10 Advanced Bioremediation Strategies for Mitigation of Chromium and Organics Pollution in Tannery

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Abstract

Recent past has witnessed to increase in environmental pollution because of rapid urbanization and industrialization. Various organic and inorganic toxicants are present in tannery effluents such as metals and other xenobiotic compounds which cause imbalance to the ecosystem having carcinogenic effects threaten plants, human, and animals' health. Chromium is one of the major pollutants discharged from tanneries, is highly toxic, mutagenic, and carcinogenic in nature. There are several remedial measures for the removal of such toxicants. Physico-chemical approaches remove the pollutants but they are not cost-effective and eco-friendly. Microorganisms based treatment of toxic chemicals either in liquid or solid system is one of the most economic, effective, environment friendly, robust, and sustainable remediation strategy. Several microbes of different physicochemical orientation and plants may selectively be employed for such remedial measure of any type of toxic chemicals of industrial effluent. This chapter discusses the recent advances and challenges in bioremediation methods of tannery wastewater.

Keywords

Bioremediation · Chromium · Heavy metals · Tannery · Pollution

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10.1 Introduction

In the past few years, industrialization and modernization produced many problems in the form of hazardous pollutants in the environment. Industrial processes insert various types of hydrocarbons, heavy metals, chlorinated phenols, biocides, and dyes to the environment (Garg and Tripathi 2011; Nicolopoulou-Stamati et al. 2016; Tripathi et al. 2019). These pollutants cause pollution in water, soil, and air resulting in harmful effects on environment and human health (Zhang et al. 2020). Chromium has contaminated all types of water resources (Szulczewski et al. 1997). There are several other industries such as chemical, iron, and steel producing bulk of chromium pollution (Chirwa and Wang 2000, 2005; Garg et al. 2012). The excessive use of hexavalent chromium (Cr^{6+}) in industries has caused substantial environmental pollution (Sultan and Hasnain 2007). Such waste is discharged into the ecosystem through leakage and inappropriate remediation methods (Palmer and Wittbrodt 1991). Chromium is listed as a priority pollutant by United States Environmental Protection Agency with discharge limit of 0.05 mg L^{-1} (U.S. EPA 1979). While the permissible limit for Cr^{6+} is 0.1 mg L^{-1} in India (Bhide et al. 1996). Chromium exists from −2 to +6 oxidation states (Avudainayagam et al. 2003); however, the most common oxidation states of Cr are +6 and + 3 (Garg et al. 2012). Cr^{6+} is toxic, carcinogenic, mutagenic, and teratogenic (Garg et al. 2013; Tripathi et al. 2011a, b, 2019). It is important to remove such toxicants or at least transform them to nontoxic form before they release into the environment. Our ecosystem is damaging due to discharge of improperly treated large quantities of heavy metals and organics containing toxic waste. Due to their bioaccumulation, persistence, and resistance to bioremediation, metal pollution has become hazardous to all living forms of our environment. To tackle the challenges due to Cr^{6+} pollution, a concerted effort should be undertaken involving both surveillance of its use and improvements in remediation processes (Garg et al. 2012).

Another major toxicant is pentachlorophenol, also discharged from tannery effluent which is highly toxic and recalcitrant (Srivastava and Thakur 2007; Thakur et al. 2001; Tripathi et al. 2014a, b). Due to its toxicity, US EPA listed PCP in the list of priority pollutants. According to the ISI, the standard limit for phenolics is 0.002 mg L^{-1} in surface waters (Tripathi and Garg 2013). Phenolic compounds are accumulated in biological food chains causing toxic effects (Garg et al. 2013). Thus, remediation of such pollutants from effluent is necessary. There are many strategies that have been used for preventing harmful effect of such pollutants up to certain level. Physical and chemical methods are being used to remediate these pollutants but due to some limitations such as cost and non-ecofriendly nature, it has not been applied successfully. Despite this, microbiological methods or bioremediation are currently applied to decrease the toxicity of pollutants from soil, water, and environment.

Bioremediation is the application of live forms of organisms, particularly microbes, to remove pollutants and transform them into innocuous forms in the environment (Garg et al. 2012). Microbe based remediation has been developed to degrade toxicants through various biosynthetic pathways. A number of bacteria, fungi, algae, actinomycetes, etc. are being used for bioremediation. This process is facilitated by two ways, in situ (on site) and ex situ (away from site). Microbial systems are being introduced to the contaminated site to enhance the remediation process known as bioaugmentation (Vidali 2001) which are mechanized by bioreduction, biosorption, and bioaccumulation (Rehman et al. 2007). Bioreduction is another approach of bioremediation in which the toxic Cr^{6+} is reduced to Cr^{3+} using microbial enzyme chromate reductase (Tripathi and Garg 2014a, b). The main benefits of bioremediation over traditional methods include cost effective, less amounts of secondary pollutants, good efficiency, and regeneration of biomass for further use (Garg et al. 2013). This chapter discusses different advanced methods of bioremediation, and their mechanisms using potential microorganisms in the treatment of hexavalent chromium and organic pollutants from the tannery wastewater.

10.2 Physicochemical Characteristics of Tannery Wastewater

Tannery wastewater causes serious problems to ecosystem because of various toxic components. Such toxicants came in the environment through discharge from industries affecting almost all living systems. Some researchers discussed common characteristics of the organic pollutants (Yadav et al. 2016). There are several parameters like biological oxygen demand (BOD), chemical oxygen demand (COD), total dissolved solid (TDS), residual chlorine, sulphide, nitrate, phenol, total chromium along with other heavy metals, oil and grease were found above than the standard permissible levels of tannery wastewater (Table 10.1). Heavy metals cause serious toxicological concerns to human health (Davis et al. 2000; Yadav et al. 2017).

