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ORIGINAL ARTICLE

Chemical characterization and toxicity assessment for the sustainable management of end of life cathode ray tubes

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Abstract

Cathode ray tube (CRT) monitors represent currently one of the most produced category of electronic waste. In CRTs most of the glass components contain lead, posing serious concern for its possible release during improper management of end-of-life devices. Nevertheless the fluorescent powders, forming a layer on CRT panel glass, may cause further adverse effects on the environment. Although lead leachability from CRT glass is well known, the hazard for the release of the fluorescent powders into the environment has not been evaluated, as the ecotoxicity potential of this matrix is not fully understood yet. The aim of the present study was to characterize both leaded glass and fluorescent powder toxicity potential for the sustainable management of waste CRTs. Representative samples of both matrices were collected at a full-scale treatment plant and analysed by their metal content as well as their ecotoxicological properties, to identify the potential for hazard. Experimental results indicated that both leaded glass and fluorescent powders are characterized by a wide variety of metals, differently influencing their potential for hazard. Ecotoxicological responses further suggest that the environmental burdens associated with the management of these matrices can be limited through the implementation of strategies reducing the formation of leachates, pointing out the urgent need for both policies and techniques promoting resource recovery from this class of electronic waste.

Keywords Metal · Rare earth elements · Recovery · Risk · WEEE

Introduction

Economic growth has been traditionally related to the consumption of resources so that the economic pattern has been developed through the linear chain of production, consumption and trade [1]. The limited availability of resources has marked such approach as unsustainable, addressing the search for proper strategies to separate the socio-economic development from the depletion of natural resources. The need for a sustainable use of resources has thus promoted the transition from the linear economy model to the circular one, aiming at the implementation of a greener economy, characterized by a new business model that moves from the concept of selling products to that of selling services [2, 3]. In the field of waste management, such approach is meant to improve both reuse and recycling practices, in order to recover materials while minimizing the demand for natural resources.

The importance of a circular approach is particularly crucial for materials that are at high supply risk, like the rare earth elements (REEs), whose demand is expected to grow at an annual rate of 5% by 2020 [4]. REEs are largely used in a wide variety of electric and electronic devices and related components [5–8] so that several categories of waste electrical and electronic equipment (WEEE) are now regarded as a potential urban stock for the recovery of these resources [9].

Cathode ray tube (CRT) monitors represent one of the most interesting WEEE classes for their content in REEs and other valuable materials [10]. CRT is indeed an obsolete technology for the projection of images, which are obtained by the striking of electron beams onto a phosphorescent surface. It has been largely used in both television and computer display screens, but in the past decades it has been

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continuously replaced by either liquid crystal or plasma display panels,so that increasing amounts of CRT devices have been entering the waste streams [11]. The peak in CRT waste production was expected in the period 2015–2020 [12], but in most regions of Asia-Pacific, Eastern Europe, Middle East and Africa, low-income consumers are still demanding CRT monitors, which are not as expensive as other technologies for image projection [13].

The CRT is a tube with a conical shape, which has been reported to constitute approximately 60% of the weight of a television or a computer monitor. It is made up of 85% glass, of which the front panel contributes 65%, funnel 30% and neck glass 5% [14]; the remaining 15% of a CRT consists of plastic and metals [15]. CRT glass is mainly composed of silicate glass, with complex formulations including different oxides: a wide variety of metals are mixed into the glass matrix to confer specific properties upon the glass itself [16]. The glass fraction can be indeed distinguished into: leaded glass, which composes the hidden part of the monitor, namely the funnel and the neck; barium (Ba) and strontium (Sr) based glasses, constituting the screen monitors [17]. The frit, joining the front panel and the funnel, also consists of up to 85% lead [18]. REEs are mainly concentrated on the CRT front panel, where they constitute the powdery, fluorescent surface enabling image creation. After the dismantling of discharged CRT devices, the front panel is separated from the funnel glass, so that the fluorescent layer coating the panel glass can be easily sucked and destined to recovery [19]. Nevertheless, the recycling of valuable materials, namely glass and REEs, from discharged CRT devices still poses some challenges.

Nowadays, fluorescent powders are disposed of in landfill sites for hazardous materials [20, 21]. Similarly, the chemical composition of the glass fraction limits its proper recovery and, as the CRT production is rather limited, the glass-to-glass recycling is no longer a feasible option. Several techniques for the removal of lead from CRT glass have been proposed [22–25], but they are still not cost competitive and a great portion of CRT glass ends up in landfills. Although the number of end-of-life CRT televisions is expected to decrease in developed countries, large amounts of second-hand CRT televisions have been shipped to developing countries, where they are often handled under uncontrolled conditions [20].

