Research article

Ecotoxicity attenuation by acid-resistant nanofiltration in scandium recovery from TiO$_2$ production waste

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ABSTRACT

The lack of high-grade scandium (Sc) ores and recovery strategies has stimulated research on the exploitation of non-ore-related secondary sources that have great potential to safeguard the critical raw materials supply of the EU's economy. Waste materials may satisfy the growing global Sc demand, specifically residues from titanium dioxide (TiO$_2$) production. New technologies are being developed for the recovery of Sc from such residues; however, the possible environmental impacts of intermediary products and residues are usually not considered. In order to provide a comprehensive ecotoxicity characterisation of the wastes and intermediate residues resulting from one promising new technology, acid-resistant nanofiltration (arNF), a waste-specific eco-toxicity toolkit was established. Three ecotoxicity assays were selected with specific test parameters providing the most diverse outcome for toxicity characterisation at different trophic levels: *Aliivibrio fischeri* (bacteria) bioluminescence inhibition (30 min exposure), *Daphnia magna* (crustacean) lethality and immobilisation (24 h exposure) and *Lemna minor* (plant) growth inhibition with determination of the frond number (7 d exposure). According to our results, the environmental impact of the generated intermediate and final residues on the aquatic ecosystem was mitigated by the consecutive steps of the filtration methods applied. High and statistically significant toxicity attenuation was achieved according to each test organism: toxicity was lowered based on EC$_{20}$ values, according to the *A. fischeri* bioluminescence inhibition assay (by 97%), *D. magna* lethality (by 99%) and *L. minor* frond number (by 100%), respectively, after the final filtration step, nanofiltration, in comparison to the original waste. Our results underline the importance of assessing chemical technologies' ecotoxicological and environmental impacts with easy-to-apply and cost-effective test methods to showcase the best available technologies.

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1. Introduction

The increasing risk of a shortage in the supply of critical raw materials (CRMs) is stimulating the identification of alternative sources and the development of recovery technologies [1,2]. These recovery technologies may ensure that future raw materials need to maintain and improve the European Union's (EU's) economy [3,4] or meet worldwide demand [5]. Since 2011, the European Commission (EC) has periodically published a list of raw materials that are considered critical to the EU, i.e. materials that are economically important and have a high supply risk. Scandium (Sc) is a crucial functional material for many industrial sectors and has been on the list since 2017, along with other rare-earth elements (REEs) [6].

The exploitation of non-ore-related secondary sources at the end of products' lives, often referred to as 'urban mining', has great potential to safeguard CRM supply [2,7–10]. On the other hand, landfilled stocks and freshly produced flows of rare-earth-containing industrial by-products represent additional CRM sources [11]. Industrial process residues, such as bauxite residue, electrical waste and electronic equipments, municipal wastes, phosphogypsum, coals and fly ashes contain considerable amounts of CRMs, including Sc [12]. These secondary resources often have low concentrations of REEs, yet they are available in very large volumes and thus could provide significant amounts of REEs, as well as Sc [13,14]. Although promising attempts have been made to recover Sc from secondary resources, such as from bauxite residues [12,15–19], further stockpiled waste materials may satisfy the growing global Sc demand. Residues from titanium dioxide (TiO_2) production, which are available in millions-of-tonnes/year [20] may satisfy this growing demand. Currently, 80% of Sc in China is obtained from titanium pigment production waste through a complex purification process [21]. The hydrogen chloride (HCl) waste of the chloride process of titanium dioxide (TiO_2) production accounts for approximately 60% of the total amount of waste generated in the HCl process. This HCl waste contains high concentrations of dissolved metals, as well as Sc. The Sc concentration found in the acid liquid waste of TiO_2 production could qualify it as an ore, of which a volume of $\sim$2.5 to $\sim$3 million m^3 would be sufficient to cover the entire future Sc demand of the EU [22].

There has been increasing interest in Sc recovery from TiO_2 production waste in recent years. Technology choices include solvent extraction [21,23–26], acid-resistant nanofiltration (arNF) [22] or the combination of solvent extraction and nanofiltration [27]. The development of technologies for the recovery of REEs, CRMs and specifically Sc from stockpiled industrial waste streams aim to promote the zero-waste valorisation concept [13] and target the reduction of landfilled stocks.

As the scandium concentration in the secondary raw materials is low compared to the coexisting elements, its recovery becomes challenging, expensive and possibly energy and chemically intensive. In addition, the diversity in the treatment processes and the consequences of applying these methodologies with respect to their environmental impact have not been appropriately discussed [28]. Even such critical issues as the environmental impacts of the conventionally applied mining processes of ilmenite ($Fe^{2+}Ti^{4+}O_3$) and rutile (O_2Ti) mining technologies in Australia have not been reported. Concerning global warming, greenhouse-gas-emissions, human health and ecotoxicity, a comprehensive analysis of the environmental impacts of these mining processes should have been carried out [29]. In their critical review, Botelho et al. [12] addressed the question of the possibility of having an eco-friendly process for scandium extraction from secondary sources (mining process wastes and end-of-life products), although the environmental implications of these technologies are rather difficult to assess due to the current lack of ecotoxicity data. They also highlighted that the environmental effects of the intermediary products and residues of the developed closed-loop recovery processes are still not being considered. These intermediary products and residues are important in occupational health and safety, as well as in the case of an accidental release into the environment [28,30–32]. Therefore, the establishment of new, eco-friendly technologies combining waste valorisation with the possible reduction of the amount of stockpiled waste materials would be of outmost importance supported by sufficiently detailed ecotoxicity data. The use of solvents, such as hydrochloric or sulfuric acid as well as ionic liquids, results in additional environmental burden [33–35], while applying membrane filtration could eliminate the generation of potentially more hazardous waste streams. Nanofiltration can offer two vital advantages: selectivity and the reduction of the environmental impact caused by solvent extraction steps by reducing the volume to be extracted downstream [36].

Although several authors have confirmed that the methods designed for classifying products under Classification, Labelling and Packaging Regulation (CLP) [37] are unsuitable for testing wastes [38] a harmonised testing strategy is still not available. In addition, a combination of a suitable battery of biological test methods and chemical analyses is necessary for the ecotoxicological characterisation of waste [39–41].

A revised Appendix III of the Waste Framework Directive 2008/98/EC [42] was published in 2014, with 14 out of 15 redefined hazardous properties for waste. However, the assessment of hazard property HP14 ('Ecotoxic': may present risks for one or more sectors of the environment) has been left unchanged [43] without any improvement of assessment and testing strategy or specific threshold values [39]. Suitable test methods for the biological assessment of waste and waste eluates are recommended by the CEN (European Committee for Standardization) guideline 14735.

Our research assessed the environmental efficiency of a Sc recovery technology exclusively based on filtration (arNF) using a problem-specific ecotoxicity toolkit of standardised test methods recommended by the CEN guideline 14735. We compared the possible environmental impacts of the generated residues on the aquatic ecosystem in each filtration step to the effect of the initial technology input material. We consider it a novelty, keeping in mind the lack of ecotoxicity characterisation in similar recovery technology-oriented articles. Ecotoxicity characterisation of the technology residues was performed by direct toxicity assessment (DTA) [44,45] which took into account the aggregated effect of the multicomponent waste streams (including their often extreme pH). In order to carry out the most comprehensive risk assessment possible, aquatic test organisms from three different trophic levels (*A. fischeri* bioluminescent bacterium, *D. magna* freshwater crustacean and *L. minor* aquatic macrophyte) were selected under specific test conditions that provided the most diverse assessment outcomes to determine the potential environmental risk upon accidental leakage. The selection of the best applicable ecotoxicological test conditions was carried out with great emphasis on statistical

approaches, which we also considered unique for publications on similar topics. The aim of this paper was to emphasise the importance of understanding the ecotoxicological and potential environmental effects in developing eco-friendly and environmentally benign technologies. For this reason, we also aimed to find the most time- and cost-efficient methods that can be applied to follow industrial processes during the developmental stage to prove the possible toxicity reduction of the wastes, which also means lower deposition and treatment costs for waste owners and industrial stakeholders.

