SAFETY DISPOSAL OF TANNERY EFFLUENT SLUDGE: CHALLENGES TO RESEARCHERS- A REVIEW

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Abstract:

All sectors of our society generate waste: industry, agriculture, mining, energy, transportation, construction and consumers. Waste contains pollutants which are discarded materials, process materials or chemicals. Pollution could be caused by these pollutants when they are released beyond the assimilation capacity of the environment. Industrial wastes are generated from different processes and the amount and toxicity of waste released varies with its own specific industrial processes. Tannery effluents are ranked as the highest pollutants among all industrial wastes. They are especially large contributors of chromium pollution. For instance, in India alone about 2000–3000 tone of chromium escapes into the environment annually from tannery industries, with chromium concentrations ranging between 2000 and 5000 mg/l in the aqueous effluent compared to the recommended permissible discharge limits of 2 mg/l in public sewers.

Keywords: Tannery effluent sludge; hexavalent chromium: pollution.

Introduction:

Tanneries are one of the most prominent sources of chromium pollution to the aquatic environment. If not adequately treated, wastewater from tanneries contaminates surface water and sediments to an unacceptable level, as shown by numerous studies from Poland (Ward et al., 1999; Molik et al., 2004) India (Hwaja et al., 2001) and many other countries. In India, there are about 3000 tanneries processing around 600 million kg of raw skin and hide per annum generating around 50 MLD (Million Litres per Day) of liquid waste and 305 million kg of solid waste. The pollution load in wastewater from tanneries is of the order of 30 – 120 kg of BOD_5 and 75 – 320 kg of COD per tonne of raw hide or skin processed. The environmental problems in the tanning industry have become more challenging after the Supreme Court verdict leading to the closure of polluting tanneries during 1995. Although the liquid waste could be managed satisfactorily through the Common Effluent Treatment Plants / Effluent Treatment Plants (CETPs/ETPs), the solid waste from tanneries causes a major environmental problem through contamination of the soil, and groundwater apart from emission of huge quantities of green house gases to the atmosphere.

Fleshing and sludge are the two major solid wastes emanating from tanning and treatment of tannery wastewater. It is reported that about 140-200 kg of fleshing, which are putrescible by nature, are generated for every tonne of leather processed. It contains about 80-90% moisture, 6-12% dry volatile matter and 4-8% ash and minerals. Large-scale leather processing activity in the country employing mechanical removal of fleshing has led to the generation of large quantity of fleshing which poses serious disposal problem.

Similarly large quantity of sludge is produced when wastewater from tanneries is treated. In Tamil Nadu alone, the ETPs generate about 100 tonnes of sludge per day (dry basis). As the sludge contains chromium, it is classified as hazardous material. In view of non-availability of secured landfill sites, solid waste and sludge are dumped in low-lying areas in an inappropriate and uncontrolled manner or are just piled up within the tannery / CETP premises. Therefore the disposal of solid wastes including chrome-containing wastes poses serious problem due to stringent environmental regulations. The current management of these solid wastes triggers some secondary and tertiary environmental impacts.

The world's ever increasing population and progressive adoption of industrial based life style leads to an increased anthropogenic impact on biosphere. A large proportion of the environmental issues are related to the usage and discharge of wastewater. Tanneries are such industries which contributes a major part in water usage. Obviously the waste water from this unit contains considerable amounts of hazardous compounds and where heavy metals are very common. Today 70% of available water in India has been polluted and two thirds of illness in India is related to water-borne diseases. Effluents from the tanneries contain high concentrations of inorganic and organic chemicals and are characterized with residual COD and high TDS.

The tanning process is carried out with the use of chromium tanning agents, principally basic chromium sulphates. As a result of proteolysis and condensation processes in water solution, these salts form a mixture of hydroxo- and aquacomplexes. The presence of sulphate radicals, showing also complexing properties, increases the stability of collagen and tannin fixations. The reaction of cationic complexes of chromium (III) with ionized carboxyl groups (COO-) of asparganine and glutamine acid radicals is central for the tanning process. These reactions lead to the crosslinking (coordination bonds) of collagen fibres, giving the leather its durable finish and stability. Chromium from tanneries is thus discharged principally as Cr (III) bound to organic and inorganic ligands (Walsh et al., 1996). At neutral or slightly basic pH, chromium is relatively immobile in tannery sludge (Chuan et al 1996). In receiving waters, chromium is found essentially as hydroxy-complexes of low solubility associated with the particulate phase and concentrates in sediments. In the proximity of tannery effluents, river sediment contains more than 1 mg Cr per g (Szalinska et al., 2003; Barakat et al., 2003).

