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# CHROMIUM REMOVAL FROM TANNERY WASTEWATER: A REVIEW

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## ABSTRACT

*Tanning process generates high strength wastewater containing heavy metals, nutrients, organic and inorganic contaminants, which may adversely affect public health and the environment. The wastewater contains considerable amounts of heavy metals including Cr(VI) which is carcinogenic, mutagenic and teratogenic, and persistent in the environment. Several physico-chemical treatment approaches were employed in tannery wastewater treatment and proved to considerably reduce the level of toxic Cr and other pollutants to low concentrations. Despite the capabilities of physico-chemical treatment methods in treating high concentrations of toxic effluents, they are associated with setbacks including low removal efficiencies, high cost of chemicals, high energy requirement as well as low nutrients removal from the wastewater stream. Microalgal wastewater treatment systems can play an important role in bioremediation of tannery effluent and are considered as low-cost, efficient treatment alternatives that can potentially remove organic and inorganic contaminants, heavy metals, and possibly reduce the toxic Cr (VI) to a much less toxic Cr (III), especially when coupled with activated carbon.*

*Keywords: microalgae, effluent, chromium, activated sludge, absorption, heavy metals*

## INTRODUCTION

Tanning is the process of transforming animals hide and skin to real leather by removing water molecules from collagen (protein content) of the skin [1] and replacing it with molecules of vegetables or chrome which makes the leather stable and imputrescible leather [2]-[3]. Vegetable tanning process produces leather by repeatedly soaking in natural tannin solutions which usually takes 1-2 months to complete, and the product has a natural tone smell, longer lifespan, wider in size due to the larger sizes of vegetables molecules. However, it requires craftsmanship, extensive labour and supervision, which makes its products more technical, while colours are not livid as in chrome tanning and darken over time. It also generates a large amount of solid waste and wastewater but considered more environment-friendly due to its biodegradability [4]. Due to the setbacks of longer time of leather production using vegetable tanning, the need to cut production cost and to meet increasing demand, a new tanning method was introduced in 1958 where leather tanning process can be achieved in one day using a chemical solution, primarily containing chromium (Cr). This method has since been preferred in leather tanning, accounting for more than 90% of the world leather produced [5]-[6].

The basic tanning processes are the same in which water molecules are expelled from the collagen of the hide, using Cr salts instead of tannins. The ions of the Cr replacing the water molecules are smaller compared to the tannins used in vegetable tanning that generally makes Cr-tanned leather thinner and softer. The process is usually achieved by placing hides in acidic drums or baths, consistently in a chemical solution. This creates a load of toxic pollutants that, if not properly treated, will cause adverse environmental impacts.

Cr tanning is quick, produces thinner, softer and more abundant leather, unchanged during the lifespan, cheaper and can be automated and achieved in one day. However, it generates toxic wastewater with a high amount of Cr, that has detrimental environmental impacts, especially in the developing countries where the majority of industries discharge their effluent to the streams and rivers [7] without reaching the required discharge limit [8].

**Tannery Wastewater Generation**

Tanning process consumes a high amount of water estimated to be 34-56 $m^3$ of water per ton of hiding and skin processed and out of the huge amount consumed, usually generates 85% of the used water as effluent [9]-[10]. Tanneries generate over 40 million tonnes of waste per year throughout the globe [11], posing enormous threats to the ecosystem.

The amount of water consumed and effluent produced varies from tannery to tannery depending on the type of tanning process, raw materials employed as well as the targeted product. Interestingly, only 15-20% of the wet-salted hide/skin is converted into commercial leather, 25% becomes Cr containing leather waste; chrome tanning method gives rise to only about 50-70% Cr salts uptake [6], and the remaining become non-tanned waste and is lost in the wastewater as fat, soluble protein, and solid suspended matter.

Cr (VI), which is the most toxic form of Cr [3], is highly soluble in bacterial cells which are smaller in size than microalgae [12], is rapidly transported across cell membranes through the surface pathway and is reduced in the cytoplasm to less toxic Cr (III) by interaction with nucleic acids and protein. The biotransformed Cr (III) is far less soluble and larger than Cr (VI) [13]-[14], and does not pass through biological membranes which can be harvested easily from the treated effluent and can be converted to less quality animal and fish feeds, biofertilizer, etc.[10].