2. Materials and methods

2.1. Scandium-containing waste

The Sc-containing (~40 mg Sc/kg) waste used in the arNF experiments was a microfiltered liquid acid waste (LAW) of a titanium dioxide (TiO_2) pigment producer located in Europe. The LAW was dark blue to green coloured with a pH of 1.5. The elemental composition of LAW is presented in Supplement 1.

2.2. Experimental setup of acid-resistant nanofiltration technology and the origin of the samples

A laboratory-scale technological experiment was carried out to assess the feasibility of arNF for the treatment of acid waste. Prior to arNF, the acid waste was microfiltered to obtain the liquid acid waste (LAW). Then, the pH of the LAW was adjusted to 1.5 by the addition of a NaOH solution (40%). Afterwards, precipitated solids were removed by centrifugation (30 min, 14′000 g, Avanti J-25I, Beckman Coulter) and ultrafiltration (UF). UF was conducted in cross-flow filtration mode (10 bar, 20 °C, 5 L min-1) using a modular filtration unit (MaxiMem, PS Prozesstechnik, Switzerland) equipped with a flat sheet membrane module (active area: 200 cm^2) and a UP150 flat sheet membrane (MWCO: 150 kDa, UP150, Microdyn-Nadir, Germany). The ultrafiltration permeate was diluted 1:5 using HCl (pH = 1.5) to give a suitable arNF feed. Nanofiltration experiments were carried out using the same modular filtration unit, equipped with self-made hollow-fibre modules, containing six fibres (total membrane area 90 cm^2). Prior to use, the fibres (poly-ethersulfone, type: UFCLE, Pentair, Enschede, Netherlands) were coated with oppositely charged polyelectrolytes (PE) via the layer-by-layer (LbL) method. Thus, poly-(allylamin-hydrochlorid) (PAH; MW = 65 kDa) as a cationic PE and poly(sodium 4-styrenesulfo-nate) (PSS; MW = 1000 kDa) as the anionic counterpart were alternatingly layered onto the membrane surface until three bi-layers were reached. The experiments were performed at a *trans*-membrane pressure of 9 bar in batch circulation mode, with the concen-trate fed back into the feed vessel. The recirculation flow rate was 1 L min-1 and sufficient for a turbulent flow (Reynolds number >4000). Feed temperature was kept constant at 20 °C. For the concentration experiments, a 50% permeate was recovered. For further information on LbL-nanofiltration see also Remmen et al. [22]. The nanofiltration experiments were carried out using a MaxiMem filtration unit (PS Prozesstechnik, Basel, Switzerland). Custom-made layer-by-layer (LbL) modified polyethersulfone (PES)-based hollow fibre membranes (type: UFCLE) from Pentair (Enschede, Netherlands) were used. The specific module contained six fibres (total membrane area 90 cm^2), which were coated with oppositely charged polyelectrolytes (PE). Thus, poly-(allylamin-hydrochlorid) (PAH; MW = 65 kDa) as a cationic PE and poly(sodium 4-styrenesulfonate) (PSS; MW = 1000 kDa) as the anionic counterpart were alternatingly layered onto the membrane surface until three bi-layers were reached. The experiments were performed at a *trans*-membrane pressure of 9 bar in batch circulation mode, with the concentrate fed back into the feed vessel. The recirculation flow rate was 1 L/min and sufficient for a turbulent flow (Reynolds number >4000). Feed temperature was kept constant at 20 °C. For the concentration experiments, a 50% permeate was recovered.

The block flow diagram of the filtration process is shown in Fig. 1. Table 1 presents the details of the different streams tested with different ecotoxicity assays.

An aqueous extract was prepared from the solid residue (SR) for ecotoxicity testing. The extraction procedure was carried out based on Pandard et *al.* [46] and current guidelines [47]. The solid waste sample was air dried, hand ground in a ceramic mortar and sieved (nominal pore size: 1 mm) before performing the extraction step. The extraction was carried out with boiled tap water at a 1:10 = solid: liquid ratio (1 g waste, 10 g liquid) and shaken for 24 h at 300 rpm and room temperature. Boiled tap water was the control in all cases, since it was used for extraction. All labware was cleaned 24 h prior with 5% HNO_3. The extracts were prepared from a 1 g solid sample with 10 mL of boiled and cooled tap water (750 mL of volume in Erlenmeyer flasks). After 24 h, the slurries were centrifuged for 10 min at 8500 rpm, then filtered through 4–12 μm pore size filter paper, followed by filtration through 0.22 μm pore size filter.
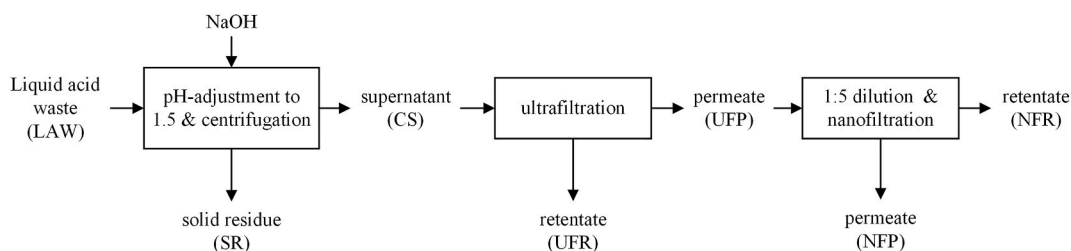

Fig. 1. Acid-resistant nanofiltration unit block flow diagram.

Table 1

Samples from the different filtration steps of acid-resistant nanofiltration technology.

Sample name	Sample abbreviation	Sample description
Liquid acid waste	LAW	Microfiltered acid waste of TiO_2 pigment production (pH = 1.5)
Solid residue	SR[a]	Solid residue of microfiltration step and after addition of 40% NaOH and centrifugation; blended product of different experiments
Centrifugation supernatant	CS[b]	Supernatant after centrifugation of the pH-adjusted (pH = 1.5) acid waste
Ultrafiltration permeate	UFP	Permeate after ultrafiltration of the pH-adjusted (pH = 1.5) centrifuged waste
Ultrafiltration retentate	UFR[b]	Retentate after ultrafiltration of the pH-adjusted (pH = 1.5) centrifuged acid waste
Nanofiltration permeate	NFP	Nanofiltration permeate after 50% permeate recovery of acid waste (dilution 1:5, pH adjustment to 1.5, centrifugation and ultrafiltration)
Nanofiltration retentate	NFR	Nanofiltration retentate after 50% permeate recovery of acid waste (dilution 1:5, pH adjustment to 1.5, centrifugation and ultrafiltration)

[a] Tested in the form of aqueous extract.
[b] Due to the small amount of centrifugation supernatant and ultrafiltration retentate (flow chart), ecotoxicity testing was not possible.

2.3. pH measurements and chemical analysis of the tested samples

The pH of the liquid phase samples and the aqueous extract was determined in three parallels using a WTW (Wissenschaftlich Technische Werkstätten GmbH) instrument containing a pH 330 instrument and a pH electrode (Electrode Sentix 81).