Both BOD and COD values indicate the level of organic pollution in wastewater (Tripathi et al. 2011a). Tiwari et al. (2012) used a bacterium, *Pediococcus acidilactici* B-25 strain for the removal of color, COD, and BOD of distillery wastewater. There are many inorganics such as Cr^{6+} along with other heavy metals which are not easily removed from the polluted sites and persist in the environment. Thus, it is very important to treat properly such toxicants from tannery effluent before discharge into the environment.

10.3 Chromium and Organics Pollution

Chromium and organics pollution may be due to several weathering of rocks, discharge of improperly treated industrial effluent such as tannery waste and leaching of soils (Oliveira 2012). However, contamination from oil spills, leakages, domestic, and industrial wastes contributes to organics pollution in the environment (Fig. 10.1). Cr^{6+}contamination in the environment adversely affects the soil microbial communities (Yadav et al. 2016).

It causes several health problems to living systems (Chandra et al. 2011; Turick et al. 1996). These contaminants are entering and increasing in our ecosystem

Table 10.1 General properties of the treated tannery wastewater (Source: Tripathi et al. 2011a)

Physicochemical parameter/heavy metal	Permissible limit[a]	Obtained value
pH	5.5–9.0	7.3 ± 0.15[b]
Temperature	<35 °C	34 ± 0.27
Total solid (mg L^{-1}) Total suspended solid (mg L^{-1}) Total dissolved solid (mg L^{-1})	– 600 2100	3468 ± 1.89 1102.25 ± 0.22 2366.62 ± 1.65
Total alkalinity (mg L^{-1})	–	340 ± 3.05
Total acidity (mg L^{-1})	–	201.33 ± 1.08
Residual chlorine (mg L^{-1})	1	5.17 ± 0.18
Hardness (mg L^{-1})	–	780.45 ± 1.02
Sulfide (mg L^{-1})	2.0–5.0	9.43 ± 0.20
Oil and grease (mg L^{-1})	10.0	19.86 ± 0.67
B.O.D. (mg L^{-1})	30.0	104.90 ± 0.25
C.O.D. (mg L^{-1})	250.0	490.93 ± 1.27
Total nitrogen (mg L^{-1})	100.0	30.64 ± 0.69
Nitrate (mg L^{-1})	10.0	15.09 ± 0.05
Phenol (mg L^{-1})	1–5.0	11.93 ± 0.17
Cr^{6+} (mg L^{-1}) Total-Cr (mg L^{-1})	0.1 2.0	1.26 ± 0.05 8.89 ± 0.74
Pb^{2+} (mg L^{-1})	0.1	0.47
Cu^{2+} (mg L^{-1})	3.0	0.006
As^{3+} (mg L^{-1})	0.2	0.39
Ni^{2+} (mg L^{-1})	3.0	0.72
Zn^{2+} (mg L^{-1})	5.0	0.36
Cd^{2+} (mg L^{-1})	2.0	0.002

[a]Permissible limits prescribed by United States Environment Protection Agency (USEPA) and Ministry of Environment and Forest (MOEF)
[b]Mean value ± SD

because of rapid industrialization and urbanization. There must be strict rules to overcome from pollution. Xenobiotics are synthesized chemicals that persist in the ecosystem for longer period at higher concentrations. They are recalcitrant compounds such as pentachlorophenol and synthetic dyes discharged from various industrial discharges (Garg et al. 2012; Garg and Tripathi 2011; Tripathi et al. 2019).

10.4 Toxicity of Chromium

Chromium of hexavalent nature is more toxic, mutagenic, and carcinogenic in aquatic systems (Losi et al. 1994; Lovely and Coates 1997; Pal et al. 2005; Ray and Ray 2009), whereas $Cr^{3+}$is innocuous form of chromium. The increased bioconcentration of metals and their toxicity to all the live forms show the urgent call for the treatment of these toxicants from the polluted soil and water. The metals are generally accumulated in living systems through the food (Perpetuo et al. 2011).

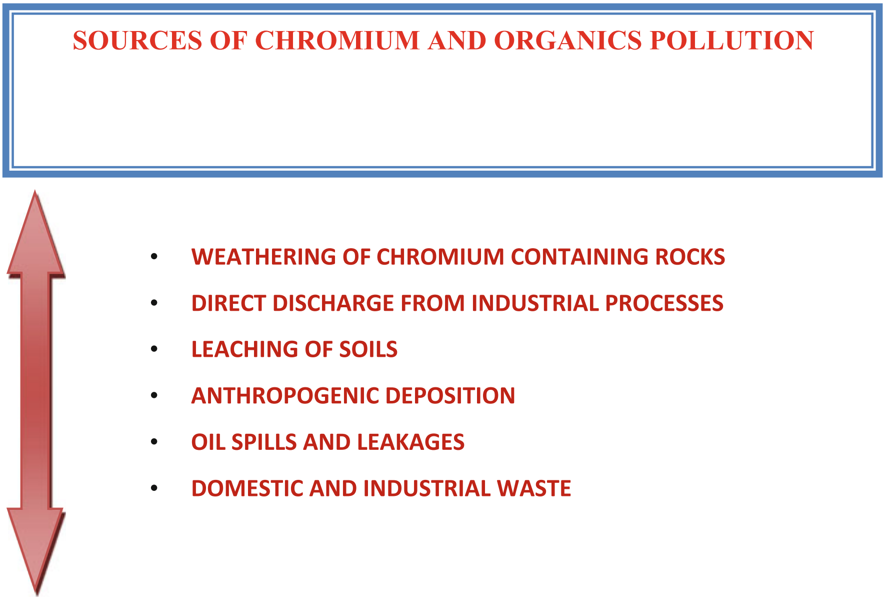

Fig. 10.1 Different sources of chromium and organics contamination in the environment

Heavy metal like Cr inhibits photosynthesis, growth and causes chlorosis in plants by hindering iron metabolism (Purakayastha and Chhonkar 2010; Upadhyay et al. 2017). Chromium affects various tissues in human and animals that include dermal, lung, liver, kidney, red blood cells, and spleen (Holmes et al. 2008). Kumar et al. (2013) reported adverse effects of heavy metals to human health. There are number of diseases such as respiratory and nephrotic ailments found in the workers of tannery industry (Maria et al. 1999).

