

Implementation of phytoremediation to remediate heavy metals from tannery waste: A review

**Shraddha Chauhan*, Manimita Das, Harshita Nigam, Poornima Pandey, P. Swati,
Archana Tiwari and Mahavir Yadav**

*School of Biotechnology (An Autonomous University Teaching Department), Rajiv Gandhi Proudyogiki
Vishwavidyalaya (State Technological University of Madhya Pradesh), Airport Road, Bhopal*

ABSTRACT

Waste management in the leather industry worldwide is a problem of major importance for both robust and fluid squanders. Leather industry one of the polluting industries because of generation of huge amount of liquid and solid wastes, also emits intolerable smell because of deprivation of proteinous material of skin and production of gases such as NH_3 , H_2S and CO_2 . Leather industry discharges solid wastes to a tune of 07 kg/kg of raw material used. The strong squanders are non tanned collage nous and tanned collage nous .Land fill method, anaerobic assimilation, warm incineration have inborn issues to execute. Leather assembling is a reproduction methodology of regular organic network. It utilizes an enormous amount of water and inorganic and natural chemicals for handling and in this manner releases strong and fluid squanders into nature. One of the guaranteeing procedures, which have been asked for irresistibly to overcome negative marks, is phytoremediation. The procedure is exceptionally powerful, eco-accommodating, simple and moderate. This technique uses the plants and its related microorganisms to sterilize the low and modesty debased locales effectively. Numerous plant species are effectively utilized for remediation of debased soil and water frameworks. This paper plans to the deeper review of biological management methodology phytoremediation of tanned waste and brings a more extensive arrangement of created techniques for treatment of contaminated soil.

Keywords: CTLs, Chromium, Leather Industry, Solid waste, Phytoremediation

INTRODUCTION

Leather is an intermediary mechanical item with unlimited applications in downstream parts. Leather industry reuses a natural waste started from the meat business into calfskin[1]. The arrangement of operation included in leather making produces significant amounts of strong, fluid, and vaporous squanders. Leather industry has been arranged as one of the unfathomably dirtying commercial enterprises and there are worries that leather producing uncertainty can have undesirable effect on nature's turf. The tannery effluents are portrayed by raised substance of disintegrated, roosted natural and inorganic solids offering enlarge to high oxygen request and possibly venomous metal salts and chromium metal particle [2].

Skin trimmings, keratin squanders, fleshing squanders, chrome shavings squanders and buffing squanders are the different robust squanders produced in cowhide industry and constitute protein as the primary part. In the event that these proteins are not treated precisely they may be hazardous to the earth.

1.1. Material flow in leather industry

The normalized inputs and outputs for different life cycle stages of leather are presented in Table 1:[3] and the figure shows the flow chart of tanning process.

Table 1: Materials used in tanning process

| Sl. No. | Parameter | Unit | Slaughtering | Preservation | Tanning and Finishing | Waste management | Electricity production | Transportation | Total |
|---------|------------------|----------------|--------------|--------------|-----------------------|------------------|------------------------|----------------|--------|
| 1 | Hide | kg | — | — | 750 | — | — | — | 750.0 |
| 2 | Water | m ³ | 0.9 | — | 15.8 | — | — | — | 16.7 |
| 3 | Chemicals | kg | — | 300 | 347.7 | — | — | — | 647.7 |
| 4 | Coal | kg | — | — | — | — | 191.2 | — | 191.2 |
| 5 | Limestone | kg | — | — | — | — | 43.6 | — | 43.6 |
| 6 | Energy | kWh | — | — | 385.3 | 37.5 | 203.1 | — | 625.9 |
| 7 | Fuel oil | kg | — | — | 0.0 | — | 4.7 | — | 4.7 |
| 8 | Finished leather | m ² | — | — | 100 | — | — | — | 100 |
| 9 | Solid waste | kg | 781 | — | 394 | — | 47.4 | — | 1222.4 |
| 10 | Wastewater | m ³ | 0.8 | — | 14.7 | — | — | — | 15.5 |
| 11 | TSS | kg | 7.6 | — | 74.2 | — | — | — | 81.8 |
| 12 | TDS | kg | — | — | 779.7 | — | — | — | 779.7 |
| 13 | BOD | kg | 10.8 | — | 33.4 | — | — | — | 44.1 |
| 14 | COD | kg | 2.2 | — | 95.9 | — | — | — | 98.1 |
| 15 | Sulphate | kg | — | — | 73.3 | — | — | — | 73.3 |
| 16 | Chloride | kg | — | — | 287.1 | — | — | — | 287.1 |
| 17 | Total chromium | kg | — | — | 8.7 | — | — | — | 8.7 |
| 18 | CO ₂ | kg | — | — | — | — | 431.5 | — | 431.5 |
| 19 | CO | kg | — | — | — | — | 0.1 | 23.6 | 23.7 |
| 20 | CH ₄ | kg | — | — | — | — | 0.4 | — | 0.4 |
| 21 | NO _x | kg | — | — | — | — | 1.4 | 44.6 | 46.0 |
| 22 | SO ₂ | kg | — | — | — | — | 2.8 | 7.8 | 10.6 |
| 23 | SPM | kg | — | — | — | — | 3.9 | 1.5 | 5.4 |

1.2. Environmental issues

1.2.1. Chrome tanned leather shavings

CTLs are minute, lean bits of leather made in the middle of shaving operation, which is, no doubt done to achieve the favored thickness for a combination of end employments of the cowhide. It comprises of 15–30% of aggregate proteinous waste produced from tannery. CLTS is a chromium cross-connected protein collagen that contains higher measure of protein [4]. Chromium is broadly utilized as a part of tannery, metallurgical and chemical industry.

Chromium (Cr) is a stiff steel gray compound with oxidation state ranging from +2 to +6Cr however normally exist as trivalent chromium Cr(III) and hexavalent chromium Cr(VI)[5]. Cr (III) is a necessary dietary supplement and Cr (VI) is the toxic form of Cr, approximately 10 to 100 times more toxic than Cr (III).

The United States Environmental Protection Agency has identified Cr⁶⁺ as one of the 17 chemicals posing the greatest threat to humans. It is considered to be one of the top 20 contaminants that need to be treated. The physical and concoction attributes of CTLs are exhibited in Table 2 by [1]. CTLs is a sinewy matter containing 30–40% moisture substance. Basic investigation information of CTLs is given in Table 3. The chromium oxide content in CLTS is around 4.4 % [6]. Vast amounts of CTLs are arranged via landfill in numerous parts of the world [7]. Diversion of area for waste transfer would be physically outlandish since regions with the biggest amassing of CTLs would likewise be the zones with genuine lack of empty area [1]. The current strategies for transfer necessitate huge transport comforts and foundation. Numerous nations have banned transfer of CTLs through landfill and incineration because of the vicinity of chromium substance.

Table 2: Physical and chemical characteristics of CTLs

| Parameters | Values |
|----------------------------------|-----------|
| % Moisture content | 35.1±0.6 |
| % Cr ₂ O ₃ | 3.12±0.12 |
| % Inorganic ash | 5.21±0.11 |
| % Nitrogen | 16.4±0.1 |
| % Oils and fat | 1.5±0.05 |
| pH (10 % aqueous leather) | 3.4±0.2 |
| Apparent density | 0.91 g/mL |

Table 3: ICP-OES multielement determination in CTLS

| Element | Concentration (g/kg) |
|---------|----------------------|
| Na | 93.86 |
| Ca | 6.91 |
| Mg | 0.60 |
| Fe | 0.80 |
| Mo | 0.008 |
| Al | 0.43 |
| Zn | 0.47 |
| Ti | 0.02 |
| V | 0.02 |
| Cd | <LOD |
| Co | <LOD |
| Cu | 0.05 |
| Li | 0.05 |
| Ni | 0.008 |
| Cr | 30.10 |
| Mn | 0.008 |
| Pb | 0.05 |

1.2.2. Soil contamination

Untreated waste waters from tanneries have been connected ashore only to contain them at one spot. The dirt holding it straightforwardly and watered with debase groundwater lose profit[8].

1.2.3. Atmospheric pollution

Tanneries are proverbially known for generating malodor. Rehydration of salted hides and skins generally emit odor of volatile fatty and amino acids evolved in the course of biological decomposition in presence of water. In addition, toxicity of hydrogen sulphide along with acids, fats, carbohydrates etc increase the toxic level. In liming, delimiting and tanning processes is predominant within tanneries. The venting out of malodorous substances transports to further distance is responsible for atmospheric pollution hydrogen sulphide at 20ppm (30mg/m³) in ambient air is lethal to human kind. Ammonia escaping from delimiting operation to atmosphere is odorous and pungent. Maximum admissible level of ammonia in air is 50 mg/m³. Phenolics (monohydric, dihydric and trihydric) are emitted into air during processing of hides in the post-tanning and finishing operations. The permissible level of phenolics as phenol (C₆H₅OH) in water is 10.2 mg/ml[2].

The concentration shall not exceed 0.3mg/ml in drinking water. The toxicity of sulphide, ammonia, phenol and chromium that are found in tannery waste water to fresh water fish has been reported[8].

2. Management

Research studies have been done to investigate secure tossing, recuperation of chromium and protein, and their reuse in different fields of industry[1]. CTLSs in combo with cotton and kraft mash were utilized to produce cowhide sheets, which are solid and adaptable and have a high stretching at break [9]. Chrome tanned leather parts and trimmings have been helpful in acquiring paste, gelatin, protein enhance and reconstituted collagen. These items could be made by treating with hydrogen peroxide to achieve paramount level of maceration and afterward pounding and extraction to yield the by items (95%) [10]. According to[11] biodiesel has also been produced by using animal fat obtained from leather industry. Chrome tanned leather, parts and trimmings have been helpful in getting paste, gelatin, protein enhance and reconstituted collagen. [12]

2.1. Use of phytoremediation to remediate heavy metal polluted soils

Our encompassing is topped off with countless in diverse structures. They sully our water, area and air where we live. Overwhelming metal contamination of soil is a critical ecological issue and has its negative effect on human wellbeing and farming[13].

An extensive variety of inorganic and natural mixes cause pollution. Significant part of inorganic defiles is substantial metals they display an alternate issue than natural contaminants. Soil microorganisms can debase natural contaminants, while metals need immobilization alternately physical evacuation[14]. Though numerous metals are vital, all metals are poisonous at higher concentration, in light of the fact that they cause oxidative stretch by arrangement of free radicals. An alternate motivation behind why metals may be dangerous is that they can supplant crucial metals in colors or proteins upsetting their capacity[15]. The most well-known substantial metal

contaminants are Cd, Cr, Cu, Hg, Pb and Ni. Metals are characteristic segments in soil with various overwhelming metals being needed by plants as micronutrients. Some overwhelming metals in follow sum are vital for typical development in both creature and plant however its get to be unsafe if taken in overabundance Metal and metalloid happen in mixture of structure as particles, compound and edifices in the earth over utilization of these metals and metal based substantial industrialization came about metal contamination in the biosphere. Contaminated soils and waters create a significant environmental and human ill health, which can be partially resolved by the rising phytoremediation technology. The utilization of plants for the removal of xenobiotics and heavy metals from spillage sites, sewage waters, sludges, soils and impure areas has become a vital experimental and sensible approach[16]. It is a low cost method for soil remediation, and some extracted metals may be recycled for value.

Green plants are the lungs of nature with interesting capacity to sanitizing debased air by photosynthesis and evacuate or minimize substantial metals poisonous quality from soil and water biological community by assimilation, gathering and biotransformation process. Vascular plant assimilate toxicant either straightforwardly from the air through the leaves or from soil or water through roots. Various plant species have been recognized and tried for their attributes in the uptake and gathering of diverse irresistible metals. Systems of metal uptake at entire plant and cell levels have been explored. Advances have been made in the robotic and pragmatic application parts of phytoremediation[17].

Many studies showed that alfalfa, sorghum, Crown of Thorns (*Euphorbia milli*) could be effective for phytoremediation of toxic heavy metals from soil[18]. Compared to conventional strategies being followed (in situ vitrification, soil incineration, excavation and landfill, soil washing, soil ushing and solidification) phytoremediation is an aesthetically pleasing, efficient and eco-friendly process in removing contaminants from low to moderate levels[19]. It is likewise a sparing strategy which lessens the expense to not exactly the large portion of the cost of the ordinary techniques. Additionally, it obliges low establishment and support costs. It moreover gives an included focal point by not just cleaning contaminated soil anyhow by likewise avoiding soil disintegration and metal draining[17, 19, 20]

3. Mechanism

Particularly, the methodology of phytoremediation is extensively partitioned into two stages for the sequestration of substantial metals from soil furthermore water: ex situ and in situ. The ex situ bioremediation process for soil and water is a two-stage technique. Firstly, it includes the uncovering of debased soil or pumping out the groundwater for treatment. The dirt and water is then subjected to a few synthetic and physical techniques like compound decrease/oxidation, dehalogenation, soil washing, fluid vapor extraction, adjustment/cementing, and dissolvable extraction to annihilate the contaminants[21]. Thereafter, the treated soil or water which is free from overwhelming metals is restored once more to the unique site. The uprooted toxins are then transported to some other site for dumping[19]. Despite the fact that, this methodology is less lengthy and can be performed under controlled conditions, because of dumping and off-site entombment of the evacuated contaminants at the time of treatment, it can go about as an alternate risk to nature at an alternate area[22]. The in situ technique then again is an engineering which expels the substantial metals from defiled soil, water and air without performing removal and transport of contaminants. The treatment administrations are done at the same site that blocks off-site entombment of the evacuated poisons and accordingly avoids tainting of the clean soil[19]. This system causes less natural unsettling influence and is likewise financially practical which brings about a significant improvement elective than ex situ engineering. This system is further isolated into diverse classes to uproot dangerous metals from soil and water: phytoextraction, phytofiltration, phytostabilization, phytovolatilization, phytodegradation, and rhizodegradation.

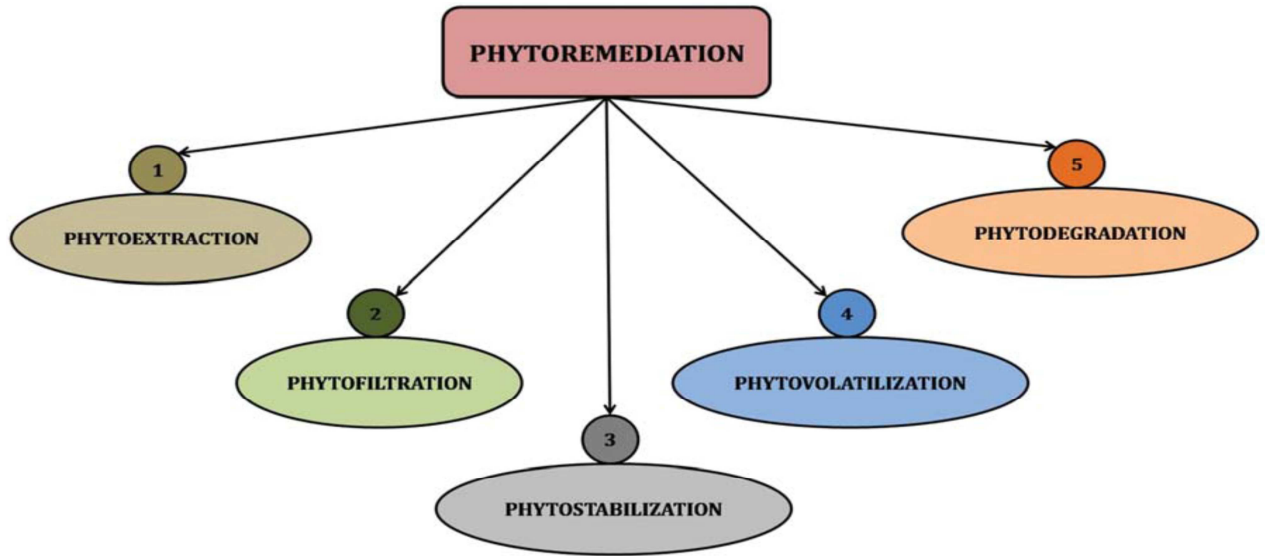


Fig :3 (a) Different mechanisms involved in phytoremediation.(modified from) [23]

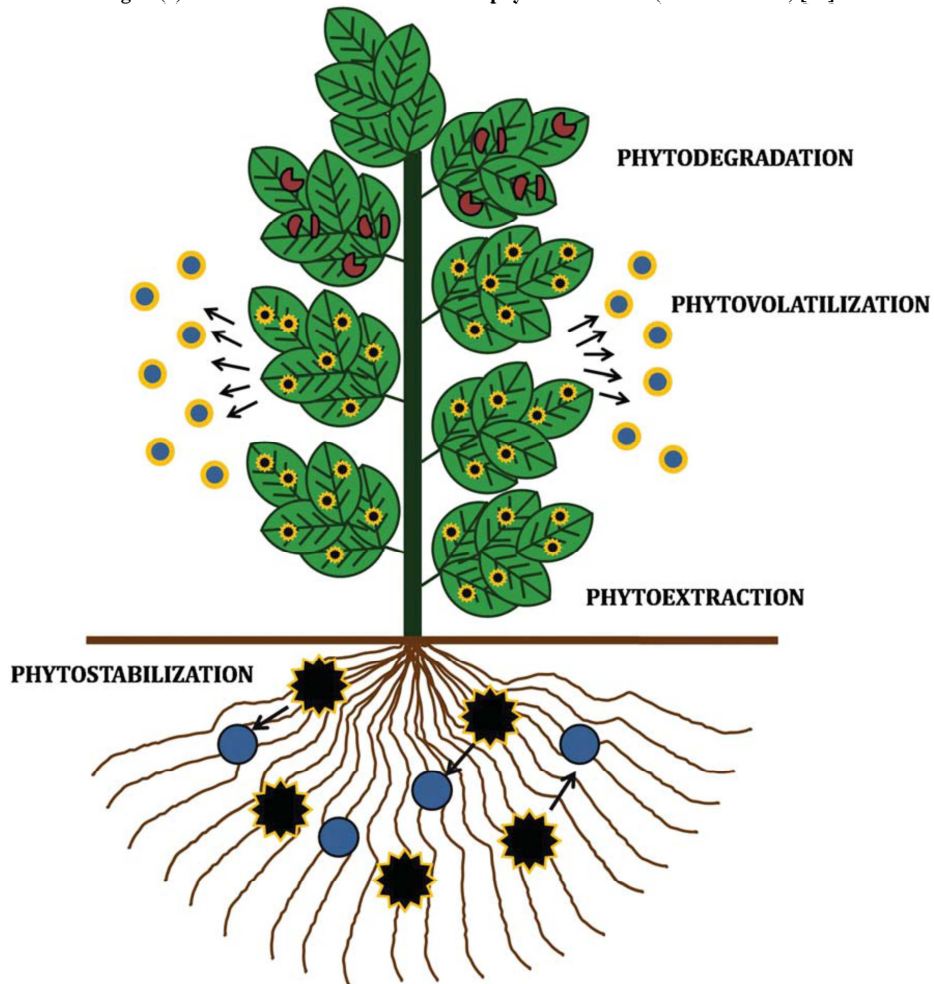


Fig : 3(b) Mechanisms of phytoremediation (modified from) [23]

3.1. Phytoextraction

Otherwise called phytoaccumulation, this procedure incorporates the extraction of lethal metals from soil and water without aggravating its respectability. The assimilation and uptake of overwhelming metals is performed by plant roots emulated by their translocation and finally aggregation and fixation over the ground in the biomass (shoots)[21]. By and large, this strategy is favored for the destinations that are carefully or superficially dirtied. The basic instrument behind phytoextraction is hyperaccumulation. The plants utilized for phytoextraction ought to have high hyper-aggregating limit and ought to be able to do developing on exceedingly dangerous soils (and water) keeping in mind the end goal to make the extraction and translocation procedure of poisonous metals in the shoots effective[24].

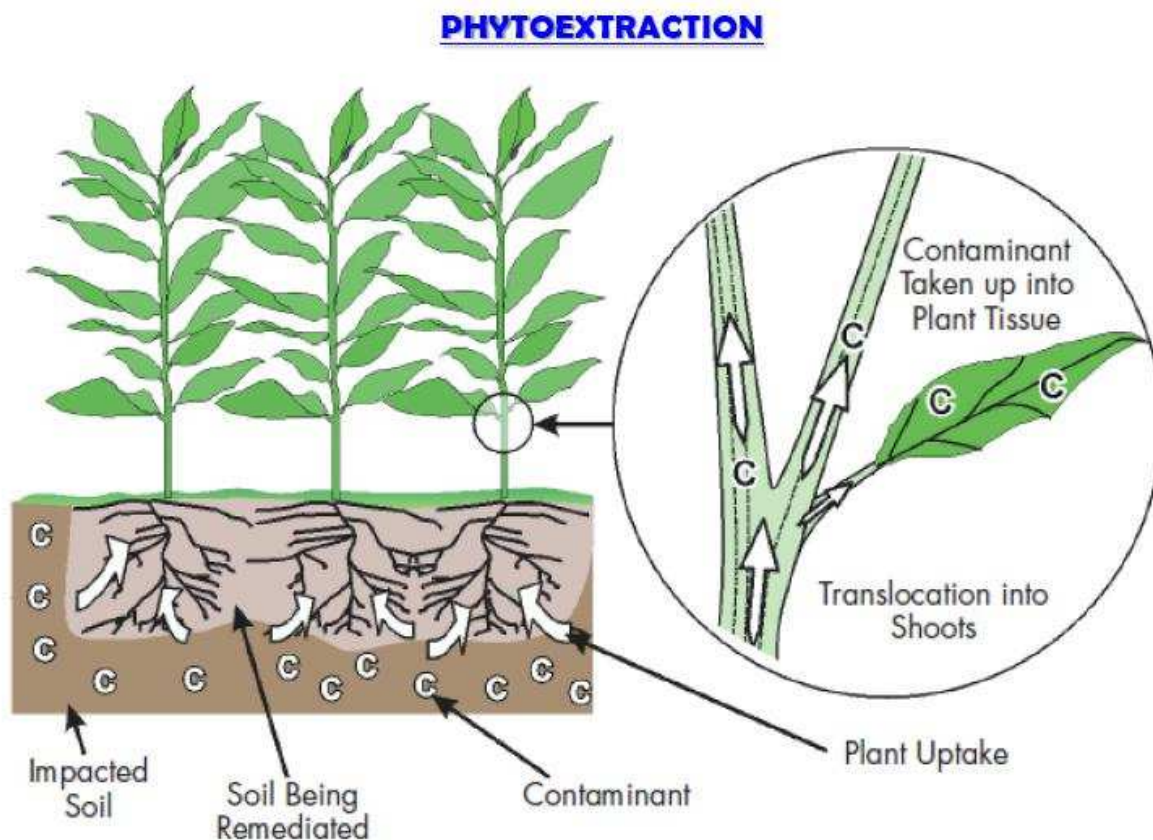


Fig:3.1(a) Phytoextraction

3.2. Phytofiltration

This procedure can be done in both physical and oceanic situations, however chiefly it is done to purge ground water or other water bodies [25]. This procedure empowers the plant roots to retain or adsorb, focus and encourage the overwhelming metals from a dirtied gushing source (mechanical release, horticultural overflow, corrosive mine seepage and so on.). In the event that plants utilization roots for remediation purposes then it is known as rhizofiltration. Such species of plants shows rapid growth of roots and evacuation time of harmful metals is insignificant [26].

This procedure includes retention of substantial metals by plants roots emulated by aggregation and transportation in the stem then again clears out. The contaminants are evacuated through gathering at a fitting time[27].

3.3. Phytostabilization

Phytostabilization is a procedure which includes retention and precipitation of contaminants like substantial metals by plants through immobilization. The procedure goes for the adjustment of the substantial metal at the debased site rather than its evacuation. This counteracts development of these contaminants by means of ground water and wind [28]. For successful phytostabilization, the plants ought to have rich root (to ingest extensive amount of water) and

shoot frameworks however a poor translocation component to counteract section of overwhelming metals into the shoots. Thick blankets of shoots have a tendency to expand transpiration which anticipates precipitation of substantial metals into the groundwater. In addition, upward stream can be kept up by quick transpiration by plants which anticipates descending filtering[27]. Types of *Spartina* indicated great phytostabilization limit towards Co in the tainted soil. [29] reported the phytostabilization capability of *Typhalatifolia* L. in modern muck. Their findings indicated that *Typhalatifolia* L. had higher potential for immobilization of Zn, Mn, Cr and As however had less phytostabilisation potential towards Ni, Cd and Co[29].

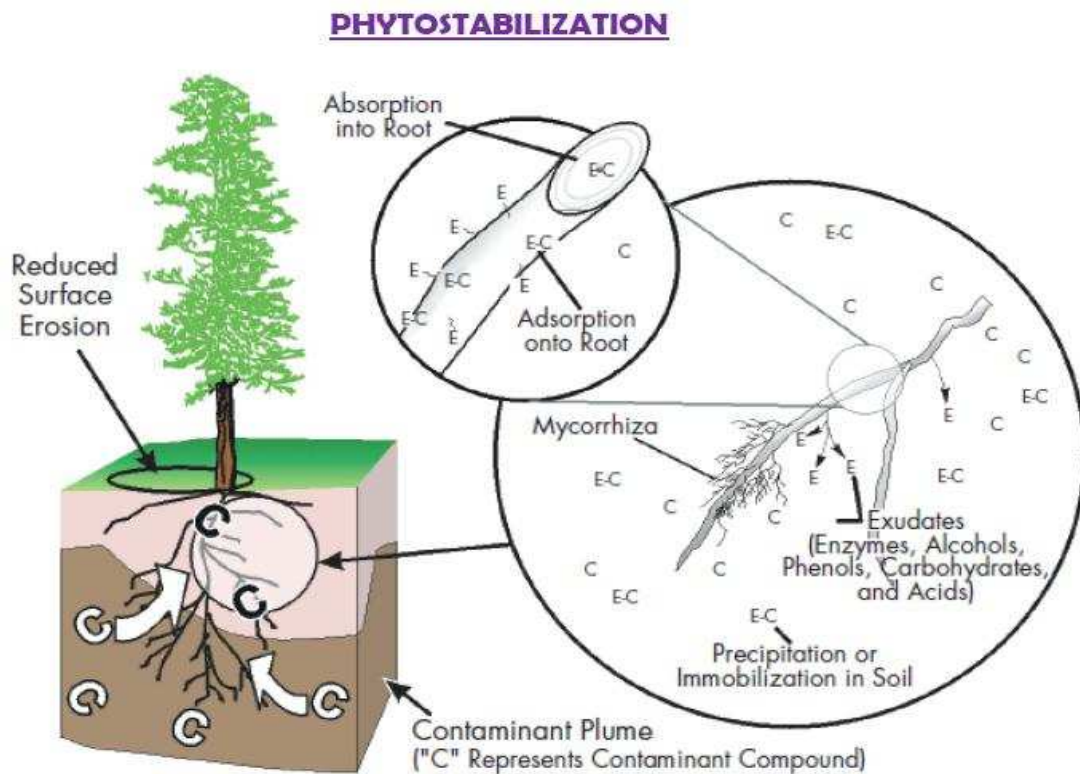


Fig 3.3 (a) Phytostabilization

3.4. Phytovolatilization

This procedure uses plants for the uptake of contaminants from soil and water took after by ensuing corruption into less dangerous structures which are then transpired into the earth[30].

Plants can volatilize both natural and inorganic contaminants given that the inorganic contaminants ought not structure methyl and hydride subordinates [31].

The instrument incorporates open stomata of the leaves to diffuse unstable contaminants in nature in less dangerous structures. The plants utilized as a part of this procedure demonstrates elevated amounts of flux of the toxin towards the environment through the transpiration process[31].

This technique not just uproots the contaminations from polluted site in an unstable structure yet the evacuation is done in more secure types of that specific contamination. Sakakibara et al. reported the destruction of As through a remediation handle by utilizing *Pteris vittata*. Carvalho et al. done studies on four amphibian plants (*Typha domingensis*, *Lemna obscura*, *Hydrilla verticillata* Royle and *Crinum americanum*) for the evacuation of watery selenium. The point of interest of this innovation is that it doesn't require transfer of any contaminant in this manner evading any site aggravation and disintegration. This procedure is limited just for cancelation of unstable mixes and can't be sought the evacuation of nonvolatile overwhelming metals.

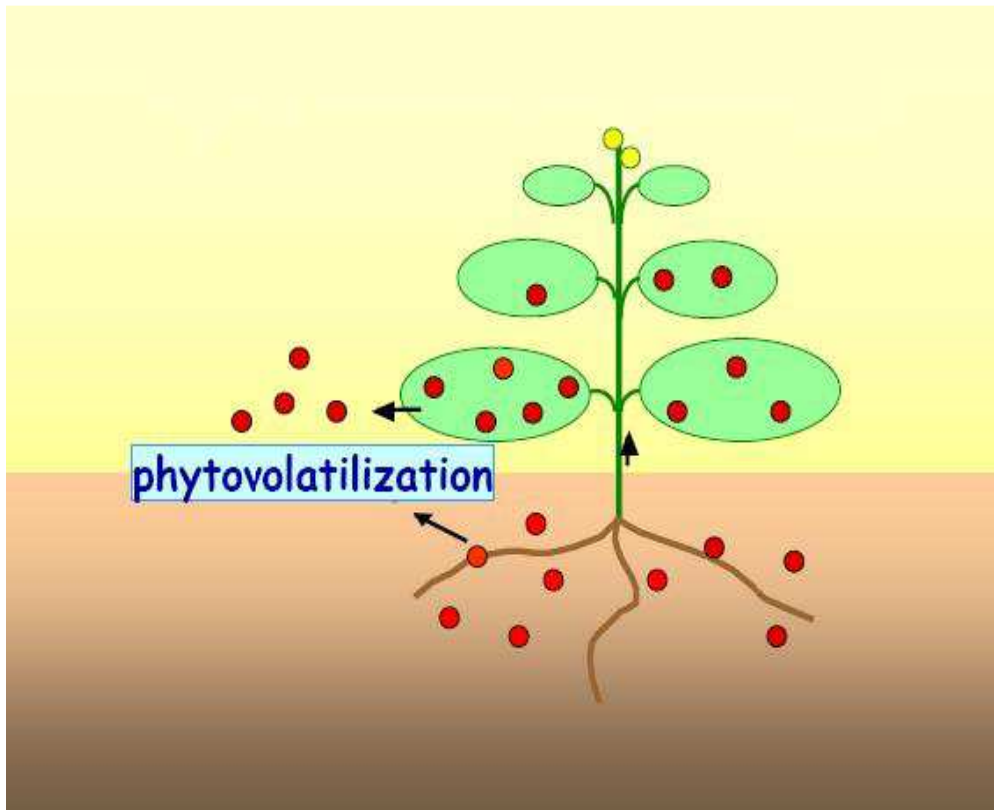


Fig: 3.4 (a) Phytovolatilization

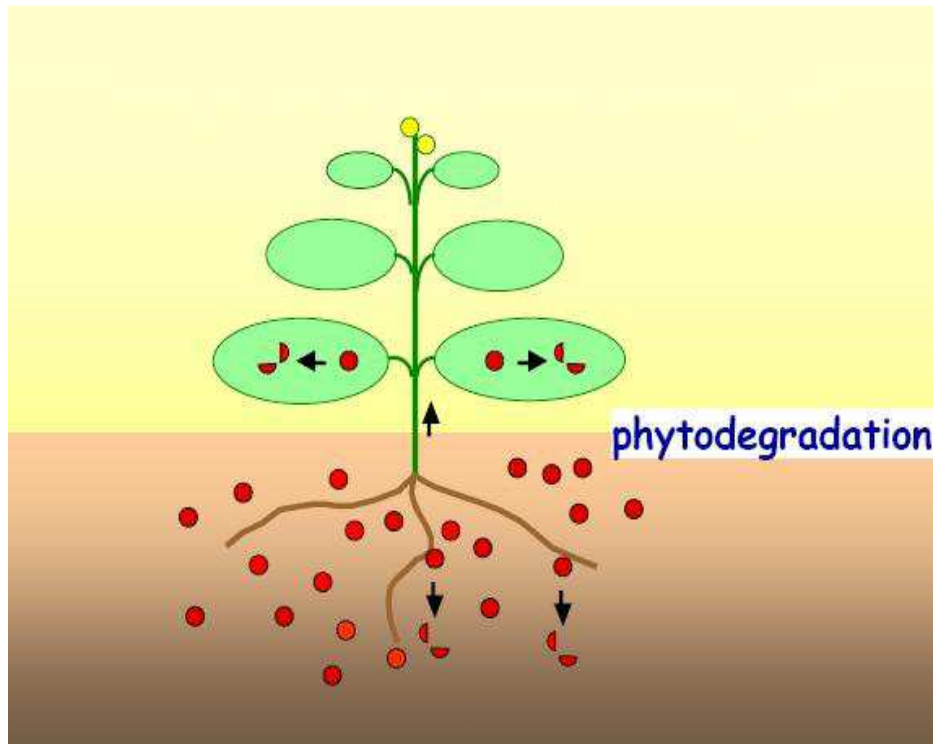


Fig: 3.5 (a) Phytodegradation

3.5. Phytodegradation

This methodology abuses the capacity of plants that have certain specific catalysts (dehalogenase, reductase and oxygenase) alternately cofactors for the corruption of contaminants from soil and groundwater[32]. This technique is constrained just to natural contaminations in light of the fact that these are biodegradable in nature. Phytodegradation contrasts from rhizodegradation basically due to the way that the previous incorporates the breakdown of contaminants with the assistance of microorganisms present in the rhizosphere and are a moderately slower system.

4. Recent development in Phytoremediation

4.1. Use of genetically modified plants (GMP)

The primary point of hereditary designing in the field of phytoremediation is to improve the limit of plants to endure, gather and ingest contaminants. Numerous qualities from distinctive life forms have been identified and portrayed that are included in procurement, portion and cleaning of metals. The recombinant proteins created by these transgenic plants assume a critical part in chelation (e.g. citrate, phytochelatins, metallothioneins, phytosiderophores and ferritin), osmosis and layer transport of metals[33].

CONCLUSION

Solid waste generated in leather industry can cause hazardous effects. The growing environmental concerns pose a new challenge towards management of these wastes. Levels of generous metals are growing regulated in light of extended current utilization making their get-together in living animals. Their appearance can bring about destructive results to organ structures through a couple of instruments (fundamentally due to period of oxidative nervousness). Oxidative anxiety prompts the generation of free radicals emulated by the decline in the level of cell reinforcements and finally prompting cell death. The industrial and agricultural waste management problem is mounting very quickly and phytoremediation can make more efficient solution for this quandary. The procedure is exceptionally powerful, eco-accommodating, simple and moderate.

REFERENCES

- [1] Pati, A., R. Chaudhary, and S. Subramani, *Environmental Science and Pollution Research*, **2014**: p. 1-17.
- [2] Kanagaraj, J., et al., *Journal of scientific and industrial research*, **2006**. **65**(7): p. 541-548.
- [3] Joseph, K. and N. Nithya, *Journal of Cleaner Production*, **2009**. **17**(7): p. 676-682.
- [4] Saravanabhavan, S., et al., *Journal of the Society of Leather Technologists and Chemists*, **2004**. **88**(5): p. 202-207.
- [5] Cheung, K. and J.-D. Gu, *International Biodeterioration & Biodegradation*, **2007**. **59**(1): p. 8-15.
- [6] Tahiri, S., et al., *The Journal of the American Leather Chemists Association*, **2002**. **97**(7): p. 261-266.
- [7] Brown, E.M., M.M. Taylor, and W.N. Marmer, *The Journal of the American Leather Chemists Association (USA)*, **1996**.
- [8] Mariappan, M., *Environmental protection initiatives in Indian tanneries—a perspective view*. Proc 30th Leath Res Ind Get Together, **1997**: p. 151-161.
- [9] Crispim, A. and M. Mota, *Leather shavings treatment-an enzymatic approach*. **2003**.
- [10] Cot, J., et al., *Journal of the Society of Leather Technologists and Chemists*, **2003**. **87**(3): p. 91-97.
- [11] Alptekin, E., M. Canakci, and H. Sanli, *Fuel*, **2012**. **95**: p. 214-220.
- [12] Cakl, J., et al., *Separation science and technology*, **1998**. **33**(9): p. 1271-1281.
- [13] He, Z.-l. and X.-e. Yang, *Journal of Zhejiang University Science B*, **2007**. **8**(3): p. 192-207.
- [14] Khan, A.G., *Journal of Trace Elements in Medicine and Biology*, **2005**. **18**(4): p. 355-364.
- [15] Abou-Shanab, R., et al., *New Phytologist*, **2003**. **158**(1): p. 219-224.
- [16] Mojiri, A., *Afr J Microbiol Res*, **2012**. **6**(3): p. 643-647.
- [17] Lone, M.I., et al., *Journal of Zhejiang University Science B*, **2008**. **9**(3): p. 210-220.
- [18] Karimi, N., *Comparative Phytoremediation of Chromium-Contaminated Soils by Alfalfa (Medicago sativa) and Sorghum bicolor (L) Moench*.
- [19] Ghosh, M. and S. Singh, *Asian J Energy Environ*, **2005**. **6**(4): p. 18.
- [20] Li, K. and W. Ramakrishna, *Journal of hazardous materials*, **2011**. **189**(1): p. 531-539.
- [21] Yusuf, M., et al., *Archives of environmental contamination and toxicology*, **2011**. **60**(1): p. 68-76.
- [22] Pavel, L.V. and M. Gavrilescu, *Environmental engineering and management journal*, **2008**. **7**(6): p. 815-834.
- [23] Gaur, N., et al., *Environmental Science: Processes & Impacts*, **2014**. **16**(2): p. 180-193.

-
- [24] McIntyre, T., *Phytoremediation of heavy metals from soils*, in *Phytoremediation*. **2003**, Springer. p. 97-123.
- [25] Islam, M.S., et al., *International journal of phytoremediation*, **2013**. **15**(10): p. 1010-1021.
- [26] Sarkar, D., R. Datta, and R. Hannigan, *Concepts and applications in environmental geochemistry*. Vol. 5. **2011**: Elsevier.
- [27] Anjum, N.A., et al., *Phytotechnologies: Remediation of environmental contaminants*. **2012**: CRC Press.
- [28] Mohee, R. and A. Mudhoo, *Bioremediation and Sustainability: Research and Applications*. **2012**: John Wiley & Sons.
- [29] Varun, M., et al., *Biotechnol Bioinf Bioeng*, **2011**. **1**(1): p. 137-145.
- [30] Rao, D.G., et al., *Wastewater treatment: advanced processes and technologies*. **2012**: CRC Press.
- [31] Singh, B.P., *Industrial crops and uses*. **2010**: Cabi.
- [32] Kulakow, P.A. and V.V. Pidlisnyuk, *Application of Phytotechnologies for Cleanup of Industrial, Agricultural and Wastewater Contamination*. **2009**: Springer Science & Business Media.
- [33] Vamerali, T., M. Bandiera, and G. Mosca, *Environmental Chemistry Letters*, **2010**. **8**(1): p. 1-17.