The addition of the carbon source in the treatment system will lower down pH and help in reducing Cr (VI) to less toxic Cr (III). Louarrat et al. [15] reported that maximum adsorption of 57.71 mg/g was attained at pH of 3 and then declined at about pH of 5 due to the decrease in protonation of the binding surfaces resulting in the reduction of adsorption. In acidic medium, the surface of the adsorbent is highly protonated and promotes the adsorption of Cr(VI) in its anionic form. At the pH less than 3, the adsorption of the predominant form of $Cr_2O_7^{2-}$ is essential.

This indicates that the adsorption cannot be by electrostatic forces, but rather by chemical forces via electron exchange between activated carbon and $Cr_2O_7^{2-}$ ions and leads to the reduction of Cr (VI) to Cr (III) by the catalytic action of carbon. Louarrat et al. [15] reported that at pH lower than 3, adsorption decreases and up to about 8 times at pH 1 due to the formation of various complexes by Cr(VI). Under the extreme acidic condition of pH less than 1.6, Cr was transformed into its natural form $H_2CrO_4$.

It was observed that tannery effluents are rich in nitrogen compounds which if not removed, will adversely affect aquatic lives [16]-[17]. Tannery wastewater also contains sulphides and Cr which impart high antibacterial activities by inhibition of biodegradation, and high concentration of these contaminants makes the possible discharge of effluent into water bodies problematic due to its mutagenic, teratogenic, carcinogenic effects and eutrophication potentials [3], [8], [11]. Most tanning facilities are strategically situated near water bodies for easy disposal of heavily polluted effluents directly to the water bodies, which in turn has adverse effects on humans and the environment [10]. Indiscriminate disposal of tannery wastes into natural water bodies is a common practice in developing countries [8], [18]-[19].

One of the emerging environmental challenges in the tanning sector is the disposal of effluent containing Cr as a by-product of leather production. At higher concentration, Cr may be toxic, mutagenic, carcinogenic and teratogenic. It exists in several oxidation states, but trivalent Cr (III) and hexavalent Cr (VI) is the most stable [3], [20]. The Cr (III) most stable form, is essential to mammals in trace amounts, biologically crucial in human metabolism, being involved in the maintenance of glucose, cholesterol and triglyceride levels, and playing a vital role for the nutrition of living organisms [21] and relatively immobile in the aquatic environment due to its low solubility [5].

Cr(VI) is much more toxic (about hundred times more toxic than Cr (III)) and found to be mutagenic, toxic and carcinogenic even in trace quantity [9], [21]-[22] to many organisms thereby inhibiting biological activity in wastewater treatment systems [9]. Most microorganisms are sensitive to Cr (VI) toxicity, but some groups possess a resistance mechanism to tolerating high concentration. Recently, the toxicity of Cr (III) has also attracted renewed attention and Wang et al. [3] ascertained that Cr (III) exhibited genotoxicity to *Eisenia fetida* (a specie of earthworm) in spiked soils after four days of exposure.

There are increasing environmental concerns against some industrial tanning activities. Discharged tannery effluents without proper treatment can contaminate surface water, groundwater and soil. Tannery wastewater can be treated using either Physico-chemical and/or biological methods. Several studies focused on the treatability of tannery effluents using chemical methods, electrochemical methods and advanced oxidation processes. Other physical or chemical treatment methods used include filtration, air stripping, chemical precipitation, adsorption, ion exchange [4], [9], [23]-[24] reverse osmosis, solvent extraction, lime coagulation [21], coagulation [25] and precipitation [3] and membrane technology [26].