The implementation of informal waste management activities can promote the release of different hazardous substances, which are contained in discharged electronic devices. Consequently, such uncontrolled practices, including open dumping, has been recognized as the source of severe environmental contamination [26]. The reported increase and bioaccumulation of metal concentration near rivers and lagoons, where uncontrolled dumping and informal recycling activities occur [27–31], indicate how some contaminants can enter the aquatic systems when leached in unregulated landfills.

The sanitary and environmental burdens that CRT devices can pose to both public health and the environment [6, 32] are mainly due to the presence of both the fluorescent powders and the leaded glass. Previous studies pointed out that some REEs, which can constitute the fluorescent powders, may display toxic effects [33–35], whereas the glass fraction can act as an important source of lead [36]. Nevertheless, the knowledge on the hazard related to the management of CRTs is still fragmented [37, 38] and the risk associated with the potential release into the environment of rare earth elements has not been assessed yet, as the ecotoxicological information on these poorly investigated elements is still not clearly identified [39]. In this regard, the application of both chemical and ecotoxicological tests could provide a more robust basis for understanding the potential hazard of CRT management as the concentration of heavy metals and REEs alone does not give adequate information on the mobility, bioavailability and potential toxicity of contaminants on the environment, because interactions between different chemicals may lead to both additive, antagonist or synergistic effects [40–42].

The present study aims at discussing the management of both the fluorescent powders and the leaded glass from discharged CRT devices in the view of their toxicity potential.

To this end, the chemical characterization of these waste components was carried out along with the assessment of their ecotoxicological properties, in order to assess the potential for hazard of both fluorescent powders and leaded glass with regard to their metal content.

Materials and methods

The experimental activity was carried out on representative samples collected at a full-scale plant, during a monitoring campaign performed over a year.

CRT treatment plant

The full-scale facility operates in Southern Italy and it treats CRT televisions and monitors by a semi-automatic processing line. The input waste is dismantled and materials are manually sorted, in order to separate plastic components, ferrous materials, cables, printed wiring boards and the electron guns. This step results in bare cathode ray tubes, which undergo the removal of the anti-implosive metal frame via an angle grinding machine. Subsequently a hot wire cutting splits the tube into the front panel and the funnel section, which are separately stored according to the chemical composition of the diverse glasses. The fluorescent powder, coating the front panel, is extracted using a special vacuum machine and collected in storage bags.

Both the leaded glass originating from the funnel disassembly and the fluorescent powders are sampled and used for experimental purposes.

Material characterization

Both leaded glass and fluorescent powder are characterized by their metal contents.

The sampled leaded glass consisted of small pieces (≤ 50 mm): before the analytical tests, they were further crushed to particles passing through a 5-mm-mesh size [43].

For each matrix, representative samples for laboratory analysis were obtained from the primary samples by means of a quartering procedure so that test portions of 3 g were analysed using the aqua regia extraction standard procedure ISO 11466:1995. The concentration of metals was determined via inductively coupled plasma-optical emission spectroscopy (ICP–OES, Thermo ICAP 6000 Series, Thermo Finnigan). The analytical device had been adequately calibrated before the measurements, using metal standard solutions provided by Sigma Aldrich. Blanks and samples at known concentrations were also measured during the instrument run for quality control.

Each analysis was repeated three times so that average values are discussed.

Leaching tests

Leaching tests for the acceptance of waste in landfills were performed following the Italian legislation, namely the Ministerial Decree 27.09.2010, on both leaded glass and fluorescent powders. For each matrix, representative samples were posed in contact with deionized water in a liquid/solid (*L*/*S*) ratio of 10 L/kg, at ambient temperature.

The leaching test consists of a nine-step extraction procedure, performed over a time set of 16 days. During this period, at nine, defined time intervals, the solid sample was separated from the deionized water, which was totally renewed to run the subsequent leaching step. At each of the nine separation phases:

- The liquid fraction was filtered (0.45 µm) and metals, anions, total dissolved solids (TDS) and dissolved organic carbon (DOC) were analysed in the resulting leachates according to standard methods (AWWA-APHA, 1998). Final results were expressed as sum of the values detected in each extraction step and were compared to the limits set by the Italian law;
- the solid residue after filtration was brought back to the solid sample destined to the subsequent leaching stage.

