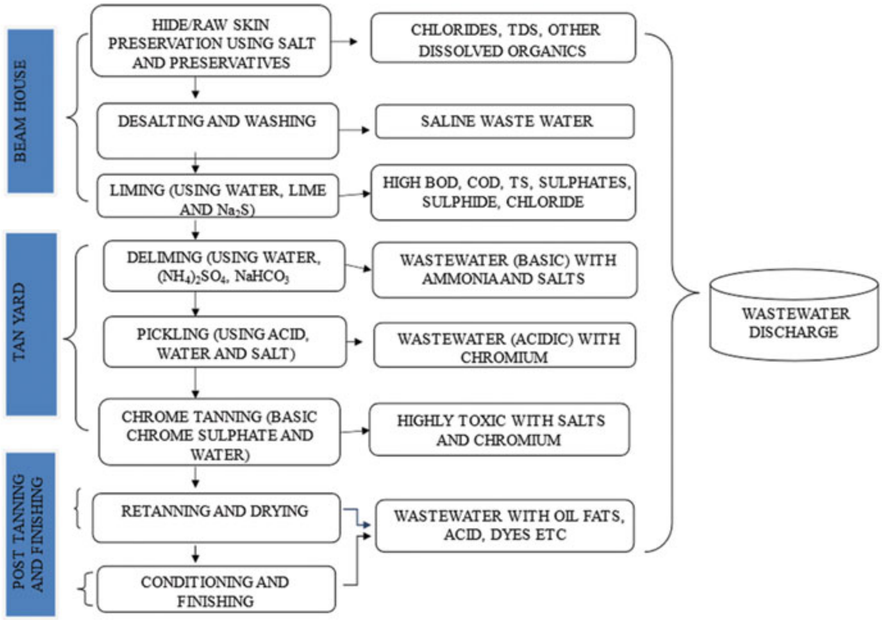

Fig. 14.1 Steps in leather production process and wastewater generated

wastes are noxious, creating a secondary problem. Furthermore, discharge from leather industry corrupts the soil and groundwater, if not treated (Chung et al. 2004).

A high level of sulphate in the discharged effluent triggers sulphate-reducing bacteria to grow, which in turn produces H_2S gas. H_2S is harmful and lethal too. Delay in disposal and decomposition of solid wastes and wastewater also produces bad odour.

14.3 Effect of Tannery Effluents

Tannery industries use various dyes and form dye-based recalcitrant pollutants that affects the ecosystem. Both the biotic and abiotic factors get seriously affected. If the effluent is dumped directly into the water body can be more harmful and cause skin allergies and other diseases. Aquatic plants and animals get affected. Many inorganic metals like Cu, Mg, Ni, Mn, V, Cr^{3+}, and Mo present in the wastewater are necessary for metabolic functions but only in trace amounts; some heavy metals such as Pb and Cr (VI) do not play an important role biologically and are noxious for biota. Many humans and animals are dependent on aquatic food so when aquatic life forms on exposure to the dissolved heavy metals such as chromium and harmful pollutants of tanneries, which can lead to the bioaccumulation of heavy metals and so on in the tissues of organisms (Aung et al. 2013). Therefore, it results in biomagnification by entering the food chain and food web.

14.3.1 Impact on Humans

Tannery discharge contains metal pollutants that promote diseases to those near the polluted area. Exposure to these contaminants imposes ill effects on skin and mental health too. Mercury, arsenic, and lead can lead to weakness, diarrhoea, anaemia, headaches, brain damage, kidney failure etc. Exposure to mercury can damage the brain and kidneys of developing foetuses permanently (Engwa et al. 2019). Heavy metals in higher concentration can cause headache, anxiety, irritability, abdominal cramps and effects the function of the nervous system, bladder, brain, liver, and kidney. Compounds with hexavalent chromium ions are more soluble in water and can move across biological membranes and interact with intracellular proteins and nucleic acids. Cr (VI) is extremely carcinogenic and mutagenic and can lead to death if infested. It is recommended to remove chromium before being dumped as it can result in oxidative DNA damage which can cause genotoxicity of Cr. As chromate shares a structural similarity with sulphate $(SO_4)^{2-}$, so it can cross the membrane through sulphate transport pathway. This can badly affect human health by causing lung cancer, dermatitis, vertigo, nausea, kidney damage, chronic liver damage, and respiratory infection. Cr also causes ulceration and perforation of the nasal septum, skin lesions, and damage to the respiratory tract (Kumar et al. 2021a, b). PCP also causes many diseases like dermatitis, chronic fatigue, impaired fertility, conjunctivitis lung cancer, intravascular haemolysis, neurological disorder, pulmonary oedema, pancreatitis, liver damage, and kidney failure (Sharma et al. 2009).