**Tannery Wastewater Treatment Approach**

Discharged tannery effluents without proper treatment can pollute surface water, groundwater and soil. As a result, there is an increasing environmental concern against tanning industrial processes. The wastewater from tannery can be treated using either Physico-chemical and/or biological methods. There are number of studies that focused on the treatability of tannery effluent include activated sludge process [27]-[28], chemical precipitation [3],[29], coagulation [25],[30], coagulation and flocculation [31], electrocoagulation [30],[32], coagulation and sedimentation [26] and chemical adsorption [33]-[36]. Haydar et al. [27] evaluate the use of activated sludge process (ASP) for tannery wastewater treatment over 267 days, 12hrs aeration period daily and at a mixed liquor volatile suspended solid (MLVSS) of 3500mgL$^{-1}$ and found that BOD and COD removal efficiencies to be 90 and 80% respectively. However, this approach exhibits high removal efficiency but was associated with longer hydraulic retention time (HRT) with only two parameters under consideration. In a related development, Hammouda et al.[28] reported relatively higher removal efficiency of BOD and COD of 90.8 and 80.7% respectively, with corresponding high removals of $NH_4$- N, $NO_3$-N, $PO_4^{3-}$-N, Ni, Cu, Zn and Cr as 98.9, 89.6, 90, 99.5, 92.2, 54.5 and 56.3% respectively when activated sludge (AS) was mixed with domestic wastewater. The combination of wastewater with AS sludge may increase the treatment efficiencies as a result of increasing microbial interactions with much consideration should be given to the ratio of AS and wastewater in order to avoid dense treatment culture that may inhibit microbial growth due to limitation of nutrients and gas exchange as $O_2$ and $CO_2$.

Chemical precipitation was also found to be suitable for the treatment of industrial effluent, in which the metal ions in the wastewater was made to react with chemical compound introduced to precipitate an insoluble chemical complex that can be easily removed by either sedimentation or filtration. Fu & Wang [29] employed the use of ferrous sulphate in order to convert toxic Cr(VI) to less toxic Cr(III) which was then precipitated with the addition of calcium hydroxide. The maximum Cr(III) precipitation occurs at pH of 8.7, and the corresponding chromate concentration was reduced from 30mgL$^{-1}$ to 0.01mgL$^{-1}$.

Sodium hydroxide was used to precipitate Cr (III) in tannery wastewater by Wang et al. [3], which observed the possibility of Cr speciation in TWW and most of Cr (III) was located within 13-100nm wavelength for colloidal samples and below 4nm for soluble samples − also established that Cr (III) was attached to either hydroxyl or carbonyl functional groups not N-groups. As such, the ability of a treatment approach to convert the most toxic and highly mobile Cr(VI) to less toxic and more stable Cr (III) will help in reducing the load of Cr (VI) to the environment. Precipitation was found to be outstanding in industrial treatment especially high concentrated up to 5000mgL-1 [3] of toxic heavy metal ions but associated with the setback of incomplete removal efficiency and excessive chemical requirements for precipitation.

In an earlier study, Vepsalainen, [30] compares the efficiencies of chemical coagulation (CC) and electrocoagulation (EC) in treating highly concentrated organic matter effluent, with consideration of current density, initial pH, electron charge per volume, temperature and electric cell construction. His findings indicated that Al is more suitable electrode material for EC applications because it produces Al(III) species that contributed more to the destabilizing pollutants with consequent low residual Al produced at the end of the process compared to that of CC. Furthermore, Sarala, [32] employed the use of Fe-Fe electrodes to treat domestic wastewater. The experiment conducted at different intervals of time between 5, 10, 15 and 20min; the current passed was 0.12, 0.25 and 0.36A. Results revealed that the batch operated at 0.25A at 20mins provided maximum removal efficiencies of COD, TDS, pH, Colour and Chloride. Electrochemical treatment was quick to be achieved in few seconds and can handle high concentration of wastewater but economic considerations in terms of energy and electrodes requirement was necessary.

Coagulation was described to be effective in the treatment of industrial effluent especially the TWW, Chowdhury et al. [25] uses Iron(III) chloride ($FeCl_3$) as a coagulant in order to treat the wastewater which was first settled by forming flocks with the subsequent settlement and filtered through sandstone and then treated with various doses of $FeCl_3$. The best coagulant dose that provides efficient removal of Physico-chemical parameters was 150mgL$^{-1}$ at near-neutral pH, and any further coagulant above 150mgL$^{-1}$ increases the pollution in the treatment system. Coagulation and flocculation treatment systems also coupled in a sequencing batch reactor (SBR) for TWW by Pire-Sierra et al. [31] and found out that 80, 82 and 99.6% of COD, TN and $NH_4$-N respectively was removed.