The leachability of lead from funnel glass samples was also characterized by a toxicity characteristic leaching procedure (TCLP) performed according to the EPA method 1311. This procedure is designed to create the worst-case leaching scenario in a municipal solid waste landfill by using a low-pH acetic acid solution [44–46] and it has been extensively applied to study the CRT toxicity by its content in leaching lead [36, 45].

Representative leaded glass samples were ground and mixed with the extraction fluid at a *S*/*L* ratio of 20/1. TCLP tests were performed at ambient temperature, using a special extractor rotating at 30 rpm, for 18 h. As lead accounts for about 80% of the toxic metals in CRT [47], the TCLP was focused on lead leachability. The resulting solutions were analysed by their lead content, measured by ICP–OES (ICAP 6000 Series, Thermo Finningan), following the EPA method 3015A.

Ecotoxicological tests

According to Tsiridis et al. [48], the leachates for toxicity tests were prepared following the 24-h short-term procedure CEN 12457-2: 2002 at a liquid to solid ratio (*L*/*S*) of 10 L/kg. A mixture of solid samples (50 g) and 500 mL of deionized water was added in polyethylene bottles and agitated for 24 ± 0.5 h at 10 rpm. Afterwards, the eluates were filtered through a 0.45-µm membrane filter.

All samples were stored at 4 °C until use for luminescence and algal growth inhibition tests as well as for acute immobilization tests. Each toxicity test was performed using different leachate concentrations obtained from the undiluted sample (100%).

The Luminescence inhibition test followed the ISO 11348-3:2007 method, which allows the evaluation of the inhibitory effect of samples on the light emitted by bioluminescent bacterium *Vibrio fischeri* (strain NRRL-B-11177) after 30-min exposure. Freeze-dried *V. fischeri* cells were reconstituted with reagent diluent at 4 °C. Sodium chloride solution (22% NaCl) was used to adjust the osmotic pressure of the sample. Three replicates were included for each sample. Luminescence *V. fischeri* measurements were performed with Microtox® Model 500 Toxicity Analyzer from Microbics Corporation (AZUR Environmental) equipped with a 30-well incubated at 15 °C ± 1 °C and with excitation source at 490 nm wavelength.

The chronic algal growth inhibition test with the unicellular algae *Raphidocelis subcapitata* was carried out according to ISO 8692:2012. The initial inoculum cell density was approximately 104 cells/mL. The growth inhibition rate considered six replicates, incubated for 72 h at 23 ± 2 °C, under continuous illumination (irradiance range of 120–60 µein/m^2 s).

Acute immobilization tests with *D. magna* were carried out according to the standard method ISO 6341:2013. Newborn daphnids (<24 h old) were exposed in four replicates for 24 h at 20 ± 1 °C in darkness. Toxicity was expressed as the percentage of immobile organisms.

In each kind of test, toxicity was expressed as the percentage of effect and, whenever possible, as EC50 along with 95% confidence limit values. Statistical analyses and graphs were carried out using GraphPad Prism software by two-way analysis of ANOVA, followed by Tukey post hoc analysis.

Furthermore, the toxicity unit (TU) of the analysed eluates was calculated as the ratio between the eluate concentration displaying toxicity to each test species and the corresponding EC50 with the formula: $\mathrm{TU} = (1/\mathrm{EC50}) \times 100$. Results were ranked into three main groups of samples, considering the weight score (WS) of toxic unit [49, 50]: (1) no acute toxicity ($\mathrm{TU} < 0.4$); (2) slight acute toxicity ($0.4 \leq \mathrm{TU} < 1$); and (3) acute toxicity ($1 \leq \mathrm{TU} < 10$).

Results and discussion

Leaded glass: characterization and leaching behaviour

The results of the leaded glass characterization, reported in Table 1, confirmed the prevailing presence of lead, as expected. The overall metal composition was found to resemble the chemical composition of leaded glass in terms of oxides: high concentrations of calcium, potassium and sodium were indeed detected.

The metal characterization showed that, beyond the lead, the most abundant heavy metals in leaded glass samples were barium, chromium, iron, nickel and strontium, whereas the average concentration of zinc was one order of magnitude lower. Conversely, cadmium was found to be below the detection limits of the analytical instruments, as it is mainly concentrated in other electronic waste components, such as the printed circuit boards (PCBs) that are selectively removed throughout the CRT disassembly line.

Experimental results further highlighted a moderate variability. In this regard, it should be pointed out that the chemical composition of CRT glass components can vary according to several factors, including the manufacturer, version and time of production [51]. The different types of treated CRT as well as the share of each one in the input material to the processing line reasonably account for the observed variability. Both these aspects are difficult to control at industrial scale, as they mainly depend on the consumer behaviour.