The samples were diluted with nitric acid (3%, trace metal analysis grade) using an autodilution device (Simprep, Teledyne Cetac Technologies) and then analyzed using triple quadrupole inductively coupled plasma mass spectrometry (QQQ-ICP-MS). The analysis was performed on an 8800 QQQ-ICP-MS system (Agilent, Basel, Switzerland) using general-purpose operational settings. Quantification was performed using multi-element standards (Sigma-Aldrich). To account for matrix effects ^{103}Rh was used as the internal standard. To quantify $^{11}B^+$, $^{23}Na^+$, $^{24}Mg^+$ and $^{43}Ca^+$, the ICP-MS was operated in single quad no-gas mode. For $^{24}Mg^+$, $^{43}Ca^+$, $^{45}Sc^+$, $^{51}V^+$, $^{52}Cr^+$, $^{55}Mn^+$, $^{56}Fe^+$, $^{59}Co^+$, $^{60}Ni^+$, $^{63}Cu^+$, $^{66}Zn^+$, $^{75}As^+$, $^{78}Se^+$, $^{88}Sr^+$, $^{95}Mo^+$, $^{111}Cd^+$, $^{118}Sn^+$, $^{121}Sb^+$, $^{137}Ba^+$, $^{201}Hg^+$, $^{208}Pb^+$, $^{232}Th^+$ and $^{238}U^+$, helium was used as a collision gas. Using oxygen (O_2) as a reaction gas, $^{27}Al^+$ and $^{47}Ti^+$ were measured in triple quad mass-shift mode. For $^{39}K^+$, hydrogen was used as a reaction gas.

2.4. Ecotoxicity assays

The liquid waste samples were diluted for testing with the growth medium necessary for the cultivation or maintenance of a particular test organism. All toxicity tests had a negative control without contaminants, which served as a reference point and quality control in an experiment. Since the extraction was done with boiled and cooled tap water (the test organisms are incompatible with distilled water or ultrapure water), tap water was used as a control in all cases. All three test organisms were selected based on their previously proven sensitivity to heavy metals [48–51] and the examples in the field of testing complex wastes, wastewaters and environmental samples, such as construction product leachates [52], wastewaters [53,54] and foundry sludge leachates [55].

2.4.1. Aliivibrio fischeri bioluminescence inhibition assay

The applied bacterial strain (NRRL B-111 77) was cultured and maintained in the laboratory under axenic conditions. The ingredients of the growth medium (pH = 7.2) were 30 g NaCl, 6.1 g $NaH_2PO_4 \cdot H_2O$, 2.75 g K_2HPO_4, 0.204 g $MgSO_4 \cdot 7\ H_2O$, 0.5 g $(NH_4)_2HPO_4$, 5 g peptone, 0.5 g yeast extract and 3 cm^3 glycerol per 1 L distilled water [56]. Tap water was applied as a control. The A. fischeri bioluminescence inhibition test was carried out as described by Fekete-Kertész et al. [57]. The luminescence intensity was measured with a Fluostar Optima BMG Labtech microplate reader (fluorescence detection limit >30 amol/well ATP) after 30, 60, 120 and 180 min incubation time. The test was carried out in 96-well microplates by pipetting 50 μL of the dilution series members of the samples and then adding 200 μL A. fischeri cell suspension in three parallels. According to the applied protocol, the time of the measurement was 1 min and 21 s/plate. Between two consecutive measurements, the microplates were stored at room temperature in the dark. The evaluation of the results was carried out as described by Ujaczki et al. [58]. Each measurement was carried out in three replicates and repeated three times. To ensure the validity of the data and the sensitivity of the A. fischeri cell culture, copper sulphate as a reference toxicant was measured in every measurement series.

2.4.2. Daphnia magna lethality and immobilisation assay

A colony of D. magna cultured in the laboratory was used in a series of experiments. The test animals were cultured in 5 L beakers in a 21.5 ± 1 °C thermostatic chamber with a 16:8 h light:dark cycle (illumination: Juwel Aquarium, Day-Lite, 15 W, 438 mm lamp, 560 Lumen, 6500 K) and fed every day by 2 mL of algal suspension of 10^9 cell/mL cultivated in the laboratory containing Chlorella sorokiniana. To maintain D. magna, natural surface water (collection site: Lake Balaton, Hungary, 46°970 N, 17°950 E, pH = 8.65, EC = 620 μS) was used. To check the sensitivity of the D. magna culture, acute toxicity tests were performed with potassium dichromate ($K_2Cr_2O_7$) as a reference toxicant at intervals of approximately six months. The range of sensitivity of D. magna culture to $K_2Cr_2O_7$ was within the limits (EC_{50}, 24 h = 0.6–2.1 mg/L) set by guideline 202 of the OECD (Organisation for Economic Co-operation and Development) [59]. The D. magna acute lethality and immobilisation tests were performed as described in the OECD 202 [59] test

protocol in three parallels. Tap water was applied as a control.

2.4.3. Lemna minor growth inhibition assay

A colony of *L. minor* cultured in the laboratory was used in this experiment. The test organism was cultured in a 20 × 30 × 7 cm glass container placed into a 21.5 ± 1 °C thermostatic chamber with a 16:8 h light:dark cycle (illumination: Juwel Aquarium, Day-Lite, 15 W, 438 mm lamp, 560 Lumen, 6500 K). For maintenance, Hoagland's nutrient medium was used, which was renewed twice a week.

On the first day, 10 healthy, two-leaf *L. minor* individuals were placed in 50 mL of each dilution member of the liquid samples. The experiment was carried out with three parallels in 150 mL beakers. Tap water was applied as a control. The beakers were covered with a translucent plastic film to avoid evaporation and concentration of the test solution during the experiment. The assembled test systems (beakers) were incubated under the same conditions used for culture and maintenance. On the seventh day, the number of fronds was determined by visual counting of the leaves, and then *L. minor* individuals were removed from the test solutions and dried on filter paper. The dried biomass was placed into ground-necked test tubes containing 5 mL of 96% ethanol. After 24 h, the optical density of the green chlorophyll-containing solutions was determined spectrophotometrically (Sanyo SP55 UV/VIS spectrophotometer) at 649 nm and 664 nm [60]. Each measurement was repeated three times, and 3,5-dichlorophenol was used as a reference chemical to check the sensitivity of the *L. minor* at least twice a year. From the measured optical density values, the total chlorophyll content was determined based on the calculation method of Lichtenthaler [61].

2.5. Data evaluation and statistical analysis

In the case of each ecotoxicity endpoint, the percentage of inhibition (H%) was calculated compared to the respective controls. One-way analysis of variance (ANOVA) was performed by STATISTICA 13® software identifying significant effects ($p < 0.05$). The homogeneity of variances was examined using Cochran's C-test. Significant effects among different treatment steps and exposure times were determined using Bonferroni's test ($\alpha = 0.05$). Statistical significance was determined using two different approaches, establishing (i) whether the length of exposure had a significant effect on the concentration–response relationship, namely the extent of inhibition compared to the control, and (ii) whether there was a significant difference in the inhibitory effect of the samples from the consecutive filtration steps of the applied filtration technology.

Effective concentration (EC_{20}, EC_{50}) values (the concentration resulting in a 20% or 50% decrease in the test endpoint compared to the control) were determined using OriginLab 8.0 software with the logistic function fitting ($y = A_2 + (A_1-A_2)/(1 + (x/x_0)^p)$), where A_1 = initial value, A_2 = final value, x_0 = centre, p = power). EC values are given in dilution factor units, which means that the minimal dilution of the original sample is necessary to cause a maximum of 20% or 50% inhibition of the test endpoint.

