Journal of Environmental Management 143 (2014) 71–79

Contents lists available at ScienceDirect

Journal of Environmental Management

journal homepage: www.elsevier.com/locate/jenvman

The effectiveness of the stabilization/solidification process on the leachability and toxicity of the tannery sludge chromium

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ARTICLE INFO

Article history:
Received 25 September 2013
Received in revised form
6 March 2014
Accepted 23 April 2014
Available online 28 May 2014

Keywords:
Tannery sludge
Stabilization/solidification
Chromium
Toxicity

ABSTRACT

A stabilization/solidification (S/S) process by using cement was applied to tannery sludge in order to find a safer way of landfilling this waste. The effects of three parameters on the process effectiveness were analysed in terms of leachate toxicity and chromium retention (%). The parameters studied were the relative amount of added water (30–50 wt.%), cement (10–60 wt.% in the solid components), and the use of three different types of cement (clinker with additions of limestone, with additions of limestone and fly ashes, and with additions of pozzolans). Statistical analysis performed by variance analysis and categorical multifactorial tests reveals that all the studied parameters significantly influence the effectiveness of the process. Results showed that chromium retention decreases as the relative amount of cement and water increases, probably due to additional chromium provided by cement and increased in the porosity of the mixtures. Leachate toxicity showed the same minimum value for mixtures with 30% or 40% cement, depending on the type of cement, showing that clinker is the main material responsible for the process effectiveness, and additives (pozzolans or fly ashes) do not improve it. The volume increase is lower as less sludge is replaced by cement and the relative amount of water decreases, and for the cement without additions of fly ashes or pozzolans. Therefore, the latter seems to be the most appropriate cement in spite of being more expensive. This is due to the fact that the minimum toxicity value is achieved with a lower amount of cement; and moreover, the volume increase in the mixtures is lower, minimizing the disposal cost to a landfill.

1. Introduction

The European Union is the world's largest supplier of leather in the international marketplace. Italy is the major leather supplying country in Europe. It accounts for 15% of the world's cattle and calf leather production and 65% of EU production. Spain ranks second and (with France, Germany and UK) accounts for most of the balance in the European leather industry (European Commission, 2003a).

The tanning industry is a potentially pollution-intensive industry. The tannery operation consists of converting the raw hide or skin into leather, which can be used in the manufacture of a wide range of products. Tanning is the process fundamental stage, which provides the stability of leather. An 80–90% of tanneries use chromium (III) salts in their tanning processes, in particular, chromium sulphate (Houshyar et al., 2012; Kiliç et al., 2011; Shakir et al., 2012; Torras et al., 2012). Hides that have been tanned with chromium salts have a good mechanical resistance, an extraordinary dying suitability and a better hydrothermal resistance in comparison with hides treated with plant substances (Krishnamoorthy et al., 2012; Nashy et al., 2012; Piccin et al., 2012; Sundarapandiyan et al., 2011). Chromium salts have also a high rate of penetration into the interfibrillar spaces of the skin, providing a saving in terms of production time and a better control of the process (Basegio et al., 2009; Cassano et al., 1996). However, the chromium toxicity is one of the most debated issues between the tanning industry and the authorities (European Commission, 2003a).

Between 30 and 50% chromium applied in conventional chromium tanneries is lost with the wastewater. Tanneries in Europe usually discharge their wastewater effluents to large wastewater treatment plants. Most tanneries discharging directly into sewer have some form of on-site effluent treatment system which usually involves the chromium precipitation. In this way, the sludge from the effluent treatment plant is approximately 500 kg (approximately 40% dry matter content) per tonne of raw hide (bovine

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http://dx.doi.org/10.1016/j.jenvman.2014.04.026
0301-4797/

salted hides) treated (Erdem and Özverdi, 2008; European Commission, 2003a).

The wastes listing in the European Waste List in the 04 01 group, are mainly from the leather and fur industry; consequently, the code 04 01 06 is described as sludges, in particular from on-site effluent treatment containing chromium (European Commission, 2000). These sludges are not included in the European Hazardous Waste List because do not possess the necessary characteristics to be classified as a hazardous waste according to European Commission. However, The United States of America environmental regulations consider chromium and chromium compounds as hazardous constituents in waste materials (US Environmental Protection Agency, 1998). Moreover, the German environmental regulations consider hazardous all wastes from the leather and hide processing (Basegio et al., 2009; Bundesrat, 1990).

One of the main environmental impacts of metal-containing sludges is the leaching of heavy metals to surface and ground water. Leaching tests therefore play a major role in the assessment of the classification, the compatibility of use and the treatment according to the environmental impact assessment of disposal or technical-economical possibilities of reuse. Spanish environmental regulations specify the DIN 38414-S4 compliance test (Spanish Government, 2002); and moreover, European regulations establish the criteria for the acceptance of waste at landfills (European Commission, 2003b).