Due to its heterogeneous composition, leaded glass is typically destined to landfill disposal: the environmental burdens associated with this practice are generally referred to the leaching properties of waste materials. Results of the leaching tests are reported in Table 2. Lead (Pb) and arsenic (As) were recognized as the most abundant heavy metals in the leaching solution. Their concentrations in leachate, along with that of mercury (Hg), antimony (Sb) and selenium (Se), exceeded the limits established for the acceptance of waste in non-hazardous landfills, forcing the disposal of CRT glass in landfill licensed for hazardous waste. Conversely, anions, total dissolved solids (TDS) and dissolved organic carbon (DOC) were found to be below the threshold limit values for non-hazardous waste landfill.

Table 1 Characterization of leaded glass metal content

Metal	Concentration (mg/kg)
Al—Aluminium	283.33 ± 5.03
Ba—Barium	250.13 ± 3.24
Be—Beryllium	< DL
Ca—Calcium	3007.00 ± 171.55
Cd—Cadmium	< DL
Co—Cobalt	4.53 ± 1.29
Cr—Chromium	292.70 ± 6.63
Cu—Copper	22.43 ± 1.41
Fe—Iron	1502.60 ± 20.68
Li—Lithium	0.41 ± 0.01
K—Potassium	3055.67 ± 131.86
Mg—Magnesium	776.13 ± 50.95
Mn—Manganese	22.10 ± 1.56
Mo—Molybdenum	51.51 ± 1.37
Na—Sodium	2763.67 ± 54.40
Ni—Nickel	122.11 ± 2.44
Pb—Lead	10263.33 ± 132.31
Sb—Antimony	4.5 ± 0.03
Sr—Strontium	243.30 ± 16.77
Ti—Titanium	3.78 ± 0.03
Zn—Zinc	17.86 ± 1.05

Leaching tests highlighted that, despite the prevailing concentration of lead in the waste glass samples, the corresponding amount available in the liquid phase is comparable with that of other heavy metals. This condition depends on the leaching properties of each contaminant as well as on the specific leaching environment. Yot and Méar [17] focused on the leachability of barium, lead and strontium from CRT glasses and found that the behaviour of tested materials varied according to the nature of the employed reduction agent.

In this view, the experimental results from the TCLP test can provide additional information on the hazardous characteristics of leaded glass. Previous studies report lead concentrations in TCLP extracts exceeding 5 ppm, which is established as the US regulatory level for the characterization of waste as hazardous. However, these results have mostly been commented as an overestimation of lead leachability, as real conditions in landfills are different from those

Table 2 Leaching tests for waste acceptance in landfills performed on leaded glass

Parameters	Value (mg/L)	Limit values for acceptance in landfill (mg/L)[a]	
		Non-hazardous waste	Hazardous waste
As	2.47	0.2	2.5
Ba	1.03	10	30
Cd	0.02	0.1	0.5
Cr	0.13	1	7
Cu	0.07	5	10
Hg	0.14	0.02	0.2
Mo	0.17	1	3
Ni	0.16	1	4
Pb	2.64	1	5
Sb	0.07	0.07	0.5
Se	0.40	0.05	0.7
Zn	0.74	5	20
Chlorides	1.62	2500	2500
Fluorides	0.60	15	50
Sulphates	1.11	5000	5000
DOC	44.68	100	100
TDS	126	10,000	10,000

[a] Italian Regulation (DM 27/09/2010)

optimizing the transfer of this metal from the solid phase to the liquid one, thus keeping its concentration into solution lower than the threshold limit values for the classification of hazardous waste.

In the present study, the concentration of lead in TCLP extracts was set at 4.82 ± 0.1 mg/L, which is double the value detected in the leaching solution produced to verify the acceptability of this waste in landfills. This outcome suggests that a further amount of lead remains available to be released. However, the lead concentration in the TCLP extract obtained in this study is lower than that obtained in previous investigations, likely due to factors related to the experimental conditions, such as the CRT sample fraction, the particle size used in the test and the CRT type [52]. The production year of CRT used can be overlooked as it was found to be not a significant factor for lead leaching [47].