14.3.2 Impact on Plants

As well-known types of irrigation water affect crop yields and productivity. However, contaminated wastewater from tanneries on disposal with the pollutants into cultivable lands drastically reduced yield and growth of crops. Total suspended solids in effluents makes water become more turbid and lead to poor photosynthetic activity. Plants can be also affected directly and indirectly by the concentration of heavy metals in soils. These noxious metals and chemicals when enter plants thereby alters physiological, genetic, and biochemical functions of the system (Dazy et al. 2008). Greater concentration of heavy metals suppress growth, induce chlorosis, epinasty, poor photosynthetic activity, chromatin condensation, necrosis, and reduced water potential during the vegetative and flowering stage of crops. Higher concentrations of arsenic interrupts the generation of ATP and also oxidative phosphorylation. Lead causes alteration in the permeability of the cell membrane. This can weaken seed germination, transpiration, cell division, root system elongation, etc. Cadmium changes the enzymatic activity involved in the Calvin cycle, carbohydrate metabolism, and carbon dioxide fixation, inhibiting photosynthesis and resulting in a short plant (Gill and Tuteja 2011). Cd toxicity may also alter metabolism in plants which can lead to inhibition of pollen germination, delay in germination, etc. Ni stress affects photosynthetic pigments and reduces the yield in plants (Kumar et al. 2021a, b).

14.3.3 Impact on Microbes

Microbes can use chemical substances as their energy source thereby can degrade naturally as well as synthetic substances in our ecosystem. That's how microbes can reduce the level of pollutants (Pavel and Gavrilescu 2008). Hence this method of microbial degradation of industrial dyes is cost-effective and efficient method (Kumar et al. 2016). But, heavy metals in soil could significantly reduce microbial activity and biodiversity. Soil contaminated with heavy metal showed adverse effects on soil respiration rate, reduced enzymatic activity, the transformation of organic matter, and altering soil pH (Wu et al. 2019). Disposal of sludge adds heavy metals to the soil and negatively affects the growth and reduces the microbial population. These metals in the soil ecosystem create selection pressure that supports specific microbes which can tolerate or develop resistance to the exposed heavy metal. Some microbes have proved themselves as significant and most promising in the bioremediation of heavy metals.

14.4 Approaches Towards Industrial Wastewater Treatment

Treatment of wastewater of tanneries is a very challenging task as it contains a high concentration of contaminants and wastes. So, it is very important to cure the effluent before discarding it. The pollutants present gets transformed into a simple and degradable form so it can be disposed of safely without causing any menace to the ecosystem (Kumar et al. 2021a, b). Tannery wastewater is treated through a series of steps.

14.4.1 Primary Treatment (Physio-Chemical Treatment)

14.4.1.1 Physical Treatment

The very first treatment step is also known as a mechanical treatment, where raw effluent is screened to remove coarse matter. Grease, sand, oils, fats in the raw waste can be removed by screening. Additionally, it also reduces the chrome and sulphides from the effluent by homogenization and sulphide oxidation.

14.4.1.2 Chemical Treatment

14.4.1.2.1 Coagulation and Flocculation

Chemicals like industrial alum, iron sulphate, iron chloride, and lime which act as coagulants are added to remove colloidal matter. Lime is used as the base to neutralize the acidic effluent (Dargo and Adhena 2014). Coagulants and flocculants being water-soluble polyelectrolyte help to form clumps of very minute and colloidal particles. For coagulation, a coagulant is mixed rapidly, and then undergoes flocculation process in which particle size is increased by gentle mixing. Size is transformed from clumps to visible suspended solids forming large macroflocs. Mixing velocity and energy should be watched to prevent the destabilization of macroflocs (Ukiwe et al. 2014). Thus, suspended solids such as girt, scum, fatty and nonfatty particles which are still left, settle faster and then can be removed from water by sedimentation. Scum is removed from the top and sludge from the bottom of settling tanks. The disadvantage of this method is the formation of sludge. Sludge is then dried by using sludge thickeners, mechanical dewatering using centrifuges, natural drying.

14.4.1.2.2 Chemical Oxidation

It is a newer technology in which oxidizing agents are used. Ozone, potassium permanganate, and hydrogen peroxide are some oxidising agents which are used to degrade organic pollutants to a manageable level but this method exhibits a lower rate of degradation. In the chemical oxidation process, it is very difficult to remove total organic carbon.

