Environmental impact of industrial sludge stabilization/solidification products: Chemical or ecotoxicological hazard evaluation?

Marcos A.R. Silva, Renan C. Testolin, Alcione P. Godinho-Castro, Albertina X.R. Corrêa, Claudemir M. Radetski *

Universidade do Vale do Itajaí, Laboratório de Remediação Ambiental, Rua Uruguai, 458, Itajaí (SC), Brazil

ABSTRACT

Nowadays, the classification of industrial solid wastes is not based on risk analysis, thus the aim of this study was to compare the toxicity classifications based on the chemical and ecotoxicological characterization of four industrial sludges submitted to a two-step stabilization/solidification (S/S) processes. To classify S/S products as hazardous or non-hazardous, values cited in Brazilian chemical waste regulations were adopted and compared to the results obtained with a battery of biotests (bacteria, alga and daphnids) which were carried out with soluble and leaching fractions. In some cases the hazardous potential of industrial sludge was underestimated, since the S/S products obtained from the metal-mechanics and automotive sludges were chemically classified as non-hazardous (but non-inert) when the ecotoxicity tests showed toxicity values for leaching and soluble fractions. In other cases, the environmental impact was overestimated, since the S/S products of the textile sludges were chemically classified as non-inert (but non-hazardous) while ecotoxicity tests did not reveal any effects on bacteria, daphnids and algae. From the results of the chemical and ecotoxicological analyses we concluded that: (i) current regulations related to solid waste classification based on leachability and solubility tests do not ensure reliable results with respect to environmental protection; (ii) the two-step process was very effective in terms of metal immobilization, even at higher metal-concentrations. Considering that S/S products will be subject to environmental conditions, it is of great interest to test the ecotoxicity potential of the contaminants release from these products with a view to avoiding environmental impact given the unreliability of ecotoxicological estimations originating from chemical analysis.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

In recent years, ecotoxicological tests have become a essential tool to evaluate the environmental impact of chemicals released into the environment, since in these tests the (eco)toxicity of the contaminants is measured, taking into account chemical speciation and bioavailability of contaminants, and synergistic or antagonistic effects of the mixture constituents [1–4]. However, in most regulations worldwide, the (eco)toxicity potential of wastes is derived from classical chemical analysis interpretation, which is used to determine the most appropriate destination or means of disposal for waste material, according to its classification as hazardous/non-hazardous and inert/non-inert properties. In Brazil, federal guidelines classify the hazard status of industrial waste based on the chemical constituents and on leaching and solubility tests [5], similarly to the USA Code of Federal Regulations (CFR Title 40, Part 260–265). Thus, Brazilian waste regulations classify solid wastes as hazardous (Class I) or non-hazardous (Class II), Class II being split into Class II A (non-inert) and Class II B (inert). In the European Union, the Hazardous Waste Council Directive 91/689/EEC has defined a set of 14 properties allowing waste classification and one of them is the ecotoxicity property (H14), which is defined as substances and preparations which present or may present immediate or delayed risks for one or more sectors of the environment [6]. However, in this directive there is no reference to specific methods for ecotoxicity evaluation. In this context, an experimental test strategy based on a battery of biotests for waste toxicity characterization was published some years ago [7].

On the other hand, the stabilization/solidification (S/S) of sludge originating from wastewater treatment can provide an alternative to waste disposal, and can originate products in a safe and profitable manner. In this regard, technology involving the S/S processes is currently being used to treat a wide variety of wastes containing contaminants such as metals, organic compounds and soluble salts [8–10], but it is most suitable for treating wastes that are predominantly inorganic, as these are considered to be more compatible with the types of cementitious materials normally used [11].

Assessment of the S/S process efficiency is generally carried out by: (i) physical characterization of the S/S products (e.g., compressive strength test) [12]; and/or (ii) solid, leachable and soluble chemical characterization of S/S products (e.g., determination of diffusion coefficients and leachability indices) [13]; and/or (iii) toxicity estimation of the leachable fraction of S/S products (e.g., toxicity characteristic leaching procedure) [14]. Recently, a series of test methods and performance thresholds were proposed for use in the evaluation of the treatability of industrial wastes by S/S, and for the optimization of S/S formulations [15].

Considering that S/S products will be subject to environmental conditions, it is of great interest to measure the ecotoxicity potential of the contaminants released from these products. The results obtained can then be compared with those of chemical analysis to verify the agreement between the two approaches, aiming to protect living organisms. Thus, the aim of this study was to compare the toxicity classification based on the (eco)toxicological and chemical analyses of four industrial sludge samples after submission to the stabilization/solidification (S/S) processes, according to the chemical limits of current Brazilian waste regulation.

2. Materials and methods

2.1. Sludge source and metal analysis

The industrial sludges used in this study came from two different textile mills, a metal-mechanics plant, and an automotive plant. Metal analysis of the sludge and aqueous samples was carried out according to standard methods [16] and the variability of measured concentrations was presented as the coefficient of variation (CV), which was calculated by dividing the Standard Deviation by the Mean value of the response, multiplied by 100 ($n = 3$). Only metals cited in Brazilian chemical waste regulations were analyzed.

