Leather Industry of Turkey, in the Adaptation Process to EU Water Framework Directive (WFD)

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Abstract

In this study, the environmental issues of the leather industry in Turkey has been scrutinized in the context of adaptation process to EU Water Framework Directive (WFD) (2000/60/EC), which sets out the strategy against chemical pollution of surface waterbodies. The EQS Directive (2008/105/EC) establishes the maximum acceptable concentration and/or annual average concentration for priority substances in river basins. For "specific pollutants", each member state shall establish their EQSs. The WFD obligate to prevent any deterioration of status, and to achieve good status, as a rule by 2015. Member States should aim to achieve the objective of at least good water status by defining and implementing the necessary measures within integrated programmes of measures, taking into account existing community requirements. Where good water status already exists, it should be maintained. Ministry of Forestry and Water Affairs, Directorate General of Water Management started a project to determine constituting dangerous substances list of Turkey, creating sector specific dangerous substances inventory.

Some parameters known to used in leather industry, and potentially exist in discharges of the wastewater of this industry are among the priority substances or will be involved in specific pollutants of Turkey, because of their toxic, persistent and bioacumulative properties. Accordingly, sector specific discharge standards might be set for some chemicals used in tanning industry such as heavy metals, chlorinated phenols, halogenated hydrocarbons, and halogenated aromatic hydrocarbons.

Introduction

The WFD establishes a framework for protection of all surface waters and groundwaters, with an obligation to prevent any deterioration of status, and to achieve good status, as a rule by 2015. Accordingly, any substances identified by EU as priority substances or by Ministry of Forestry and Water Affairs as specific pollutants will be monitored in river basins of Turkey. If their concentrations are higher than EQSs, necessary measures will be implemented. Possibly discharge standards of the substances will be set for relevant industries to control pollution at source. The tanning industry, involves a sequence of complex chemical reactions and mechanical processes. Many substances used in these processes are known toxic to aquatic environment, persistent and bioacumulative. However current legislation in Turkey

about the discharge standards of tanning industry sets standards only for Chemical Oxygen Demand, Suspended Solids, Total Kjeldahl Nitrogen, oil and grease, sulfide (S^{2-}), hexavalent chromium, total chromium, fish bio-test (toxicity dilution factor), and pH (RWPC 2004). Accordingly, new discharge standards might be set for some chemicals being used in tanning industry.

Tanning Industry

The tannery operation consists of converting the raw skin, a highly putrescible material, into leather, a stable material, which can be used in the manufacture of wide range products. The whole process involves a sequence of complex chemical reactions and mechanical processes. Amongst these, tanning is the fundamental stage, which gives to leather its stability and essential character (European Comission 2003). In this process, very sensitive hydrogen bonds are replaced by chemical bonds with tanning agents like chromium, aluminum or other mineral salts, vegetable or synthetic tanning agents to stabilize the material and to protect it against microbial attack.

The four main steps in processing hides and skins are:

- Hide and skin storage and beamhouse operations
- Tanyard operations
- Post-tanning operations
- Finishing operations
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Typically the following operations are carried out in beamhouse of a tannery; sorting, trimming, curing, soaking, unhairing and liming of bovine hides, painting and liming of sheepskins, fleshing and splitting. During these activities, raw material is prepared for tanning. Tanyard operations cover, deliming, bating, degreasing, pickling and tanning, followed by draining, samming, setting, splitting and shaving. Post-tanning involves neutralization and bleaching, followed by retanning, dyeing and fatliquoring, mostly done in a single processing vessel. The overall objective of finishing is to enhance the appearance of the leather and to provide the leather performance characteristics expected of the finished leather. Operations carried out in the beamhouse, the tanyard, and the post-tanning area are often referred to wet processes, as they are carried out in vessels (drums) filled with water or other liquids (fatliquoring). The finishing is referred to dry processing (European Comission 2003) (OECD Environment Directorate 2004).