Ozone also acts as a decolourising agent. Ozone is unstable and readily reacts (Dargo and Adhena 2014). Activated carbon as a catalyst enhances sulphide oxidation which is found to be more significant to remove sulphide from wastewater and also lowers COD, BOD, and total organic carbon (TOC) from wastewater.

14.4.1.2.3 Advanced Oxidation Process

AOPs involve technologies such as photocatalysis, Fenton, photo-Fenton, and wet oxidation in which different hydroxyl radicals are used to react for the tannery discharge treatment. Photo (solar)-Fenton process is the most efficient technology which accelerates oxidation of organic compounds in tannery effluents, but it is a much expensive process.

14.4.1.2.4 Ion Exchange

The process involves the replacement of metal ions of a species with an ion of different species attached to an insoluble resin present in the solution. The drawback of this process is that the equipment used is costly due to high operational cost and cannot remove chromium completely. It also produces chemicals not suitable for the environment.

14.4.1.2.5 Reverse Osmosis

In reverse osmosis (RO) heavy metals are removed with the help of semi-permeable membrane. Aromatic polyamide and cellulose acetate are the most commonly used membranes. In this process, the solution is passed with a greater osmotic pressure through a region of higher concentration to a diluted region through a semi-permeable membrane. Earlier this process was used to treat brackish water and for desalination. Nowadays RO is used in wastewater treatment also. But the disadvantage of this process is its high operational cost. Also, membrane leakage and membrane fouling are the other problems of this method (Ukiwe et al. 2014).

14.4.1.2.6 Electrochemical Treatment

Electrochemical treatment process is an alternative to the conventional coagulation and flocculation processes. This technique involves the use of different electrodes with varying electrolytic property giving oxidation and reduction reactions to remove sulfides, nitrogen, phosphorus, and many toxic heavy metals (Mook et al. 2012). This technology was developed to overcome the problem related to chemicals used in the coagulation/flocculation process and also during sludge formation. Safe disposal of sludge is a major concern. But it is observed that this method is more effective when applied in post-treatment stage rather than treating raw effluent (Goswami and Mazumder 2014).

14.4.1.2.7 Electrocoagulation (EC)

EC is another trendy technique that is the combination of conventional electrochemistry, coagulation, and flocculation techniques. EC involves the use of electrodes made up of iron, steel, or aluminium and submerged in tannery effluents which are to be treated. These electrodes are cheap, available, and effective. EC is efficient in the segregation of suspended solids, grease, fats, etc. It has been found EC as a useful tannery effluent treatment technique depending on the composition of the effluent, material of the electrode, etc. (Yusif et al. 2016). Primary treatment helps to get rid of settleable solids which are organic and inorganic by sedimentation, and also helps to remove floatable materials (scum) by skimming. This treatment can reduce BOD, TSS, and fats (grease) approximately by 25–50%, 50–70%, and 65%, respectively (Buljan et al. 2011).

14.4.2 Secondary Treatment (Biological Treatment)

Secondary treatment further lowers down BOD and COD and other parameters that are still present in the effluent even after the primary treatment. Then only it satisfies the standard limit to be discharged into the water bodies. In this process, polluting substances are degraded biologically but in controlled conditions.

14.4.2.1 Aerobic Biological Treatment

As the term implies, oxygen is needed to degrade substrate by using organisms such as bacteria and fungi. Bacteria and fungi release enzymes like oxygenases and peroxidases which help in the oxidation of toxicants in the effluent. These decomposers can obtain energy by decomposing organic substrates (Yusif et al. 2016). Activated sludge reactor and membrane bioreactor are aerobic biological reactors.

14.4.2.1.1 Activated Sludge Reactor

Ardern and Lockett invented this technique to treat effluent and wastewater. The process involves the use of oxygen and floc formed by bacteria and protozoans (known as biological floc). Introduction of biological floc constituting nitrifying bacteria, saprophytic bacteria, etc., and air, to the effluent not only reduces the level of organic matter but also biotransforms ammonia. But this technique always requires sufficient oxygen supply for aeration in the treatment plant. Any shortage in air supply will lead to sludge bulking. This process is costly also (Verma et al. 2019).

14.4.2.1.2 Membrane Bioreactor (MBR)

MBR is a more efficient method in which a suspended growth bioreactor with microfiltration or ultrafiltration using membrane is used. MBR is commonly used in municipal and tannery effluent treatment. For activated sludge, MBR has proven to reduce more organic pollutants and ammonia (Yusif et al. 2016). However, it is also a costlier technique as frequent membrane cleaning and replacement is needed.