The sample chemical composition is not the only factor affecting the leaching behaviour, that has been extensively investigated in scientific literature. Yamashita et al. [53] studied that of CRT funnel glass into acid, neutral and basic solutions, at 90 °C and for different periods of time. They observed the highest lead release in acid conditions, after 182 days; however, no constant leaching rate occurred in this period. In basic solutions, lead content remained high at the surface of investigated particles, suggesting the possible formation of a protective layer which may detach after temperature decrease to ambient conditions. Conversely, the increase in temperature from 100 to 180 °C was found to promote the extraction of lead into an alkaline, sulphur-containing medium up to 68 and 82%, respectively [54]. Such outcome is particularly interesting if intended to promote lead extraction and recovery from CRT glass. More recently, the recovery of CRT glass has been directed towards its possible use as sand substitute in concrete, due to the possibility of immobilizing toxic metals. However, it was proved that the inclusion of CRT glass in concrete should be controlled below 25%, to decrease the possibility of lead leaching [55].

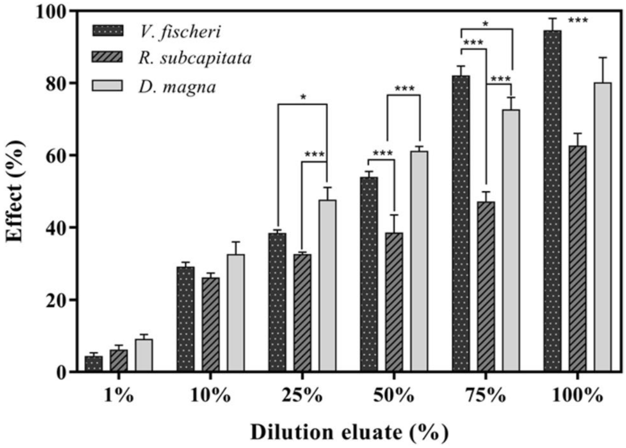

Fig. 1 Leaded glass leachate tests with *V. fischeri* (30 min), *R. subcapitata* (72 h) and *D. magna* (24 h)

The toxicity potential

The chemical characterization pointed out that leaded glass from CRT dismantling is a highly heterogeneous matrix in terms of metals, whose leachability could adversely affect the environment. In order to quantify the hazard associated with CRT leaded glass management, ecotoxicity tests were performed on the extract from leaded glass.

Toxicity data are summarized in Fig. 1, plotting the effects of leaded glass eluates on *V. fischeri, R. subcapitata* and *D. magna*. The analysis of these data evidenced that the toxic effects of undiluted eluate samples on *V. fischeri* (97% E) and *D. magna* (80% E) were more pronounced than those on *R. subcapitata* (62% E).

The comparative evaluation of the effects of leaded glass eluate on the different test species suggested that there was a little difference in the sensitivity at the lowest dilutions (1 and 10%); these effects turned to be significantly different when the dilution enhanced to 25% ($P < 0.01$).

In accordance with the toxicity results expressed as inhibition of the test species, lower EC50 were estimated for the samples tested on both *V. fischeri* and *D. magna*. The ecotoxicological assessment of leachates expressed as EC50

Table 3 Toxic unit (TU) and hazard classification for leaded glass leachates

Organism	TU	Toxicity
V. fischeri	3.4	Acute toxicity
R. subcapitata	1.4	Acute toxicity
D. magna	3.9	Acute toxicity

values showed indeed the following gradient: 29.0% dilution (21.3–39.6%) on *V. fischeri*, 25.2% dilution (21.0–29.6%) on *D. magna* and 72.6% dilution (55.9–92.6%) on *R. subcapitata*.

The WS of TU further confirmed the ecotoxicity test results. Following this approach the leaded glass leachate presented acute toxicity and consequently could be able to generate some adverse consequences on aquatic biota (Table 3).

The toxic potential of the leaded glass should be reasonably related to its content in metals. However, any direct relation was found between the chemical composition of the eluates, in terms of metal concentrations, and the inhibition effects provided on the test organisms, with the exception of the bacteria. The observed sensitivity of the organism could be reasonably attributed to the presence of 0.124 mg/L of zinc in the analysed eluate. The presence of zinc may have stimulated the uptake of lead in *D. magna* [56], which showed the ability to destroy both Na^+ and Ca^{2+} homeostasis [57]. Similarly, Tsiridis et al. [58] reported that the joint effect of zinc and lead on *V. fischeri* had synergistic effects and that a mixture of zinc and cadmium exhibited toxic effect on algal cell growth [59].

Fluorescent powder: characterization and leaching behaviour

The interest towards fluorescent powder is related to the prevailing presence of REEs. Results of the chemical characterization in terms of metals are reported in Table 4 and confirmed that the most abundant REEs are yttrium and europium, followed by samarium, gadolinium, lanthanum and erbium. Among common metals, both aluminium and zinc were detected in great concentrations: the former is the main component of the film used to ensure electronic beams strike each pixel exactly under scanning process; the latter is typically used in doped sulphide form in fluorescent powders.

