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Stabilization of tannery sludge by co-treatment with aluminum anodizing sludge and phytotoxicity of end-products

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ABSTRACT

A global demand for efficient re-utilization of produced solid wastes, which is based on the principles of re-use and recycling, results to a circular economy, where one industry's waste becomes another's raw material and it can be used in a more efficient and sustainable way. In this study, the influence of a by-product addition, such as aluminum anodizing sludge, on tannery waste (air-dried sludge) stabilization was examined. The chemical characterization of tannery waste leachate, using the EN 12457-2 standard leaching test, reveals that tannery waste cannot be accepted even in landfills for hazardous wastes, according to the EU Decision 2003/33/EC. The stabilization of tannery waste was studied applying different ratios of tannery waste and aluminum anodizing sludge, i.e. 50:50, 60:40, 70:30 and 80:20 ratios respectively. Subsequently, the stabilization rate of the qualified as optimum homogenized mixture of 50:50 ratio was also tested during time (7, 15 and 30 days). Moreover, this stabilized product was subjected to phytotoxicity tests using the *Lepidium sativum, Sinapis alba* and *Sorghum saccharatum* seeds. The experimental results showed that aluminum anodizing sludge managed to stabilize effectively chromium and organic content of tannery waste, which are the most problematic parameters influencing its subsequent disposal. As a result, tannery waste stabilized with the addition of aluminum anodizing sludge at 50:50 ratio can be accepted in non-hazardous waste landfills, as chromium and dissolved organic carbon concentrations in the respective leachate are below the relevant regulation limits, while the stabilized waste shows decreased phytotoxicity.

1. Introduction

Industrial solid wastes in Greece amounted to approximately 72×10^6 tn in 2012, of which 297×10^3 tn are hazardous solid wastes (Eurostat, 2012). Effective solid waste management is considered of great environmental concern, noting that the respective framework is changing. The waste sector faces a growing demand for waste/by-product recycling/reuse/recovery, using the produced wastes as raw-materials, closing thus the loop of circular economy (Juul et al., 2013).

Leather tanning is a general process in tanning industry in which animal skin is transformed to leather. Trivalent chromium salts are widely used in tanneries (Celary and Sobik-Szołtysek, 2014; Kilic et al., 2011; Zouboulis et al., 2012), of which only 60 wt.% reacts with the animal skin, while the rest is discharged into wastewater. The dissolved chromium and other chemicals in wastewater are commonly removed through the chemical precipitation technique, by regulating the pH value, mostly with addition of lime and inorganic coagulants, before the main biological treatment of the wastewater (Pantazopoulou et al., 2015a). The precipitated chromium, along with some organic compounds is discharged as sludge, which usually contains trivalent chromium, organic matter, proteins, fats and several salts, mainly in the form of chlorides and sulfates (Abreu and Toffoli, 2009; Swarnalatha et al., 2006). Landfilling is a common management practice of tannery sludge. The chromium level in the tannery sludge is sufficiently high and chromium may percolate through soil and pollute groundwater (Celary and Sobik-Szołtysek, 2014; Silva et al., 2010). The air-dried sludge is called "chromium-rich tannery waste" (Cr-RTW).

The application of stabilization techniques can limit the solubility or mobility of pollutants with or without change or improvement of the respective physical characteristics of waste. The process of stabilization involves the addition of materials, which ensure that the hazardous constituents are maintained in their least mobile or toxic form (Chen et al., 2009; U.S. EPA, 1986). The most commonly used stabilizing agents are cement, hydrated lime,

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phosphate compounds and pozzolanic materials, such as fly ash (Chen et al., 2009; Jing et al., 2006; Moon and Dermatas, 2007). The main stabilization/solidification methods, which have been proposed for tannery sludge, include the encapsulation in cement matrix by the addition of cement, lime and/or fly ash, as well as the incorporation of tannery sludge into ceramics and in a glassy matrix after the addition of specific reagents and the application of thermal treatment at least at 700 °C (Abreu and Toffoli, 2009; Jing et al., 2006; Swarnalatha et al., 2006). Nevertheless, the high cost of traditional stabilizing additives prompt the development of alternative materials that are more cost-effective and simultaneously, environmentally acceptable.

Anodizing of aluminum is an electrochemical method of converting aluminum surface, which is being coated with aluminum oxide (Al_2O_3). This process provides a new surface with high corrosion and abrasion resistance. However, the anodizing process results in acidic wastewaters, which have to be disposed of in an acceptable manner. The wastewaters are neutralized either by NaOH or by $Ca(OH)_2$ addition and clarified. The supernatant is discharged to a sewer and the sludge is dewatered using a filter press. This solid waste is referred either as Aluminum Anodizing Sludge (ALAS), or Aluminum-rich sludge (Al-rich sludge) (Mitrakas et al., 2012). This sludge remains as a problem in many countries, because it is difficult to manage it, due to its complex nature (Correia et al., 2005). At present, landfill is a common disposal practice.