14.4.2.2 Anaerobic Biological Treatment

The aerobic process has many advantages as it is cost-effective and reliable. It also produces stable end products but the only drawback aerobic method suffers in the treatment of high-strength effluent. Therefore, for tannery effluents, an anaerobic treatment method is followed before aerobic treatment. In this treatment, degradation of organic contaminants in oxygen deficiency by microorganisms takes place. Many anaerobic bacteria like methanogens and acidogenic bacteria convert organic substances into methane, carbon dioxide and hydrogen (Dargo and Adhena 2014). It is more efficient than aerobic degradation as it requires less reactor surface area, low energy use, less use of chemicals, less sludge handling costs; reduces BOD, COD values; and also produces renewable energy, that is, methane. There are two types of anaerobic reactors: up-flow anaerobic sludge blanket reactor and anaerobic filter reactor.

14.4.2.2.1 Up-Flow Anaerobic Sludge Blanket Reactor (UASB)

It is a methane producing digestor used in the treatment of wastewater. In the UASB reactor, the effluent passes at the bottom of the reactor and moves up throughout the granular sludge bed. During up-flow, anaerobic digestion of organic contaminant takes place, and microbes convert organic carbon to methane gas (Verma et al. 2019). The advantage of using UASB reactors to increase the efficiency and stability of this system are as follows: (a) it consists of naturally immobilized bacteria in large volume having remarkable settling properties which could help in the removal of the organic pollutants from the wastewater efficiently; (b) a large concentration of biomass can be achieved without any construction costs.

14.4.2.2.2 Anaerobic Bio-Filter

Anaerobic biofilters are high-efficiency anaerobic treatment systems that involve the use of inert support materials in reactors to provide a stable environment for anaerobic bacteria to thrive and limit turbulence, allowing detached populations to remain in the system. The following are the primary advantages: (a) The filling provides a greater area for the growth of microorganisms, and also increases the hydraulic residence time of the effluent; (b) Anaerobic biofilters also provides a large surface area between wastewater and membrane interaction. Therefore, the efficacy of this treatment method can be improved. The limitation of this system is that when it comes to high-concentration organic water, the system may collapse, especially in the water intake part (Kassab et al. 2010).

14.4.2.3 Hybrid Treatment

Hybrid or combined reactors are more proficient in the treatment of tannery effluents as compared to the use of either anaerobic or aerobic reactors. Advantages of hybrid systems are as follows: (a) the anaerobic method helps to remove organic matters as well as suspended solids from the effluent, and reduce the organic pollutants from the aerobic degradation as well as the production of sludge; (b) pre-treated wastewater by the anaerobic system is more stable as the anaerobic process could reduce the oxygen demand of aerobic decomposition; (c) the anaerobic techniques modify by altering the biochemical property of the tannery wastewater which is then followed by a better aerobic process. From many reports, hybrid reactors are more stable and efficient for degradation of pollutants and applicable to use potentially. The combined aerobic–anaerobic reactors include an oxidation ditch and constructed wetland (Verma et al. 2019).

14.4.2.3.1 Oxidation Ditch

The oxidation ditch is a process that requires low maintenance. It is a basin formed in a circular shape. In this system, activated sludge is being added followed by microbes, which start acting on the effluent. The rotating biological contactors add oxygen into the passing mixed liquor which is a mixture of raw effluent and sludge, thereby increasing the surface area and its movement in the ditch. When organic matter is reduced, mixed liquor moves out of the ditch where sludge is collected in the secondary settling tank. Aerator pumps are used to thicken the sludge (Yusif et al. 2016). A part of sludge is again used in an oxidation ditch whereas the rest is thrown as waste. This step lowers the concentration of many organic pollutants, phosphorus and nitrogen but also forms sludge bulking and foam expansion.

14.4.2.3.2 Constructed Wetland

A constructed wetland is an artificial wetland behaving as a biofilter. It helps in the removal of sediments, organic matter, and absorption of heavy metals from the effluent. A mixture of water, media, plants, microorganisms, and other animals is used. Plants supply carbon, nitrogen, phosphorus, and oxygen for an aerobic environment through their roots for microbial growth to facilitate degradation of organic matter. In the constructed wetland, approximately 90% of pollutant is removed by microbes and the rest by plants. Thus, it is supposed to be an eco-compatible, easily managed reactor. But, because of some limitations, it is not widely used. As this technique requires a large field area, its efficiency is a little less as compared to other methods, and also, a selection of plants is available to increase its efficacy (Calheiros et al. 2012).