10.5 Bioremediation

Bioremediation is one of the most important approaches for pollution mitigation. It offers the possibility of using indigenous or exogenous microbes to detoxify or degrade various toxicants that are hazardous to ecosystem. Bioremediation occurs aerobically or anaerobically. It removes pollutants which are detrimental to the environment by the application of phyto- and microbial remediation (Kumar et al. 2017). A number of bioremediation processes such as bioaugmentation, biostimulation, bioreduction, biosorption, bioaccumulation, immobilization, and phytoremediation are being used for Cr^{6+} remediation and organic pollutants.

Figure 10.2 shows the different strategies for Cr^{6+} and organic pollutants remediation from contaminated sites. These methods include physical, chemical, and biological along with modern approaches for treating contaminated sites. In general, bioremediation process can be performed by ex/in situ. In situ bioremediation

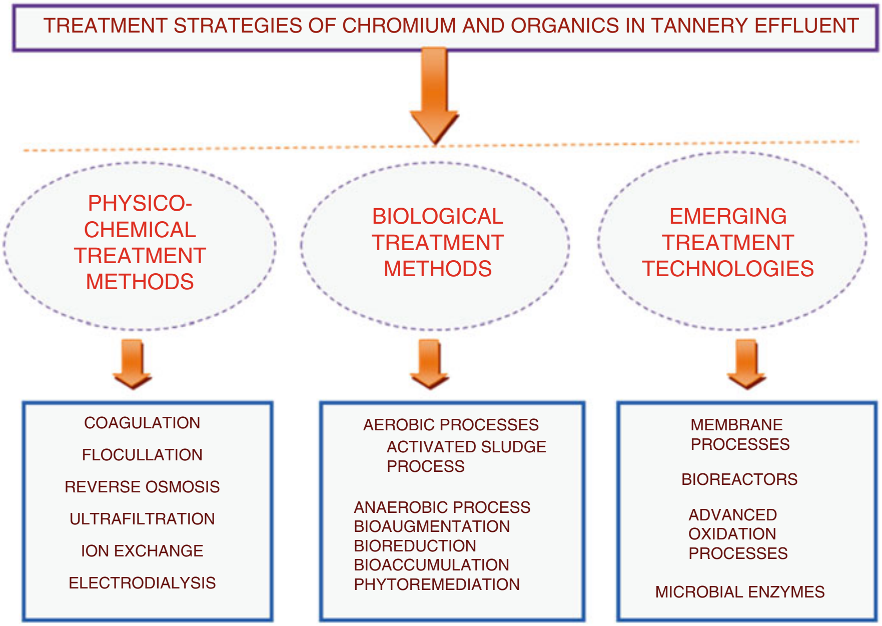

Fig. 10.2 Different methods for remediation of hexavalent chromium and organics from polluted sites

(bioventing, biosparging, phytoremediation) involves the treatment of contaminant on site of its origin. However, in ex situ bioremediation (composting, land fills, biopiles), treatment of pollutants occurs away from the contaminated origin sites that involve transportation.

Thus, in situ bioremediation is better option for treatment due to its cost effectiveness and feasibility.

It has been showed in many studies that microbes can interact with heavy metals ions (Cr^{6+}) for their removal (Garg et al. 2018; Ishibashi et al. 1990; Shen and Wang 1995; Upadhyay et al. 2017; Tripathi et al. 2018; Tripathi and Garg 2014a, b). The reduction of Cr^{6+} to $Cr^{3+}$is used to detoxify Cr^{6+} from polluted sites. Genetic engineering of microbial cells may change their characteristics in such a way that may help to bioremediation.

There are some important factors such as the use of low cost waste biomass, its immobilization and regeneration for opting bioremediation as a strategy for the removal of toxicants from industrial effluent (Quintelas et al. 2006; Garg et al. 2012; Tripathi et al. 2019). Also, there are various physicochemical and nutritional parameters that may affect the bioremediation of tannery waste (Fig. 10.3) which control the treatment process in the ecosystems that are polluted with Cr^{6+} and organic pollutants.

Different bioremediation approaches for mitigation of Cr^{6+} and organic pollutants are discussed below.

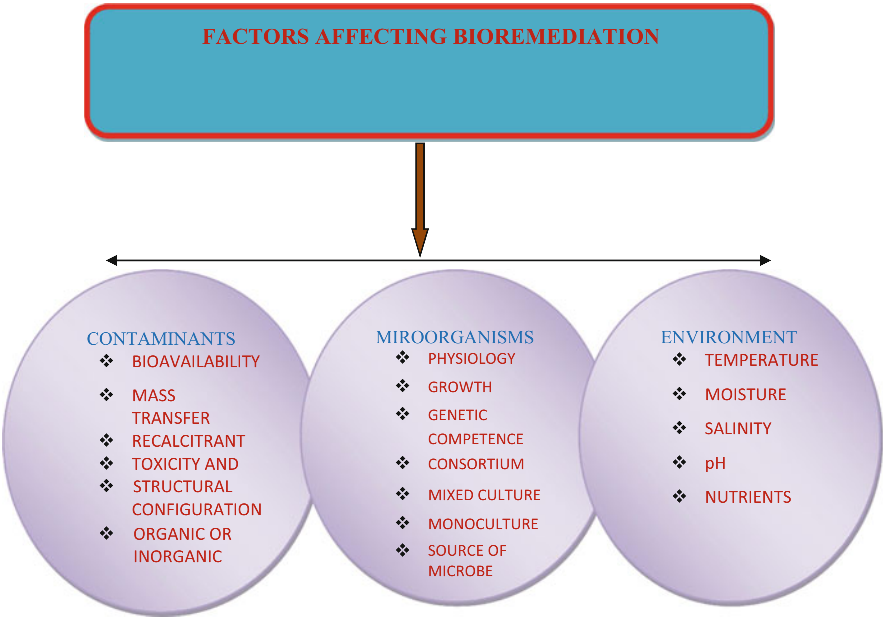

Fig. 10.3 Factors affecting bioremediation of Cr^{6+} and organic pollutants in tannery effluent

10.5.1 Mechanism of Cr^{6+}Removal by Microorganisms

Several microbes have been used with their applicability in Cr^{6+}bioremediation (Garg et al. 2013; Tripathi et al. 2011a, b, 2014a, b; Tripathi and Garg 2010, 2013). There are some important methods applied in heavy metal bioremediation by decreasing the solubility of metals by altering the pH, redox reaction, and adsorption from the contaminated sites. In redox reactions, heavy metals are transformed into the less toxic form that is less mobile and stable. The major bioremediation mechanisms of Cr^{6+} are biosorption, bioaccumulation, bioreduction, bioaugmentation, phytoremediation, and enzymatic transformation (Fig. 10.2). The efficiency of these techniques depends on several parameters that include the type and nature of organism used, the existing environmental factors, nutrients availability, and the concentration of pollutant present in that environment (Fig. 10.3).

10.5.1.1 Biosorption

It is an independent passive metabolic process in which physicochemical interaction occurs between metal species and the cellular components of microbial species (Shumate and Strandberg 1985). The biosorption process comprises different kinds of mechanisms that include physical adherence, ion exchange, and surface complexation, which differs based on the type of microorganisms used and method of processing (Srivastava and Dwivedi 2015). There are different biosorbent materials such as bacteria, yeast, algae, and fungi, which carry out the biosorption process through several mechanisms, including ion exchange, redox processes, electrostatic interactions, surface complexation, and precipitation (Beiyuan et al. 2017). Different functional groups such as carboxyl, imidazole, sulfhydryl, amino, phosphates, etc. are present on biosorbent which interact with metal species (Garg et al. 2012). The selection of biosorbent material requires certain criteria that must be followed, including low cost and reusable biosorbent, rapid movement of metals, and effective separation from the solution (Kumar et al. 2016).

Microorganisms, due to their widespread presence, play significant role in transforming toxic heavy metals into nontoxic forms. Microbes act as effective biosorbents due to their small size for removal of such toxicants. The bacterial cell wall is the main barrier which save microbes from toxic heavy metals. The cell wall carries a natural negative charge and has various functional groups that are involved in the metal binding and also regulate their movement across the membrane. These bacteria contain carboxyl and phosphate groups present in their cell wall that acts as the main binding site for metal cations (Fomina and Gadd 2014; Ayangbenro and Babalola 2017). The type of interaction involves ion exchange, chemical, and physical processes (Garg et al. 2012). The cell wall of microbes consists of proteins, lipids, and polysaccharides (Dixit et al. 2015).

Various microbial groups such as bacteria, fungi, algae, actinomycetes, etc. are applied for biosorption of toxic hexavalent chromium by many researchers. Biosorption is carried out by dead and live cells (Srinath et al. 2002; Tripathi et al. 2011b). Several researchers used microorganisms for removal of Cr^{6+} (Garg et al. 2013; Park et al. 2005; Srinath et al. 2002; Tripathi et al. 2011b). The pH specificity also plays an important role in biosorption (Volesky 1990).

Generally, industrial effluents are characterized by coexistence of many types of toxic cationic and anionic species (Garg et al. 2012). Industrial effluents generally contain numerous cations and anions of metals/non-metals, the latter of which may impart assistance in binding of the concerned heavy metals. Thus, it is important to study the influence of toxicants mixtures on the growth of microbes when studying bioremediation strategies.

10.5.1.2 Bioaccumulation

It is energy-dependent, i.e., it uses the metabolic energy of bacteria to transport heavy metals by several processes like adsorption, intracellular accumulation, and bioprecipitation mechanisms. These mechanisms are reported to be related with the transport of heavy metals. Several researchers study the bioaccumulation of Cr^{6+} by different types of microorganisms (Congeevaram et al. 2007; Srivastava and Thakur 2007; Tripathi et al. 2011b). Parameswari et al. (2009) observed the efficacy of *Azotobacter chroococcum*, *Bacillus* sp., and *Pseudomonas fluorescens* for Cr^{6+} removal. However, biosorption, as a passive process, has several advantages over bioaccumulation. In biosorption, the simple physical method of recovery of heavy metal is achieved without breaking the biosorbents structural integrity, while bioaccumulation is a passive as well as active process in which cells get disrupted during the process.

10.5.1.3 Biostimulation

Nutritional amendment also enhances the process of bioremediation. Biostimulation process facilitates the growth of native microbes of the polluted site by providing nutrients, oxygen, surfactants, and pH alteration substances which are responsible to increase the bioremediation process (Li and Li 2011). Garg et al. (2018) studied the effect of nutrient addition on Cr^{6+} removal by adding carbon and nitrogen sources in diluted tannery effluent. They observed better removal efficiency than nutrients unaided effluent.

10.5.1.4 Bioaugmentation

In this approach, exogenous microbes are added to the population of native microbes in order to increase the capability of already existing microbes to remove the pollutants. The microbes that have naturally occurring catabolic genes or that are genetically modified can be used in this process. This process is affordable, efficient, and quick, making its way among remediation experts. Garg et al. (2016) reported better Cr^{6+} ability in *Pseudomonas* sp. augmented diluted effluent medium than unaugmented medium.

10.5.1.5 Bioreduction

The oxidation state of toxic metals is affected by the activities of microorganisms for the reduction of Cr^{6+} to Cr^{3+} (Asatiani et al. 2004; Farag and Zaki 2010; Ilias et al. 2011; Liu et al. 2008; Tripathi et al. 2011a). Bacteria that grow in high Cr^{6+} containing natural environment develop chromium resistance indicate that they have ability to reduce Cr^{6+}, thereby may be isolated such resistant strain directly from ecosystem (Liu et al. 2008). Tripathi and Garg (2014a, b) reported 74.5% reduction by indigenous bacterial isolate *B. cereus* at initial 200 mg Cr^{6+} L^{-1} within 48 h incubation in minimal salt medium. However, Garg et al. (2018) found that *P. putida* strain has the ability to survive and reduce chromate in tannery effluents. The isolate survived in the native diluted tannery effluent and reduced Cr^{6+}. However, supplementation with carbon and nitrogen sources enhanced the bioremediation of Cr^{6+} in native diluted effluent. The microbial mechanisms for Cr^{6+} reduction is a detoxification mechanism that occurs intracellularly with the help of enzyme chromate reductase (Tripathi and Garg 2014a, b).

10.5.1.6 Immobilization and Elution of Chromium

The cell biomass used for biosorption as well as bioaccumulation is loaded with metals, and desorption of the loaded metal separate metal from adsorbent for reuse in industry, and the regenrated biomass is suitable for next round(s) of biosorption which make cost effective bioremediation process (Garg et al. 2012). Agar, polyacrylamide, and alginate matrices have been used in several immobilization studies (Tripathi and Garg 2013). The elution of bound chromium from cell biomass depends on its ionic state. It is normally found that when chromium is bound in hexavalent state, its simple elution by acidic solutions is based on reduction to trivalent state, which is then subsequently released into the eluent fraction (Garg et al. 2012). Some researchers reported sulfuric acid (1.0 M) and found to be the most efficient eluent (Srinath et al. 2003). Benazir et al. (2010) studied the chromium bioremediation efficiency in the consortium of *B. subtilis, P. aeruginosa,* and *S. cerevisiae* in immobilized and nonimmobilized cells. Tripathi and Garg (2013) also used immobilized cells of *B. cereus* with alginate for Cr^{6+} removal. Similarly, Garg et al. (2018) also used *Pseudomonas putida* for bioremediation of Cr^{6+} in raw diluted tannery effluent. Immobilized cells may be better option for bioremediation than free cells because free cells are more exposed to the toxicity of pollutants which may cause lesser bioremediation by them.

10.6 Methods for Removal of Organic Pollutants from Tannery Wastewater

10.6.1 Chemical Methods

10.6.1.1 Coagulation and Flocculation

The tannery wastewater contains different types of organic pollutants, solid matters, and toxic metal ions which impose serious threat to the environment when disposed off without treatment (Table 10.1). Some of the important organic pollutants present in wastewater are benzene, naphthalene sulfonates, and syntans (Lofrano et al. 2013). Syntans are synthetic tannins added to soften the leather (Lofrano et al. 2008). Syntans have complex structure composed of naphthalene-, phenol-, formaldehyde-acrylic resins and melamine (De Nicola et al. 2007; Lofrano et al. 2007; Munz et al. 2009). Besides, tannery wastewater contains the considerable amount of chromium, which is above the permissible limit of 0.1 mg L^{-1}. The different types of inorganic coagulants have been applied for the coagulation and removal of organic pollutants, total solids, and toxic metal ions from tannery wastewater before proceeding for biological treatment (Lofrano et al. 2013). Different coagulants act differently in terms of reduction in organic load (COD), BOD, total dissolved solid, suspended solids, and toxic metal ions such as chromium (Ates et al. 1997; Kabdasli et al. 1999; Song et al. 2004; Lofrano et al. 2006). Coagulants are effective at specific pH that depends on the properties of wastewater (TE) as well nature and concentration of coagulants (Song et al. 2004). Using $FeSO_4$, $FeCl_3$, and alum, more than 99% of chromium and 40–70% of COD was removed from the wastewater of leather tanning (Kabdasli et al. 1999). In another study, only 30–37% of total COD and 74–99% of chromium were removed when 800 mg $L^{-1}$of alum was used as coagulants (Song et al. 2004). Nevertheless, chemical treatment methods have been effective in limited application due to generation of TE at very large scale that requires huge quantity of chemicals increasing the pollution which limits the application of chemical treatment method.

10.6.2 Biological Treatment

Biological treatment method involves activities of mixed microbial communities to remove organic pollutants from TE. It is a friendly and less-expensive alternative to chemical treatment. However, high concentration of tannins, toxic metal ions, and persistence organic compounds hampers the microbial activities (Lofrano et al. 2013). Biological treatment processes have been categorized into aerobic or anaerobic process. This has been further sub-divided into activate sludge, anaerobic stirred tank reactors, or attached biofilm process.

10.6.2.1 Aerobic Processes

During aerobic treatment, tannery wastewater is mixed with aerobic microorganisms in the presence of oxygen. Soluble, suspended, and colloidal organic pollutants that contribute to BOD are metabolized by microorganisms leading to production of carbon dioxide and decrease in the level of BOD. Production of excess microbial biomass during the process of biodegradation is a major drawback of aerobic process. Besides higher concentration of tannins, toxic metal ions and persistence organic compounds inhibit the biological treatment process (Lofrano 2013). In a study, growth of heterotrophic bacteria was significantly inhibited in the presence of 10 mg L^{-1} Cr (VI) (Stasinakis et al. 2002). A conventional sequencing batch reactor (SBR) has specialized architecture to support various group of microorganisms for effective biological treatment processes (Farabegoli et al. 2004; Ganesh et al. 2006). The most commonly used aerobic biological treatment processes are conventional activated sludge processes and trickle filters.

Activated Sludge Processes (ASP)

The ASP was described first in the year 1914 by Arnold and Locker. In ASP, wastewater that has undergone primary treatment is treated with the flocculated suspension of mixed microbial population within aerated and agitated reactor. It is a two-step process, biological treatment, and secondary settlement. The biological treatment is carried in aerated tanks containing flocculated suspension of diverse microorganisms. In the aerated tank, microorganisms grow and clump together to form a stable flocs, activated sludge. The different types of microorganisms that are involved in ASP include nitrifying, denitrifying, carbon oxidizers, fungi, protozoans, and algae. The species of *Acinetobacter* and *Zoogloea ramigera* are important microorganisms that play a key role in formation of flocs by production of polysaccharide gels. The microflora of activated sludge must be capable of producing all enzymes that can potentially degrade soluble as well insoluble pollutants. After flocs formation, effluent is passed into a secondary settlement tanks where flocculated microorganisms settle down to form a secondary sludge. Most often, after removal of secondary sludge, supernatant is disposed, but sometime tertiary treatment is required to remove the inorganic nutrients.

Trickle Filters

In aerobic trickle filter technique, microbial biofilm is formed on an inert support material placed within a bioreactor. Effluent is continuously sprayed over the microbial biofilm and percolates down the filter bed. While passing through the bed, organic matter is degraded by the microorganisms in the biofilm. As process continues, microorganisms grow and thickness of biofilm increases penetrating downward. At a point, when threshold thickness is achieved, concentration of oxygen drops at the surface of the biofilm and decrease in the biomass called sloughing occurs. Within filter, microbial population varies, a diverse range of microorganisms are present at top including bacteria, fungi, algae, and protozoan. Within filter, carbon oxidizing microorganisms dominate, while nitrifiers are predominant group present at the bottom of the bed. For efficient operation, larger the surface area of inert material, greater would be the concentration of biomass and thus, faster rate of degradation. Secondly, large void volume is required for efficient oxygenation and to prevent the clogging while passage of water through the filter bed. Trickle filter operates under two modes, low rate and high rate filter. Low rate filter consists of stone or other denser medium that have low surface area but high density, while high rate filter uses plastic material having large void volume and high surface area.

10.6.2.2 Anaerobic Biological Treatment

Anaerobic treatment processes of sludge and heavily polluted wastewater involve the activity of facultative and obligate anaerobic microorganisms that degrade organic pollutants in the absence of oxygen. Anaerobic degradation of organic pollutants is accompanied with the production of CO_2, biomass, and energy in the form of methane. The three different groups of microorganisms are involved in this process. The fermentative or hydrolytic bacteria secrete extracellular enzymes that degrade complex polymers (polysaccharide, proteins, and lipid) to generate CO_2, H_2, methanol, and volatile fatty acids (VFAs), viz. acetic, butyric, and propionic acid. The acetogenic bacteria metabolize the end product of fermentative bacteria into acetic acid, CO_2, and H_2. The methanogenic bacteria are the terminal member in the process of anaerobic degradation. The acetotrophs are group of methanogens that causes the breakdown of acetic acid into methane and CO_2, while hydrogenotroph mediates CO_2 reduction coupled to oxidation of H_2 to generate methane. The anaerobic treatment processes are mainly carried out in simple mixed sludge reactor, upflow anaerobic sludge blanket reactors, anaerobic filters (AFs) that consist of upflow and down-flow AFs, and anaerobic baffled reactor (Lofrano 2013; Lefebvre et al. 2006; El-Sheikh et al. 2011; Zupancic and Jemec 2010).

10.6.3 Advanced Treatment Technologies

10.6.3.1 Membrane Technologies

The use of membrane technologies for treating tannery effluent is a cost-effective treatment system of chromium contaminated water. Previous studies have demonstrated that ultrafiltration and nano-filtration can be efficiently used in tanning industry for the recovery of chromium and reducing pollutant load (Ashraf et al. 1997; Cassano et al. 2001). Moreover, refractory organic compounds (sulfate and chloride) have been removed by reverse osmosis with a plane membrane (De Gisi et al. 2009). In addition, membrane bioreactor (MBR) has emerged as an alternative to activated sludge process (ASP), as no additional settling tank is required for wastewater treatment. However, the main limitation of membrane technology is clogging of membrane (Lofrano et al. 2013).

10.6.3.2 Oxidation Processes (OPs)

In recent past, role of different oxidation processes (OPs) in treatment of tannery wastewater has been well documented. Treatment method that involves OPs uses strong oxidants (H_2O_2, O_3,) and/or catalysts (TiO_2, Fe, Mn) (Schrank et al. 2004). The basic principles of oxidation processes the production of hydroxyl radicals (a powerful oxidants) that causes rapid but unselective oxidation of broad range of organic compounds leading to the reduction in the COD level. Some examples of OPs include Fenton oxidation, photooxidation, ozone oxidation, and photocatalysis (Lofrano et al. 2013). The selection of optimum OPs wastewater treatment requires proper assessment. The heavily polluted wastewaters are pre-treated before the application of OPs (Schrank et al. 2004).

10.6.3.3 Bioreactor System in Bioremediation

The vessel system which is generally known as fermenter or bioreactor provides a controlled and desired levels either physicochemical or nutritional parameters or both for the growth of a microorganism alone or in combinations at optimum level. Tannery effluent is a serious environmental problem. Khan et al. (2020) also studied the bioremediation of chromium using pilot scale sand bed bioreactor.

The development of bioreactor technology can change any process parameters economical. Bioreactor technology may depend upon the microorganisms and nature of the effluent. Bioreactor design is one of the important components in bioprocess engineering (Gaur et al. 2017). In spite of such development, still there is lack of efficient bioreactor system for effective treatment. Bioreactor system for treatment of tannery effluent through specific architecture and design specially Degrimond, Sulzer, and Aquatech has been successfully used for the treatment of such waste from industries. But these technologies must be updated on the ground of efficient recycling of active/alive microbial biomass transfer, proper treatment/recycling of heavy metals along with use of microbial consortium in a specialized vessel system within large bioreactors where entirely different environment is created for effective degradation of aromatic hydrocarbon or other xenobiotic compounds. To achieve the above parameters, any bioreactor system is optimized on the basis of these parameters either fed batch or continuous system. Most of the bioreactor for such work is designed for continuous bioremediation process including the following parameters:

1. Substrate utilization rate, where variety of substrates have been used from simple to complex requires different amount of enzymes, biomass, and retention period. These factors must be optimized in the labs and may be designed in the same bioreactor in multiple vessel systems having specialized microbial consortium, which specially degrade xenobiotic compounds, further this vessel effluent should be passed to the vessel where simple organic compounds easily utilized leading to some other organic compounds that will further degraded as long retention period will facilitate higher degradation.
2. Another parameter is biomass production and its recycling outlets with in a vessel where biomass is recycled in the initial vessel to achieve active biomass using gravity based recycling outlet as live cells are heavier, but microbial flocculation of dead or live nature must be evaluated prior to develop design/architecture.
3. This component is important but difficult to maintain, i.e., microbial metabolites mainly in the form of enzymes which act on xenobiotic/simple organic matter decomposition for effective bioremediation. These parameters generally affected by the variation of substrate concentration which generally vary in bulk treatments. For this, the temperature tolerant, aero-tolerant, acid, and alkali-tolerant with high and low substrate concentration tolerant may be isolated and used in such bioreactors. Gaur and Tiwari (2015) isolated such strains from natural ecosystem and used for the production of amylases and cellulases for effective degradation of lignocellulosics and starchy materials at very high substrate concentration as these parameters are very essential. Nature is a rich reservoir of microorganisms, therefore any desired microbial system are available, only isolation and optimization can solve this goal efficiently.
4. The ultimate effects can be minimized by designing and architecture of an effective bioreactor system. For example, most of the industrial effluent contains heavy metals that must be separated from the water bodies otherwise contaminate ground water, pond, river water, soil. It affects crops as well as human and animal health. The heavy metals are not metabolized by microbial system. Most of the microorganisms can only change its oxidation state or accumulate on the cell surface/membrane only up to some extent and further release after the death of microorganisms and their viable cells again accumulate, therefore cannot be efficiently removed from the system. Therefore, phytoremediation for heavy metal removal from aquatic system is the effective measure for the treatment because it absorbs high flux of almost all types of metals from the effluent. Various plants of aquatic origin have been grown in polluted sites and after removal of the plants from the contaminated sites, thereafter burned in furnace to get the ashes of metals for extraction. Thus, this approach must be designed in such a way the bioreactor treated effluents should be passed through such ponds attached in series by removal of weeds continuously. This is only way of effective removal of toxic heavy metals from industrial effluent especially from tanneries. The role of bioreactor in bioremediation requires upgradation in their design in which multivessel system designed in such a way that original microbial biomass should be maintained for longer period monitored by specific device and reloading of fresh culture without restricting the process. Thus, a variety of

specific consortia are required for the treatment of intermediates of the xenobiotic compounds efficiently within 48–72 h; therefore, size of the bioreactor, retention period of the effluent along with the requirement of oxygen or without oxygen can be created depending on the nature of microbial communities required for bioremediation. The main problems associated to this are blockage of pores, pipe, lives and hydrolic load which must be evaluated accordingly.

10.7 Future Prospects and Challenges in Bioremediation

Industrialization and urbanization are the social need of every country, but its proper management is equally essential and need of the hour. Industrial effluent of distillery, tannery, pulp and paper industries is highly toxic due to presence of color compounds and complex organic compounds along with heavy metals. It has been proved that bioremediation is the ultimate alternative over the physical and chemical approaches because of the cost effective as well as ecofriendly means. The management of biosystem for efficient treatment requires certain technology and management of microbial system. The microbial application strategies with combinations of microbes at different stages is the most essential part of this area. Xenobiotic compounds are also treated by co-metabolism in which some specific group converts the complex form to simple form without utilizing the original compound for carbon and energy source. The converted compound is metabolized by another group of microorganisms. Therefore, the selection of such microorganisms which can co-exist without any negative interaction with them and ability to utilize different carbon and nitrogen sources via different metabolic pathways is necessary. Such combinations are long lasting and effective for bulk treatment at industrial scale. Another important aspect is the use of thermotolerant/thermophilic microorganisms at large scale treatment of effluent in bioreactor as temperature increases from 5° to 10° C. Furthermore, the selection of microbial combination in different stages in bioreactor is another important aspect which is totally based on the organic and inorganic load of the effluent and the microbial nature. In this process, proteolytic, lipolytic along with chemolithotrophic groups are being used in combinations, because at this level, the chemoorganotrophs utilize all proteins, lipids, and fats, as keratinophilic microbial combination will liquefy the hair from follicles and short hairs present in the effluent. In this stage, large closed jacket of non-reactive metals is required in order to reduce the putrefaction odors as well as other gaseous compositions. This stage may also release several pathogenic microorganisms especially for bacteria and some surface growing fungi which may cause aeroallergenic diseases. This stage has high nutritional effluent which generates bulk of microbial groups, therefore, close jacket treatment using airlift or hydrodynamic fermenter models may be recommended. At this stage, 24–48 h retention period cuts the BOD and COD by 75 to 80% along with other easily available carbohydrate, proteins, lipids, and other minerals. A huge microbial biomass and some of xenobiotic compounds along with the inorganic components especially heavy metals like chromium, arsenic, or other may be down streamed along with open pond system for remediation. The microbes which have capability to produce peroxidases, phenoxidases, laccases, mono-, dioxygenases will be used to eliminate tannin, oils, paint compounds. Further, heavy metals may be extracted through phytoremediation within 5–10 days in small oxidation ponds attached in series of 4–5 numbers depending on the capacity of industry. The bioremediation with proper management under the supervision of microbiologist is always essential because fermentaion kinetics norms at various stages in bioreactor is very essential. Microbial system is much diversified, therefore, regular isolation and characterization of microorganisms is required to find a better strain of the diversified level, as microbial diversity is abundant and newer strains always reform through recombination process in the natural ecosystem through transformation, conjugation, and transduction especially in bacteria.

Since the microbial handling especially the cultivation without contamination and monitoring its population and application of various combinations of consortia requires strict monitoring and everyday observation under microscope regarding the existence of consortia as well as their norms set by processing and downstreamed products required for the treatment process. There are some major challenges in bioremediation such as understanding the nature of chemical compound means simple or complexity in structure, selection of potential microbial strain, and the management of environmental conditions. Further, the bioremediation requires update in the area of bioreactor design and architecture alongwith multivessel, and multi-steps bioremediation with specific group of microorganisms depending on the nature of effluents in bulk treatment. Most of the industries release bulk liquid waste which contains high organic and inorganic loads. The organic load can be best treated by using various groups of microorganisms especially those which have high capability to degrade xenobiotic compounds. Further the heavy metals of the effluent should also be remediated using different microbial system. The remedial measure is not only based on the capability of the microorganisms but also based on the design and protocol for specific effluents treatment. Such challenges require space, microbial quality, microbial differentiation, aerobic and anaerobic situations for effective remediation. The microorganisms having capability of producing degradative enzymes, etc., mono and/or dioxygenases, laccases, peroxidases by different microbial groups may be used in consortium of aerobic to anaerobic as well as mesophilic to thermophilic origin in large bioreactors.

10.8 Conclusion

Bioremediation based treatment of xenobiotic compounds either in liquid or a solid system is one of the most economic, eco-friendly, and safe method. The most diversified microbial groups in consortium have been suggested for an efficient bioremediation process. The bulk quantities of industrial solid and liquid wastes are being treated with naturally occurring microorganisms. The microbes which degrade xenobiotic compounds are limited in soil and water ecosystem, therefore, must be deliberately introduced during the treatment process. The initial population follows the co-metabolism process, through which the intermediate compounds again initiate another group of microbial process which further ultimately reduce the time limit as well as productivity of the remediation process, the deliberate introduction of some specific microbial inoculum in the ratio of 2–5% having population 50×10^6 cfu of each group depending on the nature of xenobiotic compound is suggested. In this approach, the chemical nature of xenobiotic compounds and metabolic pathways alongwith their intermediate are to be known for effective bioremediation process. Further this remedial measure requires appropriate bioreactor technology in multivessel continuous fermentation having different concentration gradients can be facilitated through airlift and hydrodynamic architecture of bioreactor. The gases released from such process are CO_2, SO_2, NO_2, and CH_4 which can be utilized for the use to reduce the air pollution. Such approach will be safe for soil, water, and air for sustainable environment. The efficient microbial groups, especially bacteria are the dominating flora of such process as they are fast multiplying and able to grow at wide range of temperature and from aerobic, facultative to anaerobic conditions, while fungi are slow growing as well as mostly aerobic but some anaerobic fungi have also been identified but very limited. The quick multiplication in all the conditions, bacteria is the dominating and potential microorganisms. The downstream processing is also not required in such process; therefore, bacteria are more appropriate than any existing microbes. The tannery effluent generally has more color compounds of aromatic hydrocarbons origin which requires higher population of specific bacteria which produce certain enzymes like mono-dioxygenases, laccases as well as peroxidase essentially required for beta keto adipic, mandelate or meta cleavage pathways where catechol and other intermediates of aromatic hydrocarbons are degraded to super compounds like muconic acid, muconolactone to pyruvate. Leading to complete degradation of xenobiotics.

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