S/S technologies use binders and additives to reduce the mobility and toxicity of the pollutants contained in wastes, and generate a final product that can be reused or deposited in landfills (Kogbara et al., 2013; Li et al., 2014; Navarro-Blasco et al., 2013; Silva et al., 2007; Ucaroglu and Talinli, 2012; Yoon et al., 2010). Stabilization refers to techniques that chemically reduce the hazard potential of a waste by converting the contaminants into less soluble, mobile, or toxic forms, while solidification refers to techniques that encapsulate the waste, forming a solid material, and does not necessarily involve a chemical interaction between the contaminants and the solidifying additives. The product of solidification may be a monolithic block, a clay-like material, granular particulates, or some other physical form commonly considered solid. Technology involving the S/S processes is currently being used to treat a wide variety of wastes from different industries, such as sludge from the tannery and from the wastewater treatment plants of electroplating and metal finishing industries (Aydin and Aydin, 2014; Erdem and Özverdi, 2008; Silva et al., 2007). These wastes usually contain contaminants such as heavy metals, organics and soluble salts (Navarro-Blasco et al., 2013; Yoon et al., 2010; Silva et al., 2007).

S/S processes are classified in terms of the binder used to encapsulate the waste, and can be divided into organic and inorganic-binder processes (Conner, 1990). The organic binders are asphalts or polymers such as polyesters, epoxy resins and polyolefins, whereas the inorganic binders are usually cement (others are lime, gypsum or zeolites).

S/S by cementation processes is used for wastes containing heavy metals. These processes, based on reactions with pozzolans or cement, are generally relatively inexpensive and easy to use (Rodríguez and Irabien, 1999). Although the S/S technology has been studied in previous works with wastes containing heavy metals, as an example with lead, arsenic, chromium, cadmium and zinc (Li et al., 2014; Peysson et al., 2005), and there are some literature in relation to the S/S of tanning industry wastes using cement (Swarnalatha et al., 2008), these studies focused on the leaching tests and did not evaluate the toxicity of the obtained solid product.

The aim of this research is to optimize the S/S process of tannery sludge by using cement for its final disposal in landfills. The effectiveness of the process is analysed in terms of leachate toxicity and percentage chromium retention: relative amount of water, cement and tannery sludge added to the mixtures, and the use of three different types of cement. Statistical analysis of the results is carried out to define the relevance of each experimental parameter on the S/S process. In this way, analysis of variance (ANOVA) is performed to prove if changes in water and cement contents are statistically significant on the analysed effectiveness variables. Additionally, categorical multifactorial experimental design is conducted to evaluate the interactions between the content and the type of cement on the S/S procedure.

2. Experimental procedure

2.1. Sludge characterization

Sludges were collected in the form of filter cakes from the water treatment plant of a conventional chromium tanning facility, located in Valencia (Spain). According to the material data sheet supplied by the tanning facility, these sludges are primarily organic wastes (41 wt.% of total solids are volatile) and they contain heavy metals, such as zinc (51 mg/kg dry matter), cadmium (<0.5 mg/kg dry matter), copper (182 mg/kg dry matter), nickel (80 mg/kg dry matter), lead (112 mg/kg dry matter), and chromium (7750 mg/kg dry matter). From the aforesaid data chromium is the major pollutant and therefore, the degree of chromium toxicity is critical.

Moisture, density, chromium content and leachate characteristics were determined for the selected sludge. Table 1 shows the mean values obtained after carrying out the analysis in triplicate. Moisture was determined in accordance with the EN 14346:2006 compliance test (EN 14346, 2006). The density value was determined to find the initial volume of the sludge in order to calculate the increase produced when it was mixed with cement. Density was obtained by introducing an amount of sludge in water and measuring the volume of water displaced. The chromium content and the leachate characteristics are the necessary parameters to calculate the effectiveness of the S/S process. In order to obtain the chromium content, an acid-digestion of the sludge using 0.5M sulphuric acid was performed prior to elementary analysis. The leaching test and the analytical techniques used are described below.

2.2. Types of cement

Three different commercial cements based on Portland cement were used to perform S/S of the tanning sludge by a cementation process. Table 2 shows the average composition of the three cements supplied by the manufacturer.

CEM II/A-L 42.5 R is the type of cement most commonly used in Spain to prepare concretes and mortars ordinary. On the other hand, additives can be used to initiate, catalyse or, in general,

Table 1
Tannery sludge characterization.

Parameter	Value
Moisture (wt.%)	58 ± 4
Density (kg/l)	1.05 ± 0.09
[Cr] (mg/kg dry matter)	7903 ± 58
Leachate characteristics	
[Cr] (mg/l)	19.3 ± 1.5
Leached Cr (mg/kg sludge)	385
Retention of Cr (%)	88.4
Leachate toxicity (EC_{50} (% leachate dilution))	0.8 ± 0.1
Leachate toxicity (EC_{50} (TU))	125
Leachate toxicity (EC_{50} (TU/(kg sludge/l)))	2501