In each case, the six measurement results for the six process samples were normalised, i.e. converted to 6-dimensional position vectors of length one, and then clustered based on their Euclidean distances. Calculations were performed using the R programming language [62]. Figures were prepared using the corrplot [63], ggdendro [64] and ggplot2 [65] packages.

Based on the results of the selected methods and the exposure times of the recommended ecotoxicity toolkit, the environmental efficiency of the applied acid-resistant filtration technology was assessed in terms of toxicity attenuation. For this purpose, relative toxicity was calculated by dividing the dilution factor corresponding to the EC_{20} value of a sample from a particular filtration step by the dilution factor, corresponding to the EC_{20} value of the initial LAW sample (e.g. y = 50%, when the dilution factor required for 20% inhibition is halved).

3. Results and discussion

3.1. Chemical characterisation of waste streams

The acid waste sample provided by the European TiO_2 manufacturer was subjected to an advanced filtration treatment, as previously published [22,27]. In terms of element concentrations, LAW was similar to the composition reported by Hedwig et al. [27] and contained substantial amounts (>1 g L^{-1}) of Al, Fe, Mn, Ti and Zr (Table S1). Furthermore, naturally occurring radioactive matter (NORM) was found in the solution (Th, U; Table S1).

By adjusting the pH of LAW to ~1.5, some impurities were precipitated, which were separated from the liquid phase by centrifugation and ultrafiltration (e.g. Th: >93%, U: >99%, Ti: >98% and Zr: >99%). As previously reported, most of the Sc (>60%, 46.7 mg/L) remained in the solution under these conditions [22,27]. The UFP stream is mostly similar to LAW but lacks the aforementioned precipitated elements (Table S1).

An aqueous extract was prepared from the solid residue after centrifugation. Although tap water was used for this purpose, the pH of the extract was ~1. Some metals were re-dissolved, such as Al, Fe, Mn, Ti and Na, whereas Na was almost twice as abundant as the other four elements combined (Table S1). Since sodium salts are usually highly soluble in water, it is unlikely that Na was precipitated to a high degree. The high content in the sludge was more likely a sign of trapped liquid or incomplete dewatering after S/L separation. Hence, when the SR was dried during the preparation of the extract, the sodium salts were concentrated in the dry matter.

During NF, a novel tailor-made LbL membrane was tested. As previously described, the UFP was diluted at 1:5 to avoid damaging the membrane, yet this reduced the metal concentrations in the stream [22].

Through NF, the total feed was divided into two equally sized (v/v) streams, the retentate (NFR) and the permeate (NFP). Most of the Sc was preserved in the NFR (retention ~95%). In contrast, Fe was more permeable (retention ~73%), leading to a partial depletion of Fe in NFR. The retentions and Sc over Fe selectivity of the tailor-made membrane were in the same range reported for the

commercial DK membrane (Suez, Germany) [27]. Due to the generally high retention of the membrane used, the NFP became the least concentrated stream in the test, with the highest pH (~1.91). Major elements in NFP were Fe (~ 1.0 g L^{-1}) and Mn (~0.3 g L^{-1}), and with some distance, Zn (0.05 g L^{-1}) and Cu (0.025 g L^{-1}). Only traces of all other elements were found (<0.01 g L^{-1} Table S1). In NFR, metal concentrations were considerably higher than in NFP. Furthermore, in addition to the aforementioned major elements in NFP, Al (0.7 g L^{-1}), Cr (0.09 g L^{-1}), Co (0.03 g L^{-1}) and Ni (0.01 g L^{-1}) were also found.

3.2. Results of the ecotoxicity assessment

A. *fischeri* is generally used for toxicity assessment of airborne heavy metal pollution, as well as waste water, surface waters and sediments contaminated with heavy metals [49]. According to the *A. fischeri* bioluminescence inhibition assay, an exposure-time-dependent increase in toxicity was found only in the case of SR, based on EC_{20} and EC_{50} values (Fig. 2, Table S2). *A. fischeri* proved to be sensitive to LAW, UFP, NFP and NFR samples, as well with relatively high EC_{20} and EC_{50} values; however, the significant exposure-time-dependent increase in effective concentration values was not examined (Fig. 2a and b). *Daphnia magna* was used for the ecotoxicity assessment of heavy metal-containing waste samples [50,51]. The *D. magna* lethality test showed a significant exposure-time-dependent increase in toxicity, mostly in the case of LAW (Fig. 2c and d). In general, it can be concluded that longer exposure times resulted in higher inhibition, both in the case of *A. fischeri* and *D. magna*; however, this phenomenon was not statistically significant in all cases.

In the case of *L. minor*, only one exposure time was applied (7 days), but the sensitivity of the two different measurement endpoints was compared. The *L. minor* growth inhibition test showed that the total chlorophyll content generally proved to be more sensitive, resulting in higher inhibition percentages and lower EC_{20} and EC_{50} values (Fig. 2e and f) compared to the conventionally used frond number measurement endpoint. The number of fronds produced during the 7-day exposure period was less affected, while subtle adverse effects of the tested samples could be detected by measuring the chlorophyll content of the leaves representing plant vitality.
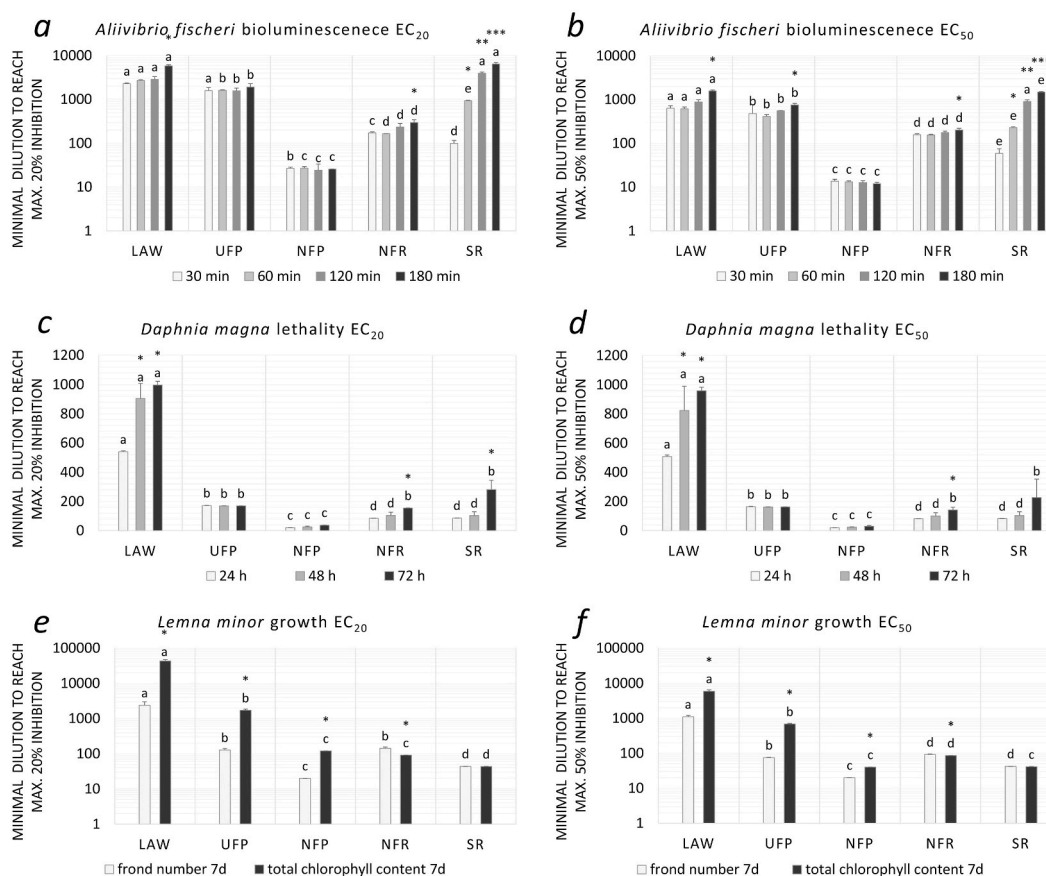
Fig. 2. EC_{20} and EC_{50} values given in dilution factor units determined for the samples of the arNF technology process. In the case of *A. fischeri* and *D. magna* asterisks (*) stand for statistical significance between EC values of a particular sample at different exposure times. In the case of *L. minor* asterisk (*) stands for statistical significance between EC values of total chlorophyll content and frond number measurement endpoints. In the diagram statistical significance between EC values of the samples within a particular exposure time or applied measurement endpoint is marked by lower case letters. Sample abbreviations: LAW - Liquid acid waste, UFP – Ultrafiltration permeate, NFP – Nanofiltration permeate, NFR – Nanofiltration retentate, SR – Solid residue.