2.2. Stabilization/solidification treatment

The following experimental design for the stabilization/solidification of the industrial sludge was optimized in a previous study (results not published).

2.2.1. Step 1

The industrial sludge (3 kg-dry weight) was placed in a 20-L mixer. Clay (1 kg) and quicklime (2 kg) were added and the mixture was stirred for 2 h. The quicklime was added 30 min after the clay. After homogenization, the mixture was allowed to stabilize/solidify for 7 days (exothermic phase). Initially, a clod mixture was formed, but after 7 days (end of exothermic phase) a fine powder was obtained. The optimized composition of the components stabilized in Step 1 was quicklime 33.33%, clay 16.66%, and raw sludge 50.00%.

2.2.2. Step 2

The stabilized solid waste product obtained in Step 1 (6 kg) was re-solidified by mixing with Portland cement (4 kg), sand (2 kg), and water (6 L). After homogenization, the concrete block manufactured was allowed to stabilize/solidify for 28 days (curing time) at $25 \pm 2\,°C$ and a relative humidity of $83 \pm 3\%$. The Portland cement used was type CPV-ARI (extra strong for use in structures). The optimized composition of the components solidified in Step 2 was cement (22.22%), sand (11.11%), water (33.33%) and stabilized sludge (33.33%).

2.3. Leachability and solubility tests

One concrete block was fragmented (sieved at 0.1 mm), homogenized and used to carry out the leachability and solubility tests.

The leachability and solubility tests were carried out according to the Brazilian standard methods [17,18]. In the leachability test, a solid sample (20 g) was placed in a 500 mL bottle and 320 mL of distilled water was added along with a sufficient quantity of acetic acid (80 mL, 0.5 N) to adjust the pH to 5.0. The initial pH was 11.2, which was adjusted under stirring to 5.0, and the final pH was 5.1. The suspension was stirred for 24 h. After filtration with a GF membrane (20 μm) the leached contaminants were analyzed. In the solubility test, a solid sample size of 25 g was placed in a 500 mL bottle with the addition of 100 mL of distilled water. After 1 h of homogenization, the suspension was allowed to stand for 7 days. After filtration, soluble contaminant concentrations were determined according to the standard methods [16].

2.4. Ecotoxicity tests

The ecotoxicity tests were carried out with leachate and soluble fractions of S/S products, i.e., after Step 2 treatment of the different sludges. To carry out these tests, the S/S product fractions were adjusted according to the different standardized protocols applied in the assays.

2.4.1. Algae

The algal species used was *Scenedesmus subspicatus* Chodat (strain 86.81 SAG, Göttingen, Germany). Three algal tests for leachate samples were conducted according to the ISO standardized protocol [19] with three replicates per concentration (or control). Aqueous samples were tested at the following dilutions (%): 3.1; 6.2; 12.5; 25.0; 50.0 and 80.0, i.e., the percentage of leachate or soluble fraction in the dilution tested. Potassium dichromate was used as a positive control. The cell density of the mixture was adjusted to 10,000 cells mL^{-1} by dilution with ISO freshwater algal test medium. Each test consisted of seven filtered leachate dilutions and a control group. The test flasks were incubated on a shaker (100 rpm) with continuous illumination of 70 μE m^{-2} s^{-1} (cool-white fluorescent lamps) at $23 \pm 2\,°C$. After 72 h of incubation, the inhibitory effect based on fluorescent activity was measured at $\lambda = 685$ nm with a Shimadzu RF-551 (Kyoto, Japan) spectrofluorimeter.

2.4.2. Lumistox test

The bacterial (*Vibrio fischeri*) luminescence inhibition (i.e., Lumistox, Dr. Bruno Lange, Düsseldorf, Germany) test was conducted according to ISO guidelines [20] at $15 \pm 1\,°C$ on water samples with salinity adjustment to 35 ppt at pH 7. Aqueous samples were tested at the following dilutions (%): 3.1; 6.2; 12.5; 25.0; 50.0 and 80.0, i.e., the percentage of leaching or soluble fraction in the dilution tested. The exposure time was 30 min. The lyophilized bacterial reagent was obtained from Deutsche Sammlung von Mikroorganismen und Zellkulturen (German Collection of Microorganisms and Cell Cultures) (DSM N# 7151, Braunschweig, Germany). Each dilution sample (or control) was performed in triplicate.

2.4.3. Daphnia magna immobility test

The 48-h immobilization test with *Daphnia magna* was performed in accordance with the ISO standard [21] at $25 \pm 2\,°C$ using 5 individuals per replicate (less than 24 h old) in 50-mL glass beakers with 30 mL of test medium. Three different tests (with triplicates) were performed for each sample dilution (or control) in order to evaluate the variability of the procedure. Aqueous samples were tested at the following dilutions (%): 3.1; 6.2; 12.5; 25.0; 50.0 and 80.0, i.e., percentage of leachate or soluble fraction in the dilution tested. Potassium dichromate was used as a positive control.