BIOSORPTION OF CHROMIUM FROM TANNERY WASTEWATER: AN APPROACH FOR
CHROME RECOVERY AND REUSE

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ECO-CONSTRAINTS POSED BY LEATHER INDUSTRY
The process employed in the manufacturing of leather in several developing countries still remains
traditional, often not optimized for chemical and water usage. The industry has environmental
concern with respect to its pollution potential and therefore is facing a severe challenge. The unit
processes that cause tanners the most difficulty, with regard to perceived environmental impact are
unhairing and chrome tanning.

BASIC CHROMIUM SULFATE: IT’S ROLE IN LEATHER INDUSTRY
Chrome tanning is a major and commonly employed method for permanent preservation of hide
and skins. The chrome-tanned leathers are characterized by high hydrothermal stability and
excellent physical properties. The currently used BCS salts and methods show an uptake of 60-
70% of chromium used for tanning. This has been attributed to high kinetic lability and poor
thermodynamic affinity of some of the species contained in BCS salts. Basic chromium salt is a
mixture of many molecular species. Depending upon the manufacturing conditions the exhaustion behaviour of BCS may vary.
When the exhaustion levels are low, higher amounts of chromium
along with neutral salts are discharged, which increase the COD, TS
and SO₄²⁻ content in the spent chrome liquor. Although the oxidation
state of chromium in the tanning salt is only trivalent, discharge norms
do not often specify the redox states, because of the concerns of
possible conversion of the trivalent state to the more toxic hexavalent form. The spent chrome
liquors have become a major waste stream from tanning industries. The presence of chromium in
the effluent is a major concern for the tanning industry.
CHROME MANAGEMENT

The untreated effluents emanating from the chrome tanning sectional stream have been found to contain 1500-3000 ppm of chromium(III). But the discharge limit of chromium in tannery wastewater is 2 ppm. This has called for technological interventions for skirmishing chromium pollution. There are many options available for chromium management.

OPTIONS FOR THE TREATMENT OF WASTEWATER CONTAINING CHROMIUM

At present, two methods of chromium recovery are practiced. The first is a direct recycling approach, which involves filtration of the waste liquor followed by chemical replenishment. The second method leads to precipitation of chromium in the waste liquor as the tri hydroxy form, filtration and subsequent dissolution in sulfuric acid to form chromic sulfate for reuse in the tanning process. Both the methods offer significant advantages and disadvantages depending on the size of the tanning operation. The various other methods followed for the removal or recovery of chromium from wastewaters are chemical reduction and precipitation, ion exchange, membrane technologies and adsorption by several types of adsorbents; such as activated carbon, bone charcoal, cork and yohimbe bark wastes, waste activated sludge, fly ash and natural zeolites. Most of these materials and methods suffer from drawbacks such as high capital or operational costs. Therefore, there is a need for the development of a methodology with low cost, easily available materials, which can adsorb chromium economically.

BIOSORPTION OF CHROMIUM: A VIABLE OPTION FOR TANNERY EFFLUENT TREATMENT

Biological materials, both living and dead are capable of removing heavy metals from solutions through a process involving a number of diverse mechanisms collectively known as biosorption. Biosorption refers to the passive uptake of metal ions by biological materials. Biosorption is characteristically rapid and with the appropriate types of biomass, it can remove a high percentage of individual metallic cations from wastewater streams.
Biosorption is defined as the accumulation and concentration of pollutants from aqueous solutions by the use of biological materials, thus allowing the recovery and/or environmentally acceptable disposal of the pollutants. Biosorption utilizes the ability of biological materials to accumulate heavy metal from wastewater by either metabolically mediated or physicochemical pathways of uptake. Because of the problems inherent in maintaining active microbial populations under highly variable conditions of wastewater, living systems are often unpredictable. A number of workers have investigated the feasibility of using cheaply available marine or fresh water algae for heavy metal removal. Among these, the marine macro algae, otherwise known as seaweeds, has attracted much attention. The seaweed species *Sargassum wightii* was found to be very effective in the removal of chromium from the tannery wastewaters, which is available in plenty in the southern coastal region of India.

*Sargassum* seaweeds have been used for the treatment of commercial chrome tanning effluent. An optimum of 50 g of seaweeds has been used in 5 stages (10g per stage) for the treatment of 1L of chrome bearing tannery wastewater containing 750 ppm of chromium. After 5 stages of treatment with seaweeds, the treated liquor is found to contain < 2ppm of chromium, which means the discharge meets the stipulated norms for chromium. The studies on desorption reveal that only 47% of bound chromium is displaced by H+ ions when high concentration of sulfuric acid is used as an eluent. Biosorption of chromium from wastewater alone does not ensure combating chrome pollution. Suitable methodologies for the proper disposal or reuse of the chromium loaded seaweed needs to be addressed in order to ensure a holistic approach to avoid chrome pollution. However, these chrome bearing seaweeds could be advantageously used as reductant in the preparation of BCS.
The novelty of the work lies in the recovery of chromium in wastewaters by naturally occurring seaweed and further reusing the chromium loaded seaweed as a reductant in the preparation of a chrome tanning salt. This tanning salt has been used for making leathers, which are comparable to the leathers produced using commercial chrome tanning salts. This forms a green route for the recovery and reuse of chromium in tanning industry. Although there is no successful industrial exploitation of biosorption technology because reusing of the metal loaded biosorbents has limitation, in our study, the chromium loaded seaweed (organic based material) forms a suitable reductant for the reduction of chromium(VI) to chromium(III) during the preparation of chrome tanning salts commercially (organically reduced chrome tanning salt, reference included). Hence, this methodology could form a viable alternative for commercial exploitation. Hence, this strategy of using seaweeds for removal of chromium from chrome bearing effluent and subsequent recouping of the same for BCS production provides a secured means of chromium utilization through biosorption.

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