High sensitivity of *L. minor* had been reported previously in the investigation into the effect of 10 heavy metals under standardised test conditions and [66] by Radic et al. [67], assessing the toxic effects of industrial effluents containing a mixture of heavy metals (Fe, Cu, Zn, Ni, Pb and Cr).

The elements that were removed the most by arNF with regard to the initial material LAW were Ti, U, Th and Zr. Although the primary aim of this manuscript was not to provide a detailed analysis of the relationship between element content and toxicity, keeping in mind the idea of DTA, it is worth considering the results of previous studies on metals and radioactive elements that have been removed to the greatest extent. The ecotoxicity threshold value for U was determined to be the predicted no-effect concentration (PNEC) = 0.005 mg/L for freshwater plants and invertebrates, and it was also revealed that for U, there can be a greater risk of chemical toxicity than radiological toxicity (depending on the isotopic composition) [68]. In addition, U can be bioaccumulated by the *Lemna species* [69]. Uranium was shown to adversely affect the growth of *L. minor* in a dose-dependent manner with EC_{50} value of 19.4–37.2 mM U, depending on the growth endpoint (frond area, frond number, fresh weight and dry weight) [70]. The U concentration investigated by Horemans et al. [70] was of a higher magnitude than the U concentration determined in the samples of the arNF technology process; therefore, we consider it justified that considering single elements, toxicity cannot stem from U in our case. Limited ecotoxicity data are available for Th. Ma et al. [71] determined $EC_{50(24\ h)}$ to be 7.3 μM and highlighted the different chemical forms and bioavailability; hence, the toxic mechanisms on *D. magna* would be totally different.

The results of short-term toxicity tests with zirconium dioxide (ZrO_2) were reported by the European Chemicals Agency [72]. No acute effect was found based on the OECD 202 test protocol on *D. magna* at an initial loading rate of 100 mg ZrO_2/L (74.03 mg Zr/L). The other available studies support the non-toxic effect of zirconium on aquatic invertebrates. No reliable acute toxicity data are available to aquatic invertebrates for Ti metal [73]; therefore, a read-across approach was used between Ti metal and TiO_2. Based on the ECHA registration dossier of titanium, all reliable acute toxicity tests to invertebrates for TiO_2 resulted in unbounded $L(E)C_{50}$ values ranging from >10 to > 10,000 mg TiO_2/L (equivalent to > 6 to > 6000 mg Ti/L). It is also stated in the registration dossier that "These reliable results cover a range of TiO_2 products with varying particle size (from nano-particles to bulk powders). All these results are taken together in a weight of evidence approach, and it is concluded that TiO_2 is not toxic to aquatic invertebrates at > 1000 mg TiO_2/L and at > 10,000 mg TiO_2/L in freshwater and marine water, respectively." [73].

The example of the toxicity data above shows how difficult it is, based on the chemical composition of a complex technology sample, to determine which elements, in what concentration or even the efficiency of their removal are the determining factors for decreased or increased toxicity [44]. This underlines the importance of using direct contact ecotoxicity tests to estimate the potential environmental impacts.

Taking into account the higher concentrations of Al, Ce, Cr, Fe, Mn, Ni, Sc, Th and U in NFR compared to NFP (and also increased toxicity of NFR compared to NFP due to higher element content) highlights our finding that arNF is a key technology for recovery, especially in the case of Sc. Scandium can be found in the retentate (NFR) that serves as an input material flow for further technology processes of Sc purification, while NFP (the 'waste stream' of the arNF technology process) was found to be the less toxic sample of all those tested during the complete technology process. It has to be noted that with regard to Sc recovery technologies based on solvent extraction and ion exchange, metal concentrations in strip liquors and raffinates are virtually the same, as these processes are tailored to extract mainly targeted metals. Although these recovery technologies are successful in the case of the selective recovery of a target component from the original waste, no significant toxicity attenuation can be expected in the final waste by the use of the technology itself. For the elemental composition of NF and a solvent extraction process, please refer to the previous results of Hedwig et al. [27].

Comparing the effect of samples from the consecutive filtration steps of the applied filtration technology, a significant decrease in the toxic effect was revealed in the cases of all three test organisms at different trophic levels (Fig. 2), despite the different sensitivity to the tested samples based on the effective concentration values. Contrary to this finding, a former study on the toxicity removal efficiency of a highly hydrophilic NF membrane found increased toxicity of the post-filtration (permeate) samples compared to pre-filtration samples (retentate) of industrial wastewaters containing several types of organic compounds (based on *A. fischeri* light emission [74]. The most sensitive test organism was found to be *A. fischeri*, followed by *L. minor* and *D. magna.* Considering that 20% inhibition was achieved after a relatively short exposure time (30 min), the *A. fischeri* bioluminescence inhibition assay may be recommended as a general screening method for samples of similar composition and with aggregated toxicity effects. In addition, the *A. fischeri* tests have the following advantages: (i) they are more robust than eukaryotic systems, (ii) require much shorter exposure times, therefore it is time- and cost-effective for general industrial application (iii) can be automated, standardised and well validated [75]. These arguments also support their choice of initial screening for the detection of highly toxic samples in the first stage of the test strategy [76].

3.3. Ecotoxicity toolkit for toxicity characterisation of samples from acid-resistant nanofiltration technology

During the ecotoxicity assessment, samples from various steps of the recovery process were tested with all three test organisms under various test conditions. The reason for varying the test conditions was to enable the selection of results from a variety of test conditions for each test organism and thus provide the most diverse assessment outcomes. These selected test conditions (one for each organism) were then used to evaluate the ecotoxicity impact of the filtration process. Two approaches were considered to find these test conditions: correlation analysis and cluster analysis. We assumed that the endpoints that correlated least with each other provided the most diverse assessment outcomes. The same question was also explored through cluster analysis, and the various assay protocols were compared through hierarchical clustering. Again, EC_{20} and EC_{50} values were analyzed separately.

poPairwise Pearson correlation coefficients of EC values were calculated and visualised with correlation plots (Fig. 3). The most diverse assessment outcomes were provided by the endpoints that correlated the least with each other. The correlation plots highlight

that some methods produced similar results, while for others, the correlation was quite low.

According to the correlation plots, the sets of test conditions that provided the most diverse outcomes for both EC_{20} and EC_{50} assessments were the ones in which *A. fischeri* bioluminescence inhibition was measured after 30 min and the frond number instead of chlorophyll content was measured in the *L. minor* growth inhibition assay. Fig. 3 shows that the correlations between the *D. magna* immobilisation assays and the other toxicity endpoints were very similar for all three *D. magna* exposure times. Therefore, to minimise the overall turnaround time for a prospective standardised procedure, the immobilisation assay applying the lowest exposure time was selected for further investigation.

