Best available technology for chrome effluent treatment

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Abstract

Chrome tanning is the most common type of tanning in the world. Residual Chrome in the effluent and the high chrome sludge disposal costs however poses a significant discharge and disposal problem. The legislative limits on chrome in effluents remain strictly regulated throughout the world with discharge limits of < 1mg/l in most countries. Common practice is to remove chrome in a batch process by precipitation of chrome effluents at pH < 9 and settlement of the chrome containing sludge. Using chrome precipitation is difficult to consistently reach the chrome discharge limit as fats and small fibre tend to float and not to settle.

A new promising approach for tanyard effluents is a continues chrome effluent treatment with DAF (Dissolved Air Flotation) treatment. A Dissolved Air Flotation installed at a wet-blue tannery, has shown to efficiently remove chrome from tanyard wastewater, achieving a clear effluent with <0,25 mg/l chrome. The chrome treatment is completely automated, reducing chemical usage and chrome sludge generation and is operated at ideal pH and adjusted coagulant and flocculant addition to allow for complete chrome precipitation. The highly concentrated chrome sludge has a high degree of dryness of 8-10 g/l, which reduces sludge volumes for chrome sludge de-watering. The implementation of continues chrome effluent treatment using Dissolved Air Flotation, removes efficiently chrome and keeps the biological sludge chrome free, opening new disposal routes and allowing to use the biological sludge for biogas generation.

Keywords: Chromium, Tannery effluent, chrome removal, DAF treatment, Product Development

Introduction

The conventional method of chrome recovery is chrome precipitation with an alkali by adjustment of pH to 9 following settlement in a clarifier and de-watering of the chrome sludge. The main disadvantage of the common settlement method is that small chrome masked fibres and fats and grease cannot be removed efficiently with settlement, resulting in elevated chrome concentration of 4 - 12 mg/l in the effluent (UNIDO, 2019). The common limit of chrome < 1 mg/l can be only achieved by combing all residual effluents and with biological treatment leading to cross contaminations of the biological sludge (IUE 5). The performance of chrome recovery can be improved significantly with the application of Dissolved Air Flotation with chrome < 0,25 mg/l achieved, as floating fibres and fats are completely removed. A further advantage of DAF treatment is that less sludge with a higher sludge dryness of 8-10% DM is achieved compared to 3-5 % DM achieved when settling the chrome sludge (Scholz, 2009).

Materials and Methods of Chrome effluent treatment with Dissolved Air Flotation – DAF

Primary treatment of chrome effluents is a physical and chemical separation, which leads to settlement or flotation of precipitated chrome, suspended solids and colloidal substances. Sedimentation occurs, when the velocity of effluent is reduced below the point at which it can transport the suspended solids matter. The precipitated chrome settles and can be removed as sludge. The physical removal of the precipitated chrome and colloidal substances from the wastewater is enhanced by chemical conditioning of the wastewater. The effluent is pre-treated by adding alkali and dosing of a coagulant, such as aluminium salts, followed by polyelectrolyte flocculants, which aid the phase separation (TAN, 2011).

Dissolved air flotation (DAF), is nowadays the preferred method of removing precipitated chrome and solids. (IUE Tannery effluent treatment videos, 2019, TAN, 2011). The main advantages are less space requirements and better performance compared with settlement techniques. As its name suggests it works on the reverse principle to sedimentation, employing fine air or gas bubbles to lift suspended solids, which were not removed by the prior settlement, to the surface from where they may be removed. Especially fine solids as hair and fibres or fats and proteins can be very efficiently removed by flotation.

Photo 1: Dissolved Air Flotation DAF with Flocculator and sludge holding tank

The flotation process relies on coagulant and flocculent chemical conditioning of the feed stream, as for sedimentation, in order to enhance the solids separation process (Scholz, 2009). The tanning effluent feed is pH 9 adjusted for chrome precipitation, followed by dosing of a suitable coagulant. A suitable polyelectrolyte flocculant is also required for optimum phase separation, especially of colloidal solids, and will require inline dosing at adjusted pH, prior to the effluent entering the flotation tank. After chemical dosing the effluent flows into the flotation tank and is mixed with the rising air bubbles stream. The air-saturated stream is formed by pumping of the treated effluent into a pressurisation chamber along with air, which under pressure, dissolves in the water. The sudden release of pressure in the flotation tank causes the dissolved air to form 'clouds' of tiny air bubbles, which come up to the surface carrying the suspended and colloidal solids with it to form a surface sludge 'blanket', which is regularly scraped off.