The chemical characterization of fluorescent powders is consistent with that provided in previous studies [10, 60, 61] and the observed variability is likely to be attributed to both the type and the brand of CRT device [18] from which the powder has been removed.

Table 4 Characterization of fluorescent powder metal content

	Concentration (mg/kg)
Common metals	
Al—Aluminium	15,845 ± 3064
Cd—Cadmium	3126 ± 626
Cr—Chromium	< DL
Cu—Copper	58.49 ± 18.36
Fe—Iron	2.458 ± 734
Ni—Nickel	80.78 ± 6.86
Pb—Lead	2955 ± 981
Zn—Zinc	197,177 ± 17,625
Precious metals	
Ag—Silver	1039 ± 386
Au—Gold	2.34 ± 0.25
Pd—Palladium	0.46 ± 0.15
Pt—Platinum	< DL
Rare earth elements	
Ce—Cerium	< DL
Er—Erbium	1.50 ± 0.48
Eu—Europium	6057 ± 3435
Gd—Gadolinium	3.05 ± 0.81
La—Lanthanum	1.66 ± 0.24
Lu—Luterium	< DL
Nd—Neodymium	0.12 ± 0.02
Pr—Praseodymium	< DL
Sc—Scandium	< DL
Sm—Samarium	50.89 ± 1.84
Y—Yttrium	12,017 ± 299
Yb—Ytterbium	< DL

The recycling potential of these valuable elements, especially REEs, is of great interest so that several methods are being studied [10, 61]. However, either their economic competitiveness or their technical feasibility still needs to be improved for industrial-scale applications. Table 5 reports the results of the leaching tests performed on representative fluorescent powder samples. All the parameters were found to be within the limits for waste acceptance in non hazardous waste landfills, with the exception of barium. Due to the significant concentration of this metal in the solution, the fluorescent powders should be disposed in hazardous waste landfills.

The content of heavy metals in leachate was found to be rather low, especially if compared with that obtained from the leaching of other WEEE components. Karnchanawong and Limpiteeprakan [62] investigated the leaching behaviour of spent batteries, that can be regarded as metal-rich waste, and pointed out that during the periods of low pH values, some metals like arsenic, mercury, nickel and zinc leached out at higher concentrations so that their mobility was higher.

Table 5 Leaching tests for waste acceptance in landfills performed on fluorescent powders

Parameters	Value (mg/L)	Limit values for acceptance in landfill (mg/L)[a]	
		Non-hazardous waste	Hazardous waste
As	0.03	0.2	2.5
Ba	29.95	10	30
Cd	0.01	0.1	0.5
Cr	< DL	1	7
Cu	0.03	5	10
Hg	< DL	0.02	0.2
Mo	0.03	1	3
Ni	0.10	1	4
Pb	0.50	1	5
Sb	0.03	0.07	0.5
Se	0.03	0.05	0.7
Zn	0.67	5	20
Chlorides	10.40	2500	2500
Fluorides	1.96	15	50
Sulphates	110.16	5000	5000
DOC	46.37	100	100
TDS	912.57	10,000	10,000

[a] Italian Regulation (DM 27/09/2010)

Material composition and acid conditions were thus the conditions promoting the extraction of these metals from solid matrix as well as that of REEs. In this view, the leachability of both metals and REEs from fluorescent powders has been largely investigated for the purposes of valuable material recovery via acid leaching [63]. De Michelis et al. [64] studied the recovery of yttrium from powders from spent fluorescent lamps with several types of acids (nitric, sulfuric and hydrochloric). Zinc and yttrium were the target metals in the study of Innocenzi et al. [61], investigating their extraction from spent fluorescent powders by sulphuric acid in the presence of hydrogen peroxide. After leaching, a step of precipitation with sodium sulphide to remove impurities from leach liquors, such as calcium, was carried out and the addition of oxalic acid was provided to precipitate yttrium oxalates.

The extreme condition that could promote the extraction of these materials from fluorescent powders are unlikely to occur in landfills so that most REEs mainly remain as urban stocks within the disposal sites of fluorescent powders. However, the simultaneous presence of potentially hazardous substances in fluorescent powders makes the characterization of their overall toxic potential worth to be identified.