Selecting toxicity tests (one for each organism) that correlate the least with each other may be based on hierarchical clustering. Test protocols that produce similar EC_{20} and EC_{50} test results should cluster close to each other, while test protocols that behave differently should be more separated. This can be captured by clustering test protocols based on their normalised Euclidean distances (where the elements of each vector are all the EC_{20} or EC_{50} dilution factors calculated within each test protocol; these elements are normalised such that each normalised vector will have a length of one). Dendrograms for EC_{20} and EC_{50} are shown in Fig. 4. Based on the results, the most diverse assessment outcomes for toxicity characterisation were provided by the following endpoints that correlated the least with each other: *A. fischeri* bioluminescence inhibition (30 min exposure), *D. magna* lethality and immobilisation (24 h exposure) and *L. minor* growth inhibition with the determination of the frond number (7 d exposure).

### 3.4. Ecotoxicity of arNF permeates

Based on the results of the selected methods and the exposure times of the recommended ecotoxicity toolkit (Section 3.3), the efficiency of the applied acid-resistant filtration technology was assessed in terms of toxicity attenuation.

According to the relative toxicity of the samples from different filtration steps compared to the technology input material (LAW) (Fig. 5), in terms of EC_{20} values, the consecutive steps of ultrafiltration and nanofiltration lowered toxicity by 23% and 96%, respectively, as determined by the *A. fischeri* bioluminescence inhibition assay.

According to the *D. magna* and *L. minor* tests, the rates of toxicity attenuation were 68% and 96%, and 95% and 99%, respectively. All values of toxicity attenuation were statistically significant in the case of EC_{20}. In terms of EC_{50}, the *L. minor* frond number endpoint showed similar results to EC_{20}, while the *A. fischeri* and *D. magna* assays showed nearly the same rate of toxicity attenuation after nanofiltration in terms of EC_{50} and EC_{20}. Based on these results, the consecutive steps of the different filtration methods resulted in high and statistically significant toxicity attenuation according to each test organism, which also means that these wastes and intermediate products are getting safer to handle from an environmental perspective. The selected ecotoxicity test methods also proved to be feasible for the environmental efficiency characterisation of the arNF technology process of TiO_2 production liquid waste.

3.5. Dependence of toxicity on pH sample in different filtration steps

The relationship between the pH values determined in the assembled test systems and the inhibition percentage (%) values are
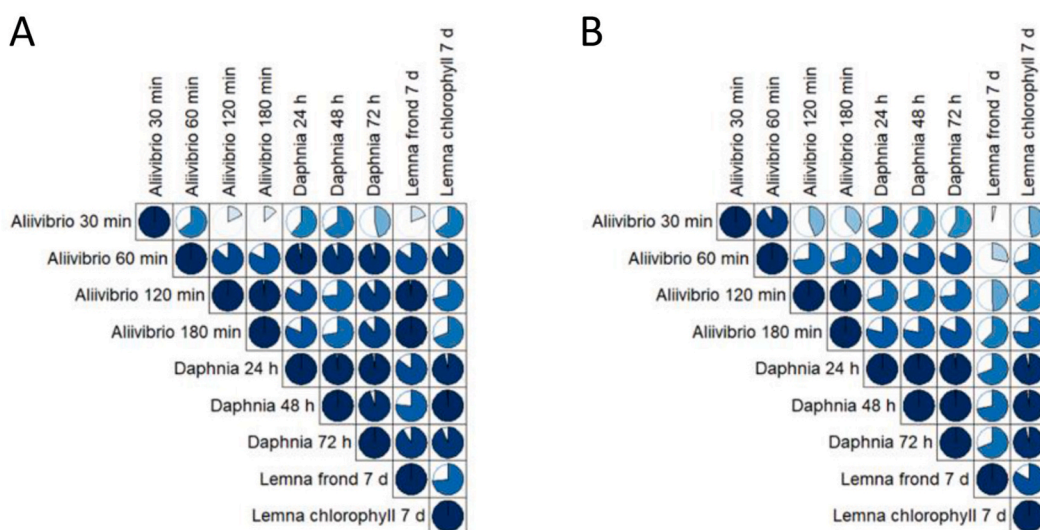

Fig. 3. Pearson correlation between EC_{20} (A) and EC_{50} (B) test results with *A. fischeri*, *D. magna* and *L. minor* at various exposure times (30, 60, 120 and 180 min for *A. fischeri* and 24, 48 and 72 h for *D. magna*) and measurands (frond and chlorophyll for *L. minor*). Each correlation is represented by a pie chart that is lighter and less saturated when the correlation is low and is darker and more saturated when the correlation is high. All correlations within the figures are positive. Correlation values are summarised in detail in Table S.3. The figure was prepared in R 4.0.3 and corrplot 0.84.
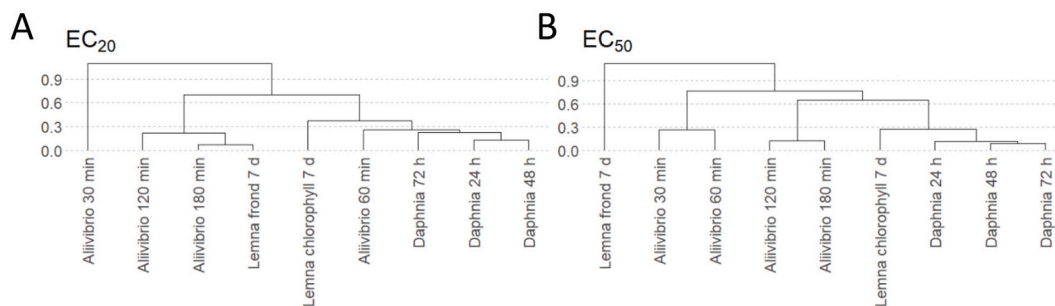
Fig. 4. Eucledian distances between EC_{20} (A) and EC_{50} (B) measurement results, with *A. fischeri, D. magna* and *L. minor* at various exposure times (30, 60, 120 and 180 min for *A. fischeri* and 24, 48 and 72 h for *D. magna*) and measurands (frond and chlorophyll for *L. minor*). The test methods that are clustered together on the dendrogram produced similar results.
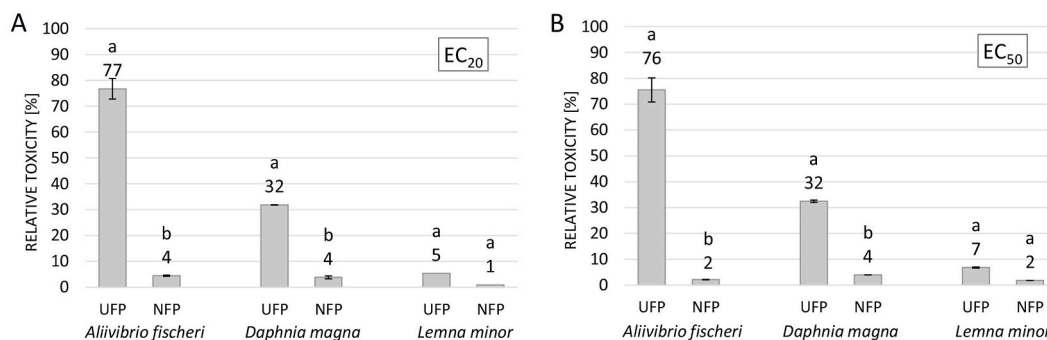