Moreover, Fettig et al. [26] incorporated coagulation and sedimentation to treat TWW. This approach involves pre-treatment of the effluent with sulphuric acid, ferrous sulphate, poly-aluminium chloride, organic polymer, dissolved air floatation and introduced to membrane bioreactor (MBR) before the influent from MBR was polished with granulated activated carbon. It was observed that an average organic substance removal was 81%, while only 36% of N removed, and this connected to the low carbon content in the treatment. However, despite the series of treatments, lower nutrients removal was reported, if discharged without further treatment, could risk the eutrophication problem in our natural watercourse [37].

In a related development to remediate tannery effluent, adsorption was widely employed as a tool for industrial effluent treatment as appeared to have a significant influence on heavy metals transportation, bioavailability and toxicity [38] and as such was found to be effective in the removal substantial amount of metal ions in the wastewater. As described by Gadd, [39], adsorption involves substance incorporation from one state of matter to other as adhesion physically or ions bonding of adsorbate to the adsorbent. Functional groups including hydroxyl, carboxyl, sulfhydryl and many more with negatively charged surfaces [40]-[41] were present for the majority of the solids including microorganisms that promote the adsorption of the highly positively charged metal ions to their surfaces from the solutions.

Dhungana & Yadav [33], proposed the use of formaldehyde-treated saw-dust at a ratio of 1:4 (saw-dust: formaldehyde) and sugarcane bagasse for the adsorption of hexavalent chromium ($Cr^{+6}$) ions at a concentration of 5-40 $mgL^{-1}$ for optimum pH of about 1 and also reported that the $Cr^{+6}$ ions adsorption increases with an increasing initial concentration of ions. Also, the effect of zeolite (Clinoptilolite) material on adsorption of $Cr^{+6}$ ions in TWW was investigated by Rangasamy et al. [35] and the mechanism involved in the removal of toxic heavy metal ions include ion exchange. $Cr^{+6}$ ions were adsorbed by zeolite up to about 92% from the solution.

The ability of rice husk silica (RHS) to remediate $Cr^{+6}$ ions by Sivakumar, [36] was investigated, with consideration of contact time, pH and initial $Cr^{+6}$ ions concentration 292 $mgL^{-1}$ in TWW. The maximum removal efficiencies of $Cr^{+6}$ ions was found to be about 88.3% at the optimum dosage of the RHS powder of 15g pH of 4.0 during 120mins. More recently, the adsorption of chromate ions on octacalcium phosphate (OCP) was determined with respect to the contact time, surface coverage and pH

**Table 1** Summary of some tannery wastewater treatment approaches

| S/No | Treatment | Major Findings | Reference |
|---|---|---|---|
| 1 | Activated sludge process at 3500$mgL^{-1}$ MLVSS | BOD and COD removal efficiencies to be 90 and 80% | Haydar et al. [27] |
| 2 | Couple activated sludge and domestic wastewater | Removal of BOD, COD, $NH_4$- N, $NO_3$-N, $PO_4^{3}$-N, Ni, Cu, Zn and Cr as 90.8, 80.7, 98.9, 89.6, 90, 99.5, 92.2, 54.5 and 56.3% respectively. | Hammouda et al. [28] |
| 3 | Chemical precipitation using ferrous sulphate at pH of 8.7 | Chromate concentration was reduced from 30$mgL^{-1}$ to 0.01$mgL^{-1}$ | Fu & Wang, [29] |
| 4 | Precipitation using NaOH | Cr (III) was coordinated with hydroxyl or carbonyl functional groups | Wang et al. [3] |
| 5 | Chemical coagulation (CC) and electrocoagulation (EC) | Al is more suitable electrode in EC due to $Al^{3+}$ species for pollutant destabilization | Vepsalainen [30] |
| 6 | Electrocoagulation using Fe-Fe Electrodes | Maximum removal efficiencies of COD, TDS, pH, Colour and Chloride was found at 0.25A at 20mins | Sarala [32] |
| 7 | Coagulation using Iron(III) chloride ($FeCl_3$) | Best removal efficiencies at coagulant dose of 150$mgL^{-1}$ | Chowdhury et al. [42] |
| 8 | Coagulation and flocculation in SBR | Removal of 80, 82 and 99.6% of COD, TN and $NH_4$-N respectively | Pire-Sierra et al. [31] |
| 9 | Coagulation and sedimentation in MBR | Organic substance and nitrogen removal was 81 and 36% | Fetting et al. [26] |
| 10 | Adsorption using formaldehyde-treated saw-dust and sugarcane bagasse | reported that the $Cr^{+6}$ ions adsorption increases with an increasing initial concentration of ions | Dhungana & Yadav [33] |
| 11 | Adsorption using zeolite (Clinoptilolite) | 92% of $Cr^{+6}$ ions was adsorbed | Rangasamy et al. [35] |
| 12 | Adsorption using rice husk silica (RHS) | 88.3% of $Cr^{+6}$ ions at an optimum RHS of 15 | Sivakumar [36] |
| 13 | Adsorption of chromate ions on octacalcium phosphate (OCP) | $H^+/OH^-$ was evaluated at a pH range of 3-10, and obtained values ranging from 0 to 1 | Elyahyaoui et al. [34] |

by Elyahyaoui et al. [34]. The exchange of $H^+/OH^-$ was evaluated at a pH range of 3-10, and obtained values ranged between 0.0 to 1.0 and the surface complexes produced by chromate and OCP were $S(HCrO_4)$ and $S(CrO_4)$. The adsorption method in heavy metal ions polluted effluent treatment was reported to be useful, but the need to provide a cheaper and renewable adsorbent is highly anticipated. The details of the reviews for TWW was summarized in Table 1.

Apart from being heavily polluted with numerous pollutants, TWW is also identified with variable strength of effluent even within a single tanning process, and the majority of the treatment approach has high selectivity among the pollutants [41], [43].

Despite the credit associated with some chemical methods for treating high concentrations of the toxic heavy metals like Ni, Cu, Cr, Pb and Zn, especially Cr(VI) [3], with corresponding BOD, COD, TN and $NH_4$-N removals, the failure of these treatment methods to remove pollutants in smaller concentrations, coupled with the fact that physio-chemical methods are expensive in terms of energy consumption and chemical employed, operating and maintenance cost as well as excessive harmful sludge production, that leads to secondary pollution and considering socio-economic importance of tanning and environmental impacts generated by the Cr in the effluent and its deteriorating effects for the health of animals and human, and also the economic value of tanning industries especially for developing countries [11], [13]. There is a need for urgent development of an efficient treatment system which will not only reduce the Cr pollution but completely eliminate it from the environment due to its chronic effects even on smaller concentrations above 0.5mg/$L^{-1}$ by Nigerian Environmental Standards and Regulations Enforcement Agency (NESREA) [47].

**Microalgal Tannery Wastewater Treatment Prospects**

The microalgal treatment system can provide alternative treatment due to the potentials of microalgae to grow even in wastewater, uptake nutrients and heavy metals, utilizing $CO_2$ to mitigate global warming, produce more biomass, and achieving efficient wastewater treatment [48]-[49]. Several types of research have been conducted in order to treat tannery wastewater using an individual species as well as a mixture of the microalgae for economical, efficient and sustainable treatment. In addition to being capable of self-nourishment from simple organic substances, algae may grow heterotrophically and/or mixotrophically in the dark and/or presence of organic carbon source [50].

Apart from the gas exchange and nutrients accumulation [51], algae are also important microorganisms for bioremediation of wastewater as they absorb plant nutrients and accumulate Cu, Pb, Ni, Fe and Cr, organic and inorganic toxic substances, due to their high tolerance and absorption capability [52]. Moreover, their large surface-to-volume ratio makes them good candidates for wastewater treatment. Algae are also composed of carboxyl, phosphoryl, sulfhydryl and polysaccharides which facilitate heavy metals absorption due to the presence of these anionic ligands in their cell walls and larger cytoplasm [21], [44]. Their high tolerance to heavy metals coupled with their facultative metabolic behaviours either autotrophs or heterotrophs, makes them one of the best wastewater treatment options.