Environmental Relevance of the Tanning Industry

The tanning industry is a potentially pollution-intensive industry. Environmental concerns in a tannery include wastewater, solid waste, air pollution, soil protection, and health and safety aspects. The main releases to wastewater originate from wet processing in the beamhouse, the tanyard, and the post-tanning operations. The main releases to air are due to the dry-finishing processes, although gaseous emissions may also arise in all other parts of tannery. The main sources of solid waste originate from fleshing, splitting and shaving. A further potential source of solid waste is the sludge from the effluent treatment plant (European Comission 2003). The releases potentially contain toxic, persistent or otherwise harmful substances. The environmental effects that have to be taken into account comprise not merely the load and concentration of the classic pollutants but also the use of certain chemicals: e.g., biocides

surfactants and organic solvents (European Comission 2003). Pollution from the leather processing industries has a negative long-term impact on both the ecosystem health and functionality (Mwinyihija 2011).
1 ton of raw hide generates approximately 600 kg of solid waste, and 15-50 m^3 of effluent containing about 250 kg COD and 100 kg BOD. About 500 kg of various chemicals added(European Comission 2003).

Chemicals in Leather Industry

The amount of chemicals used varies significantly with the specification of the final product, the pelt treated and the process chosen. The potential environmental effects of each chemical will depend on many factors:

- the chemical chosen
- the medium in which it is released, i.e. solid waste, ambient air to atmosphere, aqueous environment or soil
- the actual concentration received by the environment. The quantities in the wastewater are not strictly a function of the input quantities. Some agents are almost totally absorbed, react in the process, or are precipitated in the wastewater treatment
- transformation of the chemicals due to chemical or biological process before and after discharge to the environment. The substances might react during the process or with other constituents of the effluents; or they are degraded in the wastewater treatment plant; they can also distributed to different outlets of the factory, e.g. the product, waste and wastewater
- continuous or batch discharge

Although the amount of chemicals used varies significantly depending on many factors, chemicals for a conventional tanning processes can be considered as in Table 1.

Table 1: Main and auxiliary process chemicals for a conventional tanning processes for salted bovine hides (European Comission 2003)

Chemical consumption	%
Standard inorganic (without salt from curing, acids, bases, sulphides, ammonium containing chemicals)	40
Standard organic (not mentioned below, acids, bases, salts)	7
Tanning chemicals (chrome, vegetable, and alternative tanning agents)	23
Dyeing agents and auxiliaries	4
Fatliquoring agents	8
Finishing chemicals (pigment, special effect chemicals, binders and cross linking agents)	10
Organic solvents	5
Surfactants	1
Biocides	0.2
Enzyme	1
Others (sequestering agents, wetting agents, complexing agents)	?
Total	100

Water Framework Directory and Leather Industry

As a member state, Turkey has been scrutinized in the context of adaptation process to EU Water Framework Directive (WFD) (2000/60/EC), which sets out the strategy against chemical pollution of surface waterbodies. Article 16 of the Water Framework Directive (WFD) (EC 2000) sets out the strategy against chemical pollution of surface waterbodies. The chemical status assessment is used alongside the ecological status assessment to determine the overall quality of a waterbody. Environmental Quality Standards (EQSs) are tools used for assessing the chemical status of waterbodies. The EQS Directive (2008/105/EC) establishes the maximum acceptable concentration and/or annual average concentration for 33 priority substances and 8 other pollutants which, if met, allows the chemical status of the waterbody to be described as 'good'.

EQSs for the 33 substances identified by the EU as priority substances and priority hazardous substances are derived at a European level and apply to all Member States. They are also referred to as Annex X substances of the WFD.

The Commission shall review the adopted list of priority substances at the latest four years after the date of entry into force of the directive and at least every four years thereafter, and come forward with proposals as appropriate. In this context second candidate list of the substance which includes 15 new substances, was proposed to European Parliament and the Council in 2011. Some of the substances in the entire list indicate parameter groups rather than individual parameters, accordingly the adopted list consists more than 48 individual substances, including pesticides, phenols, metals, organometalic compounds, aromatic hydrocarbons, polyaromatic hydrocarbons, halogenated hydrocarbons, halogenated organic hydrocarbons and endocrine disruptors. Member States should aim to achieve the objective of at least good water status by defining and implementing the necessary measures within integrated programmes of measures, taking into account existing community requirements. Where good water status already exists, it should be maintained.

With regard to pollution prevention and control, community water policy should be based on a combined approach using control of pollution at source through the setting of emission limit values and of environmental quality standards.

Some parameters among the priority substances, are known to used in leather industry, and potentially exist in discharge of the wastewater of this industry. Cadmium, lead, mercury and nickel are metals identified by the EU as priority substances and they are also pollutants of concern within the tanning industry. Phenolic compounds widely used in tanning industry, pentachlorophenol and nonylphenols are also identified as priority substances by WFD. Polychlorinated biphenyls were reported by Mwinyihija (Essentials of ecotoxicology in the tanning industry 2011) as tanning industry related pollutants and there are 11 different dioxin-like polychlorinated biphenyls in the list of priority substances list of EU. Perfluorooctane sulfonic acid (PFOS), of which one of the important usage area is leather tanning, is another halogenated aromatic hydrocarbon appeared on the list of priority substances. Another two dioxin-like compounds, polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) on the list together with polyaromatic hydrocarbons (PAH), were reported as tanning related air emissions(European Comission 2003). There are 8 different PAH mentioned in the priority substances list of EU.

Two solvents; trichloroethylene and tetrachloroethylene, determined by WFD as priority substances, are used in degreasing of sheepskin in tanning industry. WFD pay special attention to pesticides and there are 37 different pesticides in the list of priority substances. Among them, cypermethrin, hexachlorocyclohexane, DDT, pentachlorophenol, dieldrin are used in the preservation of raw bovine hides in tanning industry.

Parameters determined by WFD as priority substances, most probably will be part of the Turkish legislation in a couple of years. If their concentration in river basins is higher than EQSs, than probably discharge standards will be set for relevant industries.

Some chemicals widely used in tanning industry and known toxic to aquatic environment, are not defined as priority substances by WFD. However, each member state is expected to define "specific pollutants" for river basins and establish their EQSs. Chemicals selected as specific pollutants will also be monitored in river basins and concentrations will be compared with derived EQSs. Similar to priority substances, depending on the concentration levels of specific pollutants, discharge standards may be set for relevant industries in certain river basins. Accordingly, sector specific discharges standards might be set for some chemicals used in tanning industry such as chromium, cobalt, copper, antimony, barium, selenium, zinc and arsenic, although they are not identified as priority substances by EU.

Implementation of WFD in Turkey

To satisfy the WFD requirements, Ministry of Forestry and Water Affairs, Directorate General of Water Management started a project called "Determination of Dangerous Substances in Turkey's Surface Water Resources in 3 Pilot Basins (Ergene Basin, Susurluk Basin, Konya Closed Basin)". The project covers constituting dangerous substances list of Turkey, creating sector specific dangerous substances inventory and determination of EQSs, which will be the base for the discharge standards in the upcoming period.

In this context, chemicals used in leather industry have being determined by examining capacity reports, conducting surveys and literature review. Candidate list of the chemicals which includes heavy metals and organic compounds have being analyzed by applying risk assessment methods. Risk assessment procedures based on toxicology data, chemical properties, persistency and bioaccumulation of the chemicals. Determination of final sector specific dangerous substances list of leather industry will be accomplished by monitoring besides literature survey and risk assessment at the end of 2014.

Conclusion

The WFD establishes a framework for protection of all surface waters and groundwaters, with an obligation to prevent any deterioration of status, and to achieve good status, as a rule by 2015. WFD establishes the maximum acceptable concentration and/or annual average concentration for priority substances. Ministry of Forestry and Water Affairs, Directorate General of Water Management started a project to determine constituting dangerous substances list of Turkey, creating sector specific dangerous substances inventory and determination of EQSs, which will be the base for the discharge standards in the upcoming period. Some parameters known to used in leather industry, and potentially exist in discharge of the wastewater of this industry are among the priority substances or will be involved in

specific pollutants of Turkey. Accordingly, sector specific discharge standards might be set for some chemicals used in tanning industry such as heavy metals, chlorinated phenols, halogenated hydrocarbons, and halogenated aromatic hydrocarbons.

To maintain an inventory of inputs and outputs, their fate in processes and releases will help to manage the adaptation process to the WFD. Whenever possible, substitution of harmful substances by less harmful substances may be a solution. For example, alcohol etoxylates are considered main alternatives to nonylphenol etoxylates, which is the most commonly used surfactant in leather industry. Substituting by non-halogenated solvents can be a solution for halogenated solvents. However, some substitutions may require minor process changes.

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