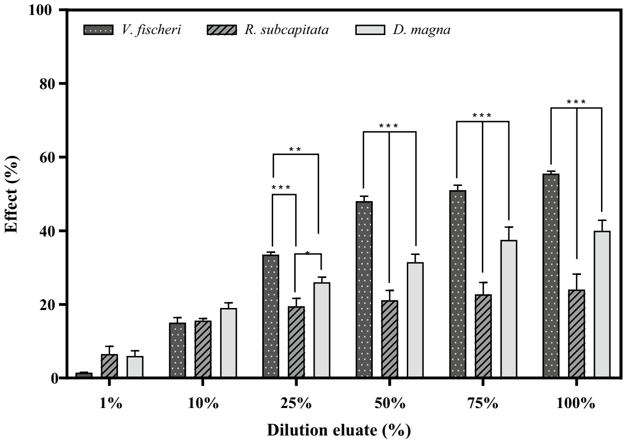

Fig. 2 Fluorescent powder leachate tests with *V. fischeri* (30 min), *R. subcapitata* (72 h) and *D. magna* (24 h)

The toxicity potential

Eluate from fluorescent powders was analysed for its ecotoxicity via *V. fischeri, R. subcapitata* and *D. magna*, as plotted in Fig. 2.

The effects expressed as the inhibition of the algal growth obtained from the tests with *R. supcapitata* pointed out a poor reduction in the proliferation of the algal cells, which was observed to be lower than 24% despite the applied dilution. Such outcome suggests a quite completely absent ecotoxicity.

As for the tests performed with *V. fischeri*, the eluate was found to inhibit the bioluminescence of 55% bacteria: the inhibition percentage decreased for increasing dilution ratio, down to 10% for a 1% dilution. The *V. fischeri* EC50 determined after a 30-min exposure to CEN eluates was 23.1% (18.8–33.9%).

Differently from what experienced with the algal species, the fluorescent powders' eluate seems to be toxic to *V. fischeri*, as well as to *D. magna*.

The test solution obtained from fluorescent powders displayed 40% *D. magna* immobilization. However, for the lower dilution factors, namely 1 and 10%, the immobilization percentage values were observed to be 6 and 19%, respectively, indicating no significant toxic effect.

The different results obtained using different test species can be reasonably related to the chemical form in which toxic metals are present in the powders that influence their bioavailability. Consequently, the uptake of the same metals could vary among the tested species, resulting in acute toxicity effects of different relevance [56–59, 65].

When considering the WS approach (Table 6), the fluorescent powders resulted to be characterized by acute toxicity. Differently from what observed for leaded glass, such result was obtained only with regard to *V. fischeri* that raise

Table 6 Toxic unit (TU) and hazard classification for fluorescent powder leachates

Organism	TU	Toxicity
V. fischeri	5.5	Acute toxicity
R. subcapitata	n.d.[a]	No acute toxicity
D. magna	n.d.[a]	No acute toxicity

[a] Not determined

as the most sensitive test species to fluorescent powders eluate.

It should be pointed out that both fluorescent powders and leaded glass displayed the most significant toxic effects on *V. fischeri*. The inhibition percentage values obtained on undiluted eluates can be indeed ordered as follows: *V. fischeri* > *D. magna* > *R. subcapitata*.

Management aspects in light of the ecotoxicity potential

The overall outcomes of ecotoxicity tests suggested that the leaded glass toxic effects cannot be referred to the prevailing presence of a specific metal, but they are likely to be determined by the synergistic effects of different ones [56, 57, 59, 65] as well as by pH, hardness and conductivity, which can have a significant influence on the leachate ecotoxicity [66].

The ecotoxicity potential to water of colour CRT, evaluated through the TRACI tool, has been attributed to the simultaneous presence of lead, antimony, cadmium, zinc and copper, with the last one providing the major contribution [67]. Synergistic effects from these metals in terms of toxicity have been often reported [68, 69], but their prediction is very complex as it depends on a wide range of parameters. Obiakor and Ezeonyejiaku [70] studied the toxicity of binary mixtures of copper and zinc, varying their relative ratio and found different results against the same animal species. Although most of the ratios displayed synergistic coergism, the combination of copper and zinc in the ratio 1:1 showed antagonistic effects when compared to the single action of copper.

Further studies could be performed to identify the no observable adverse effect level (NOAEL) concentrations for the investigated materials, so as to have a threshold leaching value driving the definition of proper handling procedures for leaded glass. However, as the leaching behaviour of different metals can differ significantly with their chemical speciation as well as with the environmental conditions, the toxicity potential of the leaded glass can be displayed differently. This condition makes the use of NOAEL a decision making supporting tool rather complicated.