Ozturk et al. [53] studied biosorption of heavy metals using *Chlorella vulgaris* and *Scenedesmus obliquus* in synthetic wastewater at a high concentration up to 250 mg/L, and the optimum biosorption was determined at pH of 5.0, 4.5 and 2.0 for copper, nickel and chromium, respectively, with Cr uptake for *Chlorella sp.* and *Scenedesmus sp.* at about 23 and 16%, respectively. This low uptake suggests further treatment. Mohammed [54], Mohammed et al. [48] and Mohammed et al. [49] developed a hybrid algae-bacteria system that treats municipal wastewater using optimized red light-emitting diodes (LED) illumination of about 580 $\mu mol.m^{-2}.s^{-1}$ in stirred-tank photobioreactors (STPBRs) with 70% organic matter and 90% nitrogen removals. However, there is a need to further study the microbial composition in the system to exploit its full capability as well as testing lower and higher hydraulic retention times (HRTs) and also checking the performance for lower and higher concentration where light attenuation could be minimized. Similar researches were conducted by [55]-[56].

Moreover, the removal of Cr from the real tannery and synthetic wastewater was conducted by Ardila et al. [57] using *Chlorella vulgaris* and *Scenedesmus acutus*. High removal efficiencies of 88.2% and 87.1% by the Chlorella and Scenedesmus, respectively, were achieved, while that of the real tannery wastewater was found to be only 30 and 26% by Chlorella and Scenedesmus, respectively. However, these findings were contrary to Mahmoud and Mohamed [58] in elevated removal efficiencies. Furthermore, Subashini and Rajiv (2018) reported high removal efficiency from tannery wastewater using *Chlorella vulgaris* with up to 40% Cr removal efficiency.

**Enhancement of Treatment Systems**

Continuous production of $O_2$ and addition of carbon source for microalgal photosynthesis will substantially decrease the cost of the algal treatment system. This will increase biomass growth rate at reduced cost, improve gas exchange and reduce or eliminate the cost of artificial aeration [62], which account for about 15% [63] of the overall cost. Algal-bacterial consortia serve another purpose of producing valuable metabolites [12], pollutants uptake and nutrients recycling.

## FUTURE PERSPECTIVE

Currently, there are many unresolved issues associated with the microalgal based treatment systems which include the identification of an efficient species or consortia that can have higher active removal capacity for heavy metals and other contaminants. These species must be able to strive in the very acidic medium since the majority of the literature indicated that the biosorption of heavy metals especially Cr(VI) was removed with a pH as low as 2.0. Therefore, the capacity and operability of the bioremediation system depend largely on the ability of the biosorbent to remove the toxic heavy metals and other related contaminants even in trace concentrations economically and efficiently for sustainable development [66], [67].

Consequently, several drawbacks exist in algal-bacterial treatment systems which include longer HRT and big footprint that increases the operating cost [61]. High biomass concentration can hamper efficient light utilization leading to process and system failure [61], [64], [65]. However, selection of efficient algal strain(s) with the corresponding optimization of growth operating conditions [68] may help in addressing some of these challenges.

## CONCLUSION

Considering the value of tanning process especially in developing countries, industrial and population growth coupled with an increase in the demand for leather products, as well as consequent higher volume of wastewater generated in every tanning circle which constitutes the toxic heavy metals like Cr (VI), there is need for the development of efficient, cost-effective and environment-friendly treatment alternatives. The application of microalgae in the biosorption of heavy metals may be an efficient and economically viable biological tool, since it can be cultured in wastewater utilizing the available nutrients therein, grow by photosynthesis, and absorb heavy metals and other pollutants. Despite the advances in tannery wastewater treatment using microalgal systems, still, there is need to optimize and develop efficient microalgae consortia with higher growth rates, capable of withstanding higher concentration of heavy metals, as well as remove nutrients and micro-pollutants even in trace amounts.

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