Chromium salts (particularly chromium sulphate) are the most widely used tanning substances today. Hides tanned with chromium salts have a good mechanical resistance, an extraordinary dyeing suitability and a better hydrothermic resistance in comparison with hides treated with vegetable substances. Unfortunately only a fraction of the chromium salts used in the tanning process react with the skins. The rest of the salts remain in the tanning exhaust bath and are subsequently sent to a depuration plant where the chromium salts end up in the sludge. One of the major emerging environmental problems in the tanning industry is the disposal of chromium contaminated sludge produced as a by-product of wastewater treatment.

At high concentrations chromium is toxic, mutagenic, carcinogenic and teratogenic. Chromium exists in oxidation states of +2, +3 and +6. The trivalent oxidation state is the most stable form of chromium and is essential to mammals in trace concentration and relatively immobile in the aquatic system due to its low water solubility. The hexavalent chromium is much more toxic to many plants, animals and bacteria inhabiting aquatic environments. Most micro-organisms are sensitive to Cr (VI) toxicity but some groups possess resistance mechanisms to tolerate high levels. A relationship was found between the total chromium content of soil and the presence of metal tolerant/resistant bacteria. In natural waters two stable oxidation states of Cr persist (III and VI), which have contrasting toxicities, motilities, and bioavailability. Cr (VI) is motile and highly toxic and soluble in water and it is a strong oxidizing agent that causes severe damage to cell membranes.

Worldwide chromium contamination of soils has arisen predominantly from the common practice of land-based disposal of tannery wastes under the assumption that the dominant species in the tannery waste would be the thermodynamically stable Cr (III) species. However, recent detection of significant levels of toxic Cr (VI) in surface water and groundwater in different part of the world raise critical questions relating to current disposal of Cr-containing wastes. Although Cr III is an essential nutrient for human beings, there is no doubt that Cr (VI) compounds are both acutely and chronically toxic. The dose threshold effect for this element has not yet been determined accurately enough to allow regulations to be defined. However some risk assessment analysis is currently being undertaken. Cr III is less toxic than some other elements (Hg, Cd, Pb, Ni and Zn) to mammalian and aquatic organism, probably due to the low solubility of this element in its trivalent form. Cr III compounds also have a very low mobility in soils and are thus relatively unavailable to plants. The direct discharge of effluents from tanneries into water bodies has become a growing environmental problem in these days. Most of these wastewaters are extremely complex mixtures containing inorganic and organic compounds that make the tanning industry potentially a pollution-intensive sector. Despite the thermodynamic stability of Cr (III), the presence of certain naturally occurring minerals, especially MnO_2, can enhance oxidation of Cr (III) to Cr (VI) in the soil environment.

This factor is of public concern because at high pH, Cr (VI) is bioavailable and it is this form that is highly mobile and therefore poses the greatest risk of groundwater contamination. Technologies used to reduce chromium in waste water such as high exhaustion process, direct or indirect chromium recycling cannot eliminate completely from effluent coming from post tanning section. In response to this challenge, replacement of chromium with combinations of metallic cations, for example titanium, magnesium, aluminium and zirconium, was tried but the results obtained at the moment are not completely satisfying for all types of leather. Synthetic organic tanning agents, alone or in combination with a metallic cation can be considered as a substitute for chromium in some types of leather, provided that environmental and workers health regulations are complied with. In general chrome waste from leather processing poses a significant disposal problem to human health and the environment. Due to the physical-chemical processes involved in the treatment, the sludge tends to concentrate heavy metals and poorly biodegradable trace organic compounds as well as potentially pathogenic organisms (viruses, bacteria etc.).

Research work engaged at present:

Today, all tanneries must thoroughly check their waste streams. Chrome discharge into those streams is one of the components that have to be strictly controlled. The environmental impact of chrome waste from tanneries has been a subject of extensive scientific and technical dispute. Statutory limits have since been set for chrome discharge and disposal, and relevant guidelines have been drawn up throughout the world. Due to high correlation between chrome tanning and its environmental impact, checking of the efficiency of processing operations and treatment plant takes on prime importance.