Procedure of DAF chrome effluent treatment

Chrome effluents are collected from the tanyard and fine screened with an automated self-cleaning screen to remove all particles > 1 mm. In the following chrome effluents are transferred to the Balancing tank, where pH is automatically adjusted with NaOH to pH 9 to achieve chrome precipitation. The balanced tanning effluent is then transferred to the Flocculator and Dissolved Air Flotation unit. Aluminium Sulphate and an anionic Polymer are dosed into the flocculation unit of the DAF system. The DAF unit has an in-line pH control with dosing pump for NaOH to re-adjust the pH automatically to an optimum for the polymer and clarification. The DAF recirculation pump, returns the treated recirculation water to the inlet of the separator. The recirculation water is pressurised (approx. 6 bar) and saturated with air. Under pressurised conditions the air dissolves into the water. In the separator de-pressurisation of the recirculation water takes place. As a result, fine air bubbles of 30-60 microns are formed. These small air-bubbles lift the flocs to the surface of the DAF unit, where a sludge layer is formed. The DAF unit has an automatic clog-free aeration system to prevent any blockages of the aeration nozzles. The floating sludge is then removed by the skimmer system and collected in the sludge auger and pumped to the mixed sludge holding tank and then de-watered.

Photo 2: DAF Sludge (8-10% DM) and skimmer

The heavier compounds of the wastewater, such as sand or settled sludge, are removed from the base of the separator by a shaft less stainless-steel auger towards the settled sludge outlet, where the sediments are discharged via a periodically activated discharge valve to a sand trap. The supernatant of the sandtrap gravity flows to the Balancing tank. The chrome-free effluents from the DAF gravity flow to the anoxic tank of the following biological treatment for de-nitrification. The biological sludge remains chrome free and is suitable for biogas production.

Photo 3: DAF effluent with less than 0,25 mg/l chrome

Results

The new chrome effluent treatment plant was started up in November 2024. The performance has been improved by adjusting the pH and aluminium sulphate dosing and using the most suitable polymer.

Table 1: Primary treatment plant performance with average reduction of Chrome and Suspended Solids achieved with Dissolved Air Flotation (2024)

Parameters (mg/l)	**Inflow**	**Outflow**	**(%) Reduction**
Chrome (mg/l)	209	0,25	99,9
Suspended Solids (mg/l)	2337	69	96,3

The implementation of the new DAF treatment for tanyard effluents has improved significantly the effluent quality and has also reduced the sludge disposal volumes and costs. The plant is fully automatic and requires the minimum of supervision.

Conclusions

The operation of a DAF system for Tanyard effluents has shown to consistently reduce chrome to < 0,25 mg/l in the effluent. This allows to keep the biological sludge chrome free and opens a new disposal route with re-use for biogas production.

Reduced chrome sludge generation as usually used Lime milk and Ferric Chloride have been replaced by Sodium Hydroxide and Aluminium Sulphate.

The chrome sludge has a high degree of dryness, thus improving the sludge de-watering and reducing the sludge management and disposal costs.

The automatic DAF system allows to reduce chemicals usage to a minimum at optimum operation.

The DAF system removes efficiently proteins and showed to reduce nitrogen concentration of the effluent by 61% thus reducing the air requirements for nitrification in the following biological treatment.

The DAF treatment requires little space and can be well integrated into existing effluent treatment plants.

Abbreviations

$Al_2(SO4)_3$	aluminium sulphate (mg,L^{-1})
Cr	chrome (mg Cr,L^{-1})
DAF	dissolved air flotation
DM	dry matter (%)
IUE	International Union of Environment of the IULTCS
NaOH	sodium hydroxide
SS	suspended solids (mg,L^{-1})

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