Dealing with Lead in Hybrid Perovskite: a Challenge to Tackle for a Bright Future of This Technology ?

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Hybrid Perovskites (HPs) semiconductors have been skyrocketing the field of new generation photovoltaics and immediately expanding into advanced optoelectronics. Perovskite photovoltaics (PV) can give a tremendous push to the energy transition, which however calls for efficient, low cost, but also environmentