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Studies on recovery of heavy metals from tannery wastewater

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Abstract

Heavy metal salts are widely used in the tanning process in the form of Chrome alum and Chromium[III] sulfate. It is a highly toxic metal and cannot be degraded thus deposited and incorporated in water, sediment and aquatic ecosystems which poses various respiratory, skin and other health issues to humans and also cause serious issues to microbial, plant and aquatic life. The cost of these heavy metal salts is high due to which the tanners need a lot of investment for the tanning process because of its abundant use. So, to overcome such issues numerous techniques have been developed for the recovery and reuse of these heavy metal salts from the wastewater of the tanneries to reduce the pollution in the wastewater streams and exempt the tanners from the high cost of these salts.

Keywords: Chrome, chromium[III] sulfates, tanneries, adsorption, membrane separation.

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1. Introduction

Heavy metal pollution is a serious issue these days due to the amounts in which these are released from the industries. These being non-renewable resource are being wasted and dumped in the environment, causing serious health issues to both humans and animals and also to aquatic and plant life. The plants and animals living in the water require oxygen for their living, which they get by the decaying process of solid waste present in the water. The heavy metal pollution can impact the fish and wildlife populations by harming them, can lead to oxygen depletion and beach closures, and also contaminates drinking water.

There are around 2,000 tanneries in the country with an annual processing capacity of over 500,000 tonnes of hides and skins. In Uttar Pradesh there are around 400 tanneries which cause pollution by discharging effluents high in organic and inorganic dissolved and suspended solids content and contain toxic metal salt residues. [The Environment Protection Rules, Schedule VI, 1986]. The effluent from leather processing contains organic matter, heavy metals, sulphide, and solid waste. The quality of soil and groundwater has effect on the fertility of soil, so the treatment of sludge is necessary for the betterment of the society.

2. Heavy metals in industrial water

Metals in wastewater when exceed the permissible limit, cause severe damage to the environment and human health like increasing levels of Cadmium causes lung damage, gastrointestinal issues, kidney damage, and death. Chromium causes skin irritations, difficulty in breathing, ulcers, anemia, and harm to the male reproductive system. Arsenic can cause skin manifestations, visceral cancers and vascular diseases. Zinc can cause depression, lethargy, neurological signs and increased thirst and Mercury leads to damage of the brain and nervous system and is very toxic to the human body. [Barakat, *et. al,* 2010].

The toxicity of heavy metals and their bioaccumulation poses a serious threat as metals cannot be broken down; their toxicity can only be reduced. Industries like Tanneries, Textile industries, Electroplating industries, etc. being the major cause of heavy metal pollution, release large concentrations of heavy metals in their effluents.

The tanneries are known to be very polluting due to the discharged effluents which have high concentration of organic and inorganic matter, dissolved and suspended solids, chromium and sulphides. A significant part of the chemicals used in the processes of leather processing are not actually absorbed, but are discharged in the environment. [Gupta, *et. al.*, 2007]. The difficulty in treatment of tannery effluent is due to the complex nature of the industry and the chemicals used in the leather processing. [Islam, *et. al*, 2014]. The step by step process of the leather processing with chemicals used and those charged in the effluent is shown in the Fig. 1 given below. In the figure it can be seen that the heavy metal salts are used in the tanning and re-tanning process iwhich is discharged in the effluent in multiple steps i.e. tanning, sammying, chrome splitting, shavings, re-tanning, sammying and buffing, trimmings.

3. Processes for recovery of metals

There are various physical, chemical, physico- chemical and biological processes which are used conventionally for the recovery of heavy metals from waste water like membrane filtration, electrodialysis, chemical precipitation, biosorption, etc. The physical separation techniques include mechanical screening, hydrodynamic classification, gravity concentration, flotation, magnetic separation, electrostatic separation, and membrane separation. [Dermont, *et al.*, 2008]. The chemical processes for removal of heavy metals mainly include chemical precipitation, adsorption, ion exchange and electrochemical deposition. The chrome recovery plants setup, under Ganga Action Plan I [Chrome recovery and reuse as a clean technology in the leather industry in Kanpur under Ganga action plan], in tanneries use chemical precipitation method for Chromium recovery in which MgO was used as an alkali for chrome precipitation. The various biological processes used include biosorption by using inactive, dead biomass of algae, bacteria, fungi and yeast, various agricultural by-products can also be used as adsorbents like adsorption on hazelnut shell, rice husk, coconut shell, maize cub, etc. [Babel, *et. al,* 2003]. There are various biopolymers which possess various different functional groups like hydroxyls and amines. The binding capacity of these biopolymers increases with higher pH due to polymerization reaction [Crini, 2005].

Due to their increasing concentrations and the issues arising, various methods have been developed for removing and reducing the heavy metal pollution. The various methods used are- chemical methods like coagulation, precipitation, etc. physical methods- filtration, membrane separation, etc. electrochemical methods- electrodialysis, biological methods- biosorption, bioaccumulation, bioreduction, etc. The processes to be discussed in this review include biosorption, membrane separation and electrochemical process.

4. Biosorption

Various researches have been carried out on different biological materials i.e. the use of micro-organisms [fungi, algae and bacteria] and plants [living or dead] for their ability to adsorb heavy metals from the wastewater. This utilizes microorganisms in living or dead state, or with chemically modified cell wall using acid or alkali treatments, or in immobilized state, for the removal and recovery of heavy metals from the wastewater streams. Mahadavan and Daniel [2018] studied biosorption on immobilized *Aspergillus awamori* and found the maximum removal of chromium to 399.13 mg/g at 25˚C and pH of 11.5 for an initial concentration of 500 mg/L. Cr [VI] removal from from aqueous solution was studied using dead algal biomass of *C. tamariscifolia*. The maximum uptake capacity of 81.96 mg/g was reported by Bellatmania et. al. [2018] . Bano et. al. [2018] studied biosorption of cadmium, copper, ferrous, manganese, lead and zinc using halophilic fungi comprising *Aspergillus flavus, Aspergillus gracilis, Aspergillus penicillioides, Aspergillus penicillioides, Aspergillus restrictus and Sterigmatomyces halophilus* out of which *A. falvus* and *S. halophilus* showed good rate of adsorption for all heavy metals studied with an average of 86% and 83% respectively [Bano, *et. al,* 2018]. In a study by Xu et. al. [2018] on multi-metal resistant *P. chrysogenum* XJ-1, whichwas used as biosorbent for removal of Cu^{2+} and Cr^{6+} The maximum biosorption capacity for Cu^{2+} was 42.83±0.57 mg/g at pH 5.0 and that for Cr6+ at pH 3 was 52.69±1.68 mg/g, [Xu, *et. al.* 2018].

5. Membrane filtration

Various types of membrane filtration processes such as ultra filtration, nano filtration and reverse osmosis have been studied depending upon the size of the particle that can be retained the membranes were designed and employed for heavy metal removal from wastewater. In a research by Peydayesh et. al. [2019] amyloid-activated carbon hybrid membranes were used for removing four heavy metals: chromium, nickel, silver and platinum. The concentration of the metals i.e. chromium, silver, nickel and platinum was reduced to 1.26, 0.3, 0.3, 0.03 ppb, respectively, when the initial concentration was 174, 212, 206 and 135 ppb respectively. Ali et. al. [2018] studied plasma- treated CNT membranes for removal of zinc. The P-CNT membranes effectively removed 100% of zinc from synthetic waters and approximately 80% of zinc from a wastewater.

The separation and recovery of heavy metals was done by Tang and Qiu [2019] using shear-induced dissociation coupling with ultrafiltration [SID-UF] for selective recovery of nickel, zinc and copper from electro-plating effluent using poly [acrylic acid] sodium [PAAS] and copolymer of maleic acid and acrylic acid [PMA] as complexants respectively. The results showed that in the case of PAA-metal complexes the order of shear stabilities is PAA-Zn> PAA-Cu> PAA-Ni, and that of PMA-metal complex is PMA-Cu> PMA-Ni> PMA-Zn. Ates and Uzal [2018] studied recovery of heavy metals: nickel, chromium, aluminium from aluminium anodic oxidation wastewaters. The removal efficiencies reported for all the heavy metals: aluminium, nickel and chromium were 99, 99 and 94 respectively using NF-270 membrane. Similarly, SW 30 RO membrane was also highly successful to remove heavy metals giving 99% efficiency for aluminium, 94% for chromium and 99% for nickel.

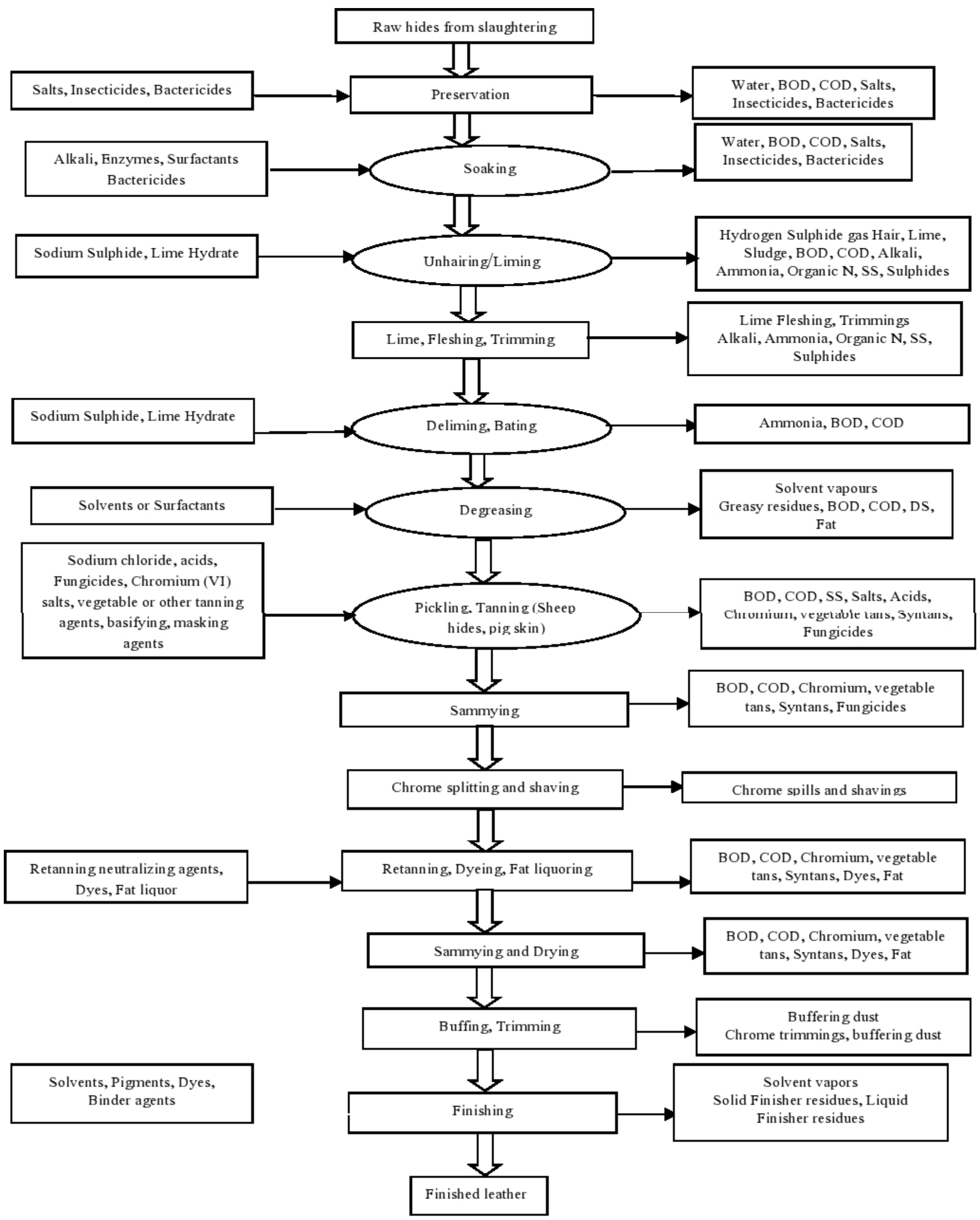

Fig. 1 An overview on the steps of leather processing [20]

Table 1. Comparison of efficiency of removal of heavy metal using different techniques

S.No.	**Technique**	**Heavy metals removed**	**Reference**
1.	Biosorption	86%	[Bano, *et. al*, 2018]
2.	Membrane Filtration	100%	[Ali, *et.al*, 2019]
3.	Electrochemical treatment	>99%	[Jakobsen *et. al, 2004*]

6. Electrochemical treatment

Electrodialysis is a technique which focuses on separation and recovery of heavy metals using charged membranes. This process basically depends on the membrane size and the physical and chemical properties of the heavy metals. Ning et al.[2019] studied recovery of copper [Cu^{+2}] from dilute Cu^{+2} concentration wastewater [500mg/L] using jet electrodeposition. The efficiency reported was more than 97.4% with a satisfied current efficiency of 77.2%, the deposited Cu was in bulk state and was easily separated from the cathode . In a study by Min et. al. [2018] the separation of heavy metals: copper [Cu^{2+}] and nickel [Ni^{2+}] was done from electroplating wastewater using electrodialysis . They analyzed that the voltage used is the key factor responsible for separation efficiency. The separation efficiency increased with increase in voltage, but excessive voltage lead to concentration polarization and the efficiency decreased. The removal efficiencies of Cu^{2+} and Ni^{2+} was >99% at 12V. Jakobsen et al. [2004] studied removal of Cadmium from wastewater using electrodialysis. A set of three experiments were done where the sludge was suspended in distilled water where removal was 69%, in citric acid where removal was 70% and in nitric acid where removal was 67%.

7. Conclusion

In recent years various new advancements have been done in the technologies being used for the recovery and removal of heavy metals from the wastewater streams. The government has also become very rigid for the treatment of effluent waste water. In the literature survey done, we conclude that in terms of removal, membrane filtration and electrodialysis give greater efficiency but the operational cost is also very high due to membrane fouling and energy consumption. Biosorption requires low operational cost as it is performed using industrial by-products and can be operated easily with high metal binding capacities.

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