Aluminum is one of the major constituents, regarding the composition of solid fraction of this sludge, along with the total sulfur content, expressed as sulfate (Correia et al., 2005). Aluminum content on dry basis in ALAS is usually ranged between 17 and 28 wt.%, while the corresponding content of sulfate is between 2 and 5 wt.%. The pH value of leachates, produced by the application of standard leaching tests, has been found in the range of 6.9–7.8 (Mitrakas et al., 2012). Potential applications of ALAS include its addition in ceramic substrates, during the synthesis of pigments and for the production of ceramics and bricks (Khezri et al., 2010; Ribeiro et al., 2009). Moreover, ALAS has also been investigated as a coagulant for the treatment of municipal wastewaters, instead of conventional inorganic compounds (Correia et al., 2005) and also as potential As(V) adsorbent (Mitrakas et al., 2012). ALAS seems to be an appealing additive for stabilization and especially for chromium stabilization, because its pH value ranges between 7 and 8, where chromium shows low solubility. Additionally, the use of ALAS as a metal adsorbent, as well as an additive in ceramics, reinforce its selection as stabilizing agent.

The objective of this study was to investigate the influence of ALAS on Cr-RTW stabilization. ALAS was used as an alternative material/additive, in order to stabilize chromium along with organic compounds in Cr-RTW, avoiding the use of supplementary stabilizing agents. To the best of our knowledge there are no studies in the literature, in which ALAS is used as a stabilizing agent and specifically for chromium and organic compounds stabilization. Additionally, the potential toxic effects of the examined wastes to the environment were also investigated by using common phytotoxicity tests. The significance of this work is the simplicity of the proposed method, combined with the encouraging results for an environmentally safe disposal of a hazardous/toxic industrial waste.

2. Materials and methods

2.1. Sample collection and characterization

Cr-RTW was produced in the central wastewater treatment unit of tanneries cluster in the industrial area of Thessaloniki in Northern Greece, located next to the city of Sindos. ALAS was supplied from an aluminum anodizing industry located also in Northern Greece. After sampling, the wastes were crushed and homogenized using a "Jaw Crusher" machine (Denver) at particle sizes below 4 mm. The moisture content ratio MC (%) of wastes was calculated as follows:

$$MC = 100 \times (M_W - M_D)/M_D \tag{1}$$

where M_W is the mass (kg) of raw waste and M_D is the mass (kg) of dried waste at 105 ± 5 °C for 1 h (European Committee for Standardization, 2002).

In order to determine the main components, as well as the trace elements in the Cr-RTW and ALAS, a 0.4 g dry sample was placed into a 100 mL PTFE beaker with 20 mL concentrated HNO_3 and heated until it was completely dissolved. Afterwards the solution was diluted to 100 mL with deionized water. Metal concentrations were determined by atomic absorption spectrophotometer (Perkin Elmer Analyst 800), either using flame or graphite furnace. X-ray Diffraction (XRD) analysis was used for structural characterization. XRD diagrams were recorded at Bragg-Brentano geometry, using a two-cycle Rigaku Ultima+ powder X-ray diffractometer with a Cu-Ka radiation operating at 40 kV/30 mA. The main functional groups, which are present in the wastes, were determined using a Perkin-Elmer Spectrum 100 Fourier Transform Infrared (FTIR) spectrophotometer. The wastes were mixed with KBr, pressed to form a disc with 10 mm diameter and 1 mm thickness and scanned in the spectral range of 4000–400 cm^{-1}.

2.2. Stabilization of Cr-RTW with ALAS

Stabilization of Cr-RTW was studied using different ratios of the waste (Cr-RTW) and the stabilization additive (ALAS), i.e. ratios of 50:50, 60:40, 70:30 and 80:20. In each case, wastes were homogenized using a laboratory ball mill at mild conditions. The stabilized products were granular with approximately 12–18 wt.% moisture. Different conditions, such as mixing time (15, 20 and 30 min) and mixing rate (40, 50 and 60 rpm) were used in order to achieve effective homogenization and stabilization of mixtures. Satisfactory results for homogenization were obtained by applying 60 rpm and 30 min mixing time, which subsequently applied for all samples. Additionally, the qualified as optimum homogenized mixture of 50:50 ratio was left for 7, 15 and 30 days, in order to test the stabilization rate during time.

2.3. Leaching tests

The evaluation of chemical toxicity of raw wastes, as well as of stabilized products was performed by the standard leaching procedure EN 12457-2. The stabilized products were subjected to the leaching test immediately after mixing, while the qualified product of 50:50 ratio was subjected to the leaching test after 7, 15 and 30 days, in order to evaluate the leaching potential of chromium, as well as of organic substances during time, which found to contribute mainly to the chemical toxicity of this waste. EN 12457-2 leaching test was applied at different periods of time in order to simulate the long-term leaching potential of these constituents.

EN 12457-2 leaching test provides information on leaching behavior of granular waste and sludge under specific experimental conditions and particularly, applying a liquid to solid ratio of 10 L/kg dry matter and a particle size below 4 mm, with or without size reduction (European Committee for Standardization, 2002). In a 1 L glass bottle, 100 g of each dry sample (oven dried at 105 °C) was mixed with 1000 mL of leaching solvent (in this case with deionized water), establishing a liquid to solid ratio (L/S) 10 L/kg. Then, the capped bottle was placed in an agitation device for 24 h with a rotational type of mixing at 10 rpm. Subsequently, the leachate was filtered through a membrane filter with pore size 0.45 μm.