A number of efforts for utilization and/or safe disposal of tannery sludge have been proposed, practiced, tested and applied at pilot and industrial scale: landfill, land application, composting, anaerobic digestion, brick making, etc., none of them proving satisfactory enough.In Tamilnadu, hazardous waste of 4 CETPs disposed of in secured landfill within their premises, of 2 other CETPs is stored on an impervious common place and of the remaining 23 CETPs is stored within CETP's premises. No other common scientific hazardous waste treatment and disposal facility has been developed.

Review of pollution:

All sectors of our society generate waste: industry, agriculture, mining, energy, transportation, construction and consumers. Waste contains pollutants which are discarded materials, process materials or chemicals. Pollution could be caused by these pollutants when they are released beyond the assimilation capacity of the environment. Industrial wastes are generated from different processes and the amount and toxicity of waste released varies with its own specific industrial processes. Tannery effluents are ranked as the highest pollutants among all industrial wastes. They are especially large contributors of chromium pollution. For instance, in India alone about 2000–3000 tone of chromium escapes into the environment annually from tannery industries, with chromium concentrations ranging between 2000 and 5000 mg/l in the aqueous effluent compared to the recommended permissible discharge limits of 2 mg/l (Ahamed et al., 2014). There are two types of tanning systems which are vegetable tanning, which does not contain chromium, and chrome tanning. However, due to the high pollution load and low treatability, conventional vegetable tanning can't be considered more environmentally friendly than chrome tanning. Moreover, vegetable tanned leathers have different physical properties and specific applications, but is biodegradable. Currently more than 90% of global leather production of 18 billion sq. ft is through chrome-tanning process.

Two main systems have been discussed and evaluated in order to comply with the many problems related to the sludge handling, including low stabilization degree, odour problems and low dewatering properties. The first system has primary clarifiers, anaerobic digestion and a new landfill as main investments and the other system is based on incineration and deposit of the ashes in a constructed landfill at the plant. The first system will solve many of the problems including a high degree of sludge stabilization, much less odour problems and better dewatering properties of the sludge.

The main drawback is that a new landfill area must be used. In many countries it will not be allowed to use landfills for deposition of sludge with an organic content above 5 %. In general, sludge disposal on landfill gets less and less acceptance. Odour problems seem mostly to depend on disposal of sludge that is not sufficiently stabilized. Aerobic stabilization, composting and anaerobic digestion seem to be cost-effective for stabilization by biological methods. If the sludge is stored for a short period before further sludge handling increase of the pH-value or addition of substances (as nitrate) that inhibits septicity of the sludge seem to be useful.

The need to reduce the volume of the sludge makes heat drying and incineration two suitable treatment ways. Both methods have their advantages and disadvantages as discussed in the report. Heat drying will within about 10-15 years fill up the constructed landfill and complementary handling of the heat dried sludge must be considered. Incineration may be used either at a plant constructed later on near the treatment plant or at a central incinerator plant in the region. Chromium recovery from heat dried sludge is also a possibility for complementary handling of the sludge. Heat drying involves certain fire risks that should be considered both during the drying process and later on if a biological reaction causes a high temperature of the sludge. Biological reactions may also induce reactions that cause bad odour.

Use of incineration produces relative small volumes of ashes and the constructed landfill may at present sludge production last more than 50 years before it is filled-up. This solution may therefore be seen as a long-range solution especially if methods can be developed to recover chromium from the ashes. If incineration is used it is recommended to use only small additions of inorganic material as these will significantly increase the volumes of ashes and to avoid oxidation of chromium(III) to chromium(VI) that occurs at high redox potentials and at high pH-values. Two other problems in use of incineration is the poor dewatering properties of the sludge that makes incineration energy consuming and the relative small size of the plant to make incineration cost-effective.

Conclusion:

The treatment of tannery effluents is by now a well established technology, and modular common effluent treatment plants servicing traditional tannery clusters or newly created leather industry zones are a widely accepted approach. However, two issues still pose serious challenges:

- High TDS (salinity) content, unaffected by treatment. This problem is especially pronounced in developing countries where mixing tannery effluent with domestic sewage or its discharge into the sea is not feasible, and the raw hides and skins are still preserved by salting. Relocation of tanneries to the seaside is often not feasible, and desalination of treated effluent by reverse osmosis is very expensive.

- Utilization or safe disposal of sludge.

Cost-effective solutions to both of these problems are still eagerly awaited.

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