14.4.3 Tertiary Treatment

In most cases still, the effluent does not meet the standard disposal quality after primary and secondary treatment. In such cases, tertiary treatment is used before effluent discharge in the water body. Tertiary treatment is a more refined and expensive method like the Fenton method where organic compounds are treated with hydrogen peroxide in the presence of ferrous sulphate and ozone. These methods help in the removal of residual BOD, COD, and many harmful microbes (Buljan et al. 2011). It removes 90–95% pollutants and thereby treated water can be used for industrial, agricultural, and domestic purposes. Further disinfection methods are also used, like chlorination, ozone, and ultraviolet light, to get good quality potable water, which could be safe for public health.

14.5 Bioremediation: A Promising Tool

Bioremediation is a technique that employs biological agents mainly microbes like bacteria and fungi to transform heavy metals to a low-risk phase (Ndeddy Aka and Babalola 2016; Kumar et al. 2018). It is a cost-effective and eco-compatible technique. In other words, bioremediation can help eliminate, attenuate, or transform pollutants by the use of biological agents via various processes. This technique is a rising innovation that utilizes organisms to remediate contaminates sites (Kumar et al. 2020). Some bioremediation techniques require aerobic conditions and some run under an anaerobic environment for the degradation of recalcitrant pollutants to a safer level (Agrawal et al. 2021; Kumar and Chandra 2018). In bioremediation processes, microbes use organic matter or pollutants as their nutrient source to get energy. Many of the studies revealed a great potential of the strains of bacteria and fungi to decolourize the colouring agents, that is dyes from the industrial wastewater (Kumar et al. 2016). However, major issue is with the degradation of heavy metals as they persist or accumulates in the soil and water critically disturbing the environment (Kumar 2018). The adoption of the bioremediation technique has been found to be an efficient method for the cleaning of noxious contaminants present in the effluent by the use of microorganisms to remediate contaminates sites. The microorganisms have the capability of carrying out metabolic machinery for the breakdown of the pollutants of the toxic effluents from the tannery industries. Chemicals have been used for exposing the activities of microorganisms by developing necessary enzymes which aid in metabolizing the compounds in wastewater. Anaerobic reactors are used for treating waste effluents from tanneries using microbial culture. A large amount of microbial biomass is used by wastewater treatment plants, which generally have anaerobic digesters using anaerobic microorganisms. UASB has been used that shows efficacy towards the treatment of strong wastewater in comparison to conventional reactors. Identification of native microorganisms and consortium that are responsible for efficient reduction of recalcitrant compounds from the wastewater of tannery industries at laboratory scale is a better choice for the environmental clean-up.

The use of microorganisms in bioremediation techniques for treating the wastewater from tannery industries has been effective due to the characteristics of the microorganisms with respect to their size, Supplementation of nutrition, water, and optimum physiological condition for the growth and multiplication of the cells. This treatment of tannery wastewater while using the microorganisms generates the biomass sludge. The decomposition of organic material helps in obtaining the nutrient supplementation for the microorganisms that aids in multiplying the cell. Hence, microorganisms are efficiently used for decaying organic wastes present in the leather waste stream by multiplying their number to show effective degradation of organic matter. Bacterial cells usually undergo biological oxidation that involves degradation of organic compounds in the waste stream and are used as nutritional supplements.

One of the major challenges while using the technique of bioremediation is the degradation of heavy metals as they persist or accumulate in the soil and water, critically disturbing the environment. Hence, different types of bioremediation techniques have been adopted by tannery industries to meet the concerned challenges. Different types of bioremediation techniques are capable of removal of heavy metals and chlorogenic contents from tannery wastewater and establish several other applications in the reuse of the wastewater. Economically valuable metals can be recovered and reused by applying bioremediation for cleaning wastewater from tannery industries. Various types of microorganisms have been proved to be effective for removal of heavy toxins from tannery wastewater. Phytoremediation is another effective method of bioremediation that involves the use of plants for accumulation, hyperaccumulation, and exclusion of heavy metals for remediation of wastewater.

The present chapter thus concludes with the fact that treatment of tannery wastewater involves several challenges concerned with ill-effects of the environment which needs to be addressed on an immediate basis. Hence, the use of eco-friendly and cost-effective techniques such as bioremediation and phytoremediation has been proved to be efficient for removal of toxins and recovery of important metals from wastewater and further capable of making the wastewater available for reuse for several purposes. The treated tannery wastewater is mainly reused for non-potable purposes such as agriculture and leather tanning. Hence, this would prove to be effective in minimizing issues of water scarcity and increase productivity.