Similar consideration raises for fluorescent powders: as already observed for the leaded glass, it was not possible to identify a linear relationship between the metal composition of the fluorescent powder eluates and the inhibition effects so that the overall toxicity response cannot be attributed to a single chemical element. In this case, the toxicity response is even more complex to be identified as not only the presence of base and heavy metals, but also that of REEs, needs to be taken into account.

The metal composition of the analysed matrices highlights that both fluorescent powders and leaded glass contained comparable amounts of base metals, with the exception of aluminium, cadmium lead and zinc. Apart from lead, their concentrations were indeed higher in fluorescent powders, which also contained REEs. However, the greatest availability of potentially harmful substances did not result in a higher toxicity potential. This evidence can be likely related to the different metal complexes that are present in both leaded glass and fluorescent powders.

Experimental results suggest that the ecotoxicological potential of the investigated materials should thus be minimized through the implementation of proper management strategies, reducing the formation of leachates which is usually associated with the landfill disposal. In the case of fluorescent powders, this practice is expected to make way for recycling, due to the strong economic interest raised by their content in REEs, whereas different consideration raises for leaded glass.

In high-income countries, the production of potentially toxic leachates from leaded glass disposal is already a remote event as the landfilling, which should be regarded as the last option for the sustainable management of waste, is also legally regulated to ensure the highest sanitary environmental protection. However, the current recourse to the leaded glass landfill disposal should be further lowered by encouraging recovery practices. To this end, the producer responsibility needs to be enhanced and the competitiveness of emerging technologies for leaded glass recycling has to be promoted. A key feature for the definition of such technologies would likely be recognized in their flexibility towards the waste materials to be treated for recovery purposes: following the development of the market of electronic appliances, the full-scale implementation of a technique exclusively devoted to CRT recycling would probably turn to be obsolete in less than a decade.

In developing regions, where the informal recycling sector of electronic devices is largely based, open dumping can result in environmental burdens much higher than those associated to formally identified disposal practices. In this case, the formation of potential toxic leachates from uncontrolled landfilling should be limited by strategies acting at either local and global level [71]. Locally, the informal sector should be included in the formal one, so as to discourage the implementation of primitive techniques entailing the release of hazardous substances. Such condition, along with specific legislation banning the import of discharged devices, would make their export a less economically attractive strategy for the management of electronic waste, thus reducing the amount destined to informal treatment and disposal.

Conclusion

In the present study, the chemical and ecotoxicological characterization of both leaded glass and fluorescent powders from CRT monitors was carried out to discuss the more suitable strategies for their management.

Experimental results confirmed that lead is the main metal in the analysed glass fraction, but significant concentrations of barium, chromium, iron, nickel and strontium were also detected. Although the amount of leachable lead is lower than the one that can be extracted under optimal conditions, the release of other heavy metals was found to contribute to the overall toxicity potential of leaded glass. Similarly, the presence of heavy metals in the fluorescent powders was observed to affect their toxicity characteristics, which cannot be exclusively attributed to the presence of REEs. Physico-chemical parameters such as hardness, conductivity and pH may have contributed to the metal eluate bioavailability among the organisms tested, also giving rise to synergistic and/or cumulative effects, which may explain the different responses obtained across the species tested. Due to the chemical complexity of these matrices, the definition of ecotoxicity-based strategies for their proper management seems difficult to implement.

A different approach should be, thus, outlined in order to reduce the formation of potentially toxic leachates, mainly from unregulated disposal practices. The results of this study clearly underlined the need for recycling techniques, diverting both components from landfills. It is worth pointing out that the strategies to ensure the recycling of the tested CRT components can vary in different geographical context. In developed countries, the environmental burdens associated with the potential formation of toxic leachate from either leaded glass or fluorescent powders is rather limited, as landfilling is operated in accordance with formally identified criteria. In this case, the development of cost-competitive and sustainable technologies would spread the recovery of materials from both leaded glass and fluorescent powders at industrial scale.

In those regions where the informal recycling is performed, the strategies to reduce the environmental burdens associated with the improper management of CRT components should not focus on the development of recovery practices. The absence of clear legislation would indeed encourage the application of primitive techniques for CRT recovery that would then produce different environmental impacts from the release of its hazardous substances. Further efforts should be provided in reducing the potential of the informal sector. The decrease in the fed amount of discharged CRT as well as the inclusion of informal recyclers into regulatory framework would indeed discourage illegal export from high-income regions as well as ensure more sustainable management strategies.

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