Fig. 5. Toxicity attenuation calculated based on EC_{20} (A) and EC_{50} (B) values in the case of the selected ecotoxicity methods with *A. fischeri, D. magna* and *L. minor* at selected exposure times. Relative toxicity was calculated by dividing the dilution factor corresponding to the EC_{20} value of a sample from a particular filtration step by the dilution factor corresponding to the EC_{20} value of the initial LAW sample (e.g. y = 50%, when the dilution factor required for 20% inhibition is halved). Significant toxicity attenuation after different filtration steps are marked by lowercase letters.

visualised in Fig. 6. The tolerable pH range for the growth limit is marked by an orange background in the case of each test organism. Based on literature data, the lower and upper pH growth limits for *A. fischeri* were 6.0 and 10.0 [77], for *D. magna* the pH growth limits were 4.66 and 10.13 [78] and for *L. minor* these were 4.0 and 10.0 [79]. Since the DTA approach was applied, the relationship between element content and inhibition rate was not investigated. The inhibition percentage values determined in our experiments represent the aggregated toxic effects of pH and toxic element content. Furthermore, during preliminary experiments, several attempts were made to adjust the pH of the original samples according to current guidelines [47], however, the pH adjustment of the samples proved to be an impasse, as the dissolved element content was immediately precipitated and sedimented and the toxicity testing became impracticable.

The results showed that, in the case of the *A. fischeri* bioluminescence inhibition assay, the pH of the tested dilutions of the samples from different filtration steps fell within the tolerable pH range of the test organism. Therefore, it can be assumed that the measured aggregated effect may be attributed mainly to the toxic element content, resulting in a dose-response-like curve for the tested dilution series of the samples. In the case of the *L. minor*, the pH values of the most concentrated dilution members fall out of the tolerable pH according to the literature data; thus, the adverse effect of extreme pH and toxic element content cannot be separated so clearly. With a pH above 7, a slight increase in sample toxicity was experienced, despite what we would expect to be a further decline and then disappearance, which may be due to the modified bioavailability of toxic elements in a slightly alkaline medium. The *D. magna* also showed a dose-response-curve-like pattern within a good tolerance pH range. In summary, if the pH is very different from the tolerable range and the inhibition is high, it can be assumed that the extreme pH itself is a driving factor for the detected inhibition, while within a good tolerance range, the toxic element content is probably the driving factor.

3.6. Our results reflecting on 'state-of-the art' recommendations for waste toxicity characterisation

Since 1998, there has been a progressive convergence of applied ecotoxicological test methods used for waste characterisation; however, important parameters of the tests are frequently modified or, if necessary, adapted to the waste type. The most frequently proposed test organisms for the characterisation of liquid wastes or leachates are *A. fischeri, Pseudokirchneriella* sp. and *D. magna* [43]. Our results support the choice of two of these test organisms: *A. fischeri* and *D. magna*. In our study, a different plant was chosen as the representative primary producer because precipitation was observed due to the modified pH in the algal test medium. This
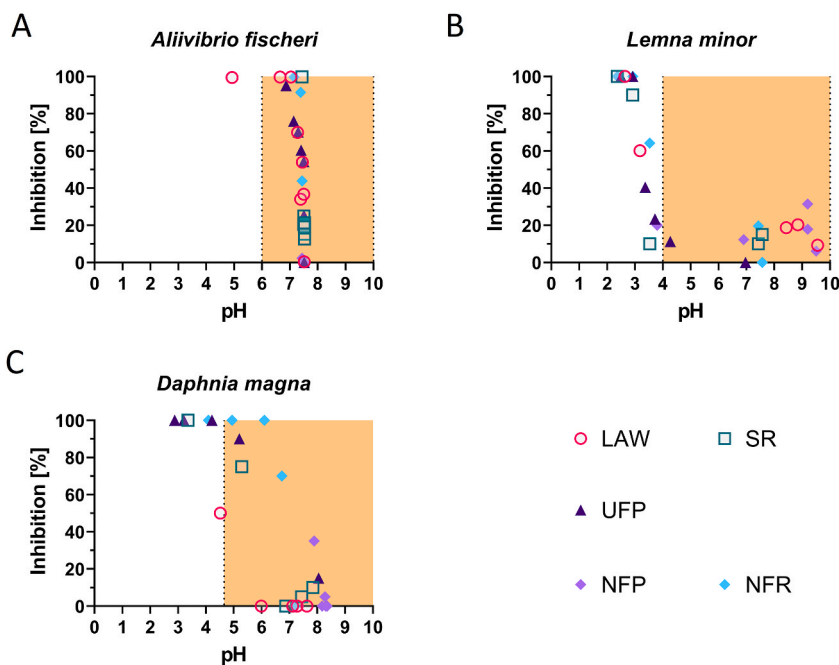
Fig. 6. Toxicity and pH of different arNF filtration steps in the case of *A. fischeri* (A), *L. minor* (B) and *D. magna* (C). The tolerable pH range for growth limits for the test organisms is marked by the orange background. Sample abbreviations: LAW - Liquid acid waste, UFP – Ultrafiltration permeate, NFP – Nanofiltration permeate, NFR – Nanofiltration retentate, SR – Solid residue of ultrafiltration.

phenomenon disturbed the spectrophotometric detection of algal cell density in the samples using the high-throughput microtitration plate method during preliminary experiments. It was decided to select the freshwater macrophyte *L. minor*, representing aquatic plant organisms, with an existing OECD test protocol instead of unicellular green algae, therefore, we recommend applying the *L. minor* growth inhibition test in the case of precipitation problems.

Proposing a strategy for the routine classification of waste, Hennebert [43] analyzed data from current literature, finding that the most sensitive test methods apply the following test species, *Pseudokirchneriella* sp.*, A. fischeri, Brassica* sp.*, D. magna, Eisenia fetida* and *Arthrobacter* sp.*, in detecting any possible toxic effect successfully. Choosing a test method is often based on cost and time efficiency [43]. Since *A. fischeri* bioluminescence is cost- and time-effective and high-throughput, it can be used in routine assessments in a stepwise approach for hazardous waste detection, while avoiding a whole battery of tests. Based on our results, we recommend the *A. fischeri* bioluminescence assay as a general screening method with 30-min exposuretime as an initial level of a tiered ecotoxicity characterisation. Therefore, if the bioluminescence inhibition assay detected any toxicity, all components of the recommended test battery could be applied for testing.

Authors prefer endpoints where results are not correlated to cover all aspects of ecotoxicity in order to provide sufficient information on the environmental hazard of the tested waste [80]. To explore the relationship between the results of the applied test endpoints, we calculated the pairwise correlation coefficients of EC values and visualised these with correlation plots to select the most diverse assessment outcomes provided by the endpoints that correlated the least with each other. We found that the combination of the (i) *A. fischeri* bioluminescence inhibition with 30 min exposure time, (ii) the frond number determined for *L. minor* growth inhibition assay and the (iii) *D. magna* immobilisation assay could be a feasible ecotoxicity toolkit covering many aspects of possible toxic effects; therefore, these methods were recommended for a prospective standardised procedure.

The United States Environmental Protection Agency (US EPA) also recommends a chemical data-based Toxicity Characteristic Leaching Procedure (TCLP), which is a chemical analysis process used to determine whether there are hazardous elements present in a waste [81]. TCLP was applied by some authors [82–84] for TiO_2 pigment production waste characterisation. Contreras et al. [83] reported that according to the TCLP limits set by US EPA, the leached metal values were clearly lower than the limits imposed by US EPA [85]. As the metal concentrations were below the TCLP toxicity limits, the general conclusion drawn was that the tested waste would not have a significant impact when this material was released into the environment without assessing the potential aggregated toxic effects of all known contaminants for realistic ecotoxicity characterisation. Therefore, in our opinion, regardless of ecotoxicity characterisation, the outcomes from the TCLP method would result in an unrealistic assessment, although ecotoxicity testing could be used for more realistic waste hazardousness classification.