14.5.1 Types of Bioremediations

Microbes are very efficient; they can transform toxic substances into less harmful intermediates or can completely degrade them into harmless end products. Microorganisms are capable enough to survive at the lowest temperature to extreme conditions and can exploit contaminants as their sole source of energy. Microbes also restore the original natural surroundings and prevent further pollution. Microorganisms grow and interact with the pollutant depends on environmental conditions like temperature, soil, water solubility, the concentration of pollutant, pH, type, and solubility of a toxic substance. Optimum pH which works best for bioremediation of the pollutant can occur from 6.5 to 8.5 in most aquatic and terrestrial environments. These factors are responsible for the degradation kinetics (Naik and Duraphe 2012).

14.5.1.1 Biosorption

The metals can be held by interactions between the metal and functional groups present on the cell surface of microbes. The various means are adsorption, ion exchange, precipitation, complexation, and crystallization. Several factors like pH, temperature, ionic strength, particle size, and biomass concentration could affect metal biosorption. Living as well as dead biomass are employed for biosorption because of its independence of cell metabolism as metals are taken up passively on the cell wall through surface complexation. The biosorption process needs to be economic as the biomass can be procured from effluent and could be restored for further use. Any biological materials which possess affinity towards metals are referred to as biosorbent. Heavy metals attach to the biomass surface and become loaded with metal ions. Some of the reports have mentioned chromium removal from tannery wastewater by chromate-resistant bacteria through biosorption, such as *Pseudomonas fluorescens* (Bopp and Ehrlich 1988).

Other bacteria such as *Enterobacter* cloacae and *Acinetobacter* sp. also showed biosorption of chromium (Srivastava and Thakur 2007). *Bacillus megatherium*, *Bacillus subtilis*, and some bacterial consortia showed biosorption of other metals like lead and cadmium from tannery effluents (Abioye et al. 2018). Kim reported *Desulfovibrio desulfuricans* for the removal of Ni, Cr (VI), and Cu metals. *Acinetobacter* and *Arthrobacter* have been reported to remove 78% of chromium from the wastewater (Bhattacharya et al. 2014). Fungi also act as biosorbents that uptake metals. *Trichoderma*, *Aspergillus*, *Penicillium*, *Rhizopus*, and *Saccharomyces* species showed remarkable biosorption potential. Approximately 97% chromate at pH 5.5 was removed by *Trichoderma* sp. (Vankar and Bajpai 2008).

14.5.1.2 Bioaccumulation

Bioaccumulation is a system that relies upon diverse physical, chemical, and organic mechanisms and those elements are intracellular and extracellular processes, Bioaccumulation, on the other hand, wishes luxurious price due to the fact the system happens inside the presence of residing cells best as it cannot be reused. Energy demand is also high which is required for cell growth. Heavy metals like chromium, nickel and cobalt were adsorbed on *R. arrhizus*, *A. niger,* and *Saccharomyces cerevisiae* (Gautam et al. 2015). Many dead biomasses of fungi such as *Aspergillus niger*, *Penicillium chrysogenum*, *Rhizopus oryzae*, and *S. cerevisiae* could transform toxic Cr (VI) to less toxic form Cr (III) (Park et al. 2005). Some yeast strains have also been used to convert Cr (VI) to Cr (III), such as *S. cerevisiae*, *Rhodotorula mucilage*, *Rhodotorula pilimanae*, *Hansenula polymorpha*, *Yarrowia lipolytica*, and *Pichia guilliermondii* (Ksheminska et al. 2008).

14.5.1.3 Methylation of Metals

Metal toxicity is increased by the methylation of metals by enhancing movement across cell membranes. Methylation by microbial cells plays a very important role in metal removal. Usually, methylated compounds are found to be explosive. Some bacteria such as *Bacillus* sp., *Escherichia* sp., and *Clostridium* sp. helped in bio methylation of mercury to gaseous methyl mercury (Ramasamy and Banu 2007).

14.5.1.4 Biostimulation

To stimulate the activity of microbes on infected sites, both soil and water is being injected with supplements (precise nutrients). Addition of stimulators, minerals, and optimizing environmental factors hurry up the microbial metabolism rate. Moreover, addition of biostimulant on suitable microbes may further efficiently degrade the pollutant (Naik and Duraphe 2012).

14.5.1.5 Bioattenuation

It is also referred to as natural attenuation of removing pollutants from the environment. This process takes place either aerobically or anaerobically. It also involves physical processes such as dispersion, diffusion etc, and chemical processes such as ion exchange, abiotic conversion. When the ecosystem gets contaminated with chemicals, nature itself works to clean itself using ways such as (1) soil microorganisms and microbes in groundwater use pollutants as their food, and after decomposing the chemicals, convert them into nontoxic gases and water. (2) Chemicals can adhere to the soil; this method does not clean up the surroundings but will prevent contamination in water. Chemicals hold the soil in a place. (3) This method also prevents the further pollution of clean water.