Currently, based on EU regulation, a waste is declared ecotoxic according to a calculation method based on its chemical composition [37]. In addition, each Member State is allowed to establish a specific experimental procedure that adds to the problem resulting in a fragmented legal framework [86]. Although the characterisation of the chemical composition of the tested samples from the arNF technology was carried out, only the results of the ecotoxicological studies were taken into consideration for toxicity assessment and

environmental efficiency characterisation. The total element concentration would lead to an overestimation of the ecotoxicity of wastes [87] since it did not consider that only a fraction might be bioavailable, contributing to the actual ecotoxic effect [44,88]. In addition, Decision 2014/955/EU (amending Decision 2000/532/EC on the list of wastes) stipulates that experimental test results will prevail over the results of calculations.

The Technical Committee for the Characterisation of Waste within the European Committee for Standardization published the EN 14735 guideline [47], describing the necessary steps to be performed before carrying out ecotoxicity tests on wastes and their eluates. Furthermore, it provides information about the application of several aquatic and terrestrial tests on wastes but without proposing a relevant test battery to assess their ecotoxicity. Pandard and Römbke [46] developed a proposal for a 'harmonised' strategy, defining the legal requirements for the ecotoxicological classification of wastes. The strategy for the assessment of HP14 property is based on a combination of two approaches: the summation of classified compounds in the waste, carried out according to the regulation on CLP [37] of substances and mixtures and the usage of the results of biotests performed on waste eluates and solid wastes. According to the strategy, if sufficient data (e.g. EC_{50}s, LC_{50}s, NOECs and M-factors) on the individual components of the waste are available, it is not necessary to perform biological tests since the waste can be classified based on its composition (CLP). However, it is often difficult to identify all components in complex and heterogeneous waste matrices; reference values are available only for a limited number of chemicals, and the summation method does not take into account the bioavailable fraction of contaminants [46,89]. Thus, ecotoxicity tests are necessary.

Based on our results and experience with the ecotoxicity testing of wastes (red mud, fly ash, waste-derived biochars, transformer oil-contaminated soil and groundwater, soil contaminated with mazout, Zn, Cd, Pb contaminated soils and mine wastes, groundwater contaminated with chlorinated aliphatic hydrocarbons, etc.) [44,58,90–95] and considering the reported, diverse challenges (in-homogeneity, phase-separation, extreme pH, precipitation of contaminants due to pH adjustment) [41,89] that often arise during the testing of complex waste samples of varying physico-chemical characteristics, in our opinion, the use of a routine ecotoxicity char-acterisation approach of wastes should not be proposed in terms of the strict restrictions on the applied test methods. Instead, the use of a set of generally sensitive, high-throughput and time- and cost-effective ecotoxicity methods could be more straightforward and efficient, with specific recommendations for the most appropriate assays to test a particular waste sample. The main guidelines should be that it should (i) cover at least three different trophic levels; (ii) use at least one bacterial, one animal and one primary producer test organism; (iii) not apply pre-treatment (pH adjustment and filtration) on the original waste samples that may modify the bioavail-ability of the toxic elements occurring in the sample, since the initial pH adjustment and the consecutive filtration stages as part of the Sc recovery technology significantly decreased the toxicity of the original acid waste (LAW) of TiO_2 production; and that (iv) a chemical analysis should always be performed but should not be taken as the sole basis of classification of ecotoxicity.

In summary, our results draw attention to the need for a test battery of harmonised experimental approaches for the ecotoxicity assessment of different kinds of wastes, as there is still no agreement at European Union level [86]. Our research also describes se-lection process of the parameter settings of the finally applied ecotoxicity experimental methods, which approach can be adapted to a suite of ecotoxicological methods for characterising wastes from other processes. The ecotoxicity test battery established in this paper supports the comprehensive characterization of wastes and intermediate products with similar characteristics to the TiO_2 production waste and technology-generated byproducts. This has considerable importance since false risk and hazard classification of a particular waste can lead to inappropriately determined environmental and human health risks, not to mention financial consequences for waste owners. Our ecotoxicological results also highlight the environmental advantages of the NF-based Sc recovery technology over traditionally applied solvent extraction-based technologies without generating additional technology waste streams.

Considering the importance of Life Cycle Assessment (LCA) in identifying the most suitable pathway for a particular product with the lowest environmental burden, our results of ecotoxicity assessment may help in assessing the effect of the input and output pa-rameters associated with the particular product and the accompanying technology for the long-term sustainability of energy sources, human health, climate and biodiversity.

4. Conclusions

We carried out the ecotoxicological characterisation of different intermediate and final wastes and the products of a laboratory-scale technological experiment. Our aim was to assess the feasibility and environmental efficiency of arNF for the treatment of acidic waste of TiO_2 production with the ultimate intention to suggest a conventional and scientifically sound procedure for the ecotoxicity assessment of similar wastes. From an environmental efficiency point of view, the consecutive steps of the three filtration methods resulted in high and statistically significant toxicity attenuation according to the selected experimental setups of each test organism, which beneficially implicated waste handling and deposition. According to the thorough ecotoxicity assessment of the applied arNF technology for Sc recovery, we consider it justified that it could be an environmentally effective aspiration towards waste valorisation with the production of Sc, a critical raw material with great future potential.

Evaluating the established problem-specific ecotoxicity test battery, the most diverse assessment outcomes for toxicity charac-terisation of the intermediate and final wastes and products of a laboratory-scale arNF were provided by the following endpoints that correlated the least with each other: the *A fischeri* bioluminescence inhibition (30 min exposure), the *D. magna* lethality and immo-bilisation (24 h exposure) and the *L. minor* growth inhibition with the determination of the frond number (7 d exposure). These three selected test methods are simple, time- and cost-effective for general industrial applications to determine effective concentration values for realistic waste hazard classification and may serve as input data for Life Cycle Assessment. The high-throughput, time- and cost-effective *A. fischeri* bioluminescence inhibition assay may be used as a general screening method for a tiered toxicity assessment of wastes with similar characteristics to the samples from arNF technology. The determination of the frond number and the total

chlorophyll content of the aquatic macrophyte *L. minor* proved to be a sensitive test endpoint for the characterisation of the aggregated effects of the toxic element content and extreme pH of the complex waste samples. Therefore, it is recommended that this method be included in the official list of current DTA protocols. The pH adjustment or filtration of the initial liquid waste samples and eluates should be avoided to eliminate the possible modification of the original sample characteristics and hence the bioavailability of the toxic elements. Our findings demonstrate the priority of ecotoxicological waste characterisation to chemical-data-oriented hazard classification. Stakeholders and waste owners may benefit by avoiding unwanted financial consequences.

Credit author statement

Ildikó Fekete-Kertész: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Tamás Stirling: Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Emese Vaszita: Wrote the paper.

Zsófia Berkl: Analyzed and interpreted the data.

Éva Farkas: Analyzed and interpreted the data.

Sebastian Hedwig: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

Kirsten Remmen: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data.

Markus Lenz: Conceived and designed the experiments; Analyzed and interpreted the data; Wrote the paper.

Mónika Molnár: Conceived and designed the experiments.

Viktória Feigl: Conceived and designed the experiments; Analyzed and interpreted the data; Wrote the paper.

Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.heliyon.2023.e15512.

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