14.5.1.6 Bioaugmentation

It is a process to create an environment of microbes with augmented biodegradative capacity so that they can act in polluted areas. This method involves natural as well as designed (engineered) microbes making them bio remediators that can rapidly clean up the site with complex pollutants. After the collection of microbes from sites, they are cultured, genetically modified, and then placed back to the location site. A wide range of digesting ability is being proved by Genetically modified microorganisms (GMM) and transforming pollutants into less harmless end products (Sayler and Ripp 2000). GMM is modified by DNA manipulation and is more efficient in comparison to the natural species to break down the contaminate at a faster rate. GMMs have proven capacity for bioremediation of soil, groundwater, and activated sludge filled with pollutants (Thapa et al. 2012).

14.5.1.7 Microbial Technology

Microbial technologies as a remediation technique are very actively growing these days. For depollution, microbe–metal interaction is primarily focussed. Genetic engineering and chemical change ought to modify the additives of cells surface and might correctly enhance the adsorption ability to target metallic species. It is a technique in which a microorganism whose genetic material is changed by recombinant DNA technology. In this procedure, genetically modified organisms are created by improving them either by eliminating toxic genes or adding useful ones under laboratory conditions. In addition, microbes are engineered with favoured traits consisting of the potential to tolerate metallic stress, overexpression of metal-chelating proteins and peptides, and cap potential of metallic accumulation. In genetic engineering techniques, metabolic pathways can be altered so that degradation kinetics can be increased or by modifying enzyme specificity. By using GEMs, hoarding of pollutants can be achieved in a shorter time. With the use of a small amount of biomass, a large area of disposal sites can be treated, decontaminated, and transformed into a purified environment. With several advantages, there are some disadvantages of GEMs. In contrast, genetic manipulation in microbes may alter microbial community resultant of whole ecosystem may affected (Kumar et al. 2021a, b).

14.6 Phytoremediation

It is also known as botanical bioremediation, involving the use of plants to depollute soil and water. Phytoremediation is implemented to detoxify the contaminants of the effluent naturally. The ability to hoard heavy metals varies among species primarily based totally on their genetic, morphological, physiological, and anatomical features. The strategy involves the employment of plants are to either accumulate, translocate, stablize, transform or degrade the heavy metals present in the environment (Chandra et al. 2018a, b). Green plants act as lungs which help sanitize atmospheric air by photosynthesis and also degrade toxic metals in soil and water by assimilation, adsorption, and biotransformation process (Chandra and Kumar 2017, 2018). Vascular plants assimilate toxicants either directly from the air through leaves or from soil or water through roots. Several plant species have been identified to absorb and collect certain heavy metals (Lone et al. 2008). The types of phytoremediation are illustrated in Table 14.1. There are some reports on the removal of colours/dyes from wastewater with the help of plants. Protein from plant *Rheum rhabarbarum* showed its capacity to detoxify sulphonated anthraquinones (Aubert and Schwitzguébel 2004). Phytoremediation along with microbial organisms has been a trendy approach towards transforming xenobiotic compounds to less harmful states. Genetically modified plants (GMP) are another innovative approach to detoxify recalcitrant compounds from the fields. The recombinant proteins created by GMP assume a critical part in chelation (e.g. citrate, phytochelatins, metallothioneins, phytosiderophores, and ferritin), osmosis, and layer transport of metals (Vamerali et al. 2010).

Table 14.1 Phytoremediation and their action

Types of phytoremediation	Action
Phytoaccumulation (Phytoextraction)	The assimilation and uptake of metals is performed by plant roots emulated by their translocation and finally aggregation and fixation over the ground in the ariel parts of plant (shoots). Accumulated metal ions in aerial parts can be removed and disposed of, or burned to recover metals
Phytofiltration (Rhizofiltration)	Plant roots are used in this procedure to remove metals from aqueous wastes
Phytostabilization	From the soil toxic substances are stored in the rhizosphere which prevents them from leaching
Phytovolatilization	It includes the use of plants to remove toxins from the environment such as Se and Hg
Phytodegradation	Utilization of plants and related microbes to degrade organic pollutants by using specialized catalysts (dehalogenase, reductase and oxygenase) alternately cofactors for the corruption of contaminants from soil and groundwater

14.6.1 Phycoremediation

Phycoremediation is the process of removing or degrading toxicants using various forms of algae and cyanobacteria. Algae are autotrophic, requires low nutrients, and are very capable to decolourise dyes of the effluent and heavy metals from the effluent. Algal species such as *Chlorella*, *Oscillatoria*, and *Spirogyra* have been mentioned in some reports as decolourisers (Romera et al. 2007). These biosorbents remove heavy metals from the effluent via adsorption or by ion-exchange methods. These functional groups such as sulphonate, sulfhydryl, hydroxyl, carboxyl, phosphate, and amino act as a binding site for metals. The degradation kinetics is dependent on the algal species and the chemical nature of the dye. The algal enzyme azo reductase can break the azo bond in azo dyes and convert them into aromatic amines and then to simpler forms. Green algae, brown algae, diatoms, and cyanobacteria can also decolourize di-azo dye (Dwivedi and Tomar 2018). Some of the organisms showing bioremediation property in removing heavy metals from effluents are listed in Table 14.2.

14.7 Conclusion

Several attempts have been made by the tannery industries for treating the discharged effluents which have evolved many challenges in the environment. The use of conventional methods has been proved to be effective with the implementation of physicochemical treatment methods remediating the metal-polluted sites. But due to the high operational costs with the requirement of large area, energy, chemicals, and labour and resulting in environmental damage, these conventional

Table 14.2 Organisms showing bioremediation

Organisms	Metal uptake	Reference
Bacillus cereus	Cr	Kanmani et al. (2012)
Bacillus subtilis	Cr	Kim et al. (2015)
Acinetobacter sp.	Cr, Ni	Bhattacharya et al. (2014)
Pseudomonas sp.	Pb, Cu, Cr, Zn, Ni	Kumaran et al. (2011)
Pseudomonas veronii	Cd, Cu, Zn	Vullo et al. (2008)
Pseudomonas aeruginosa	Cr	Kumaran et al. (2011)
Pseudomonas fluorescens	Zn	Uzel and Ozdemir (2009)
Stenotrophomonas sp.	Cr	Benazir et al. (2010)
Desulfovibrio desulfuricans	Cr, Ni, Cu	Kim et al. (2015)
Cellulosimicrobium sp.	Cr, Pb	Bharagava and Mishra (2018)
Methylobacterium sp.	Pb, Cu	Kim et al. (1996)
Micrococcus	Cr, Cu, Pb	Congeevaram et al. (2007)
Burkholderia	Cd, Pb	Jiang et al. (2008)
Agaricus bisporus	Cd, Zn	Nagy et al. (2017)
Aspergillus versicolor	Cr, Ni, Cu	Taştan et al. (2010)
Aspergillus niger	Cr, Ni, Co, Hg	Taştan et al. (2010)
Aspergillus, Penicillium, Mucor, and *Rhizopus*	Cd, Cu, Fe	Loukidou et al. (2003)
A. foetidus, *A. niger*, and *Penicillium simplicissimum*	Ni, Co, V, Fe, Zn, Mo, Mn	Anahid et al. (2011)
Aspergillus fumigatus	Pb	Kumaran et al. (2011)
Penicillium spp.	Cr	Loukidou et al. (2003)
Ganoderma lucidum	Ar	Say et al. (2003)
Saccharomyces cerevisiae	Cr	Parvathi et al. (2007)
Chlorella pyrenoidosa	U	Romera et al. (2007)
Cladophora fascicularis	Pb	Aung et al. (2013)
Fucus vesiculosus	Cr, Cd, Pb	Deng et al. (2007)
Hydrodictyon, *Oedogonium*, and *Rhizoclonium* spp.	V, As	Murphy et al. (2008)
Spirogyra spp. and *Cladophora* spp.	Pb, Cu	Lee and Chang (2011)
Spirogyra and *Spirullina* spp.	Cr, Cu, Fe, Mn, Zn	Romera et al. (2007)
Chlorella vulgaricus	Cu, Pb Ni, Cd	Mane and Bhosle (2012)
Chlorella miniate	Cr	Goher et al. (2016)
Melia azedarach, Azadirachta indica, and *Leucaena leucocephala*	Cr	Sakthivel and Vivekanandan (2009)
Brassica spp., *Sorghum bicolor*, and *Spinacia oleracea*	Cd, Cu, Cr, Zn	Firdaus and Tahira (2010)
Helianthus annuus	Cr	January et al. (2008)
Brassica spp.	Zn, Cu, Ni, Cd, Pb	Purakayastha et al. (2008)
Portulaca tuberosa and *P. oleracea*	Cr, Cd, As	Tiwari et al. (2008)

methods need to be replaced with some alternative methods that are eco-compatible and cost-effective for the clean-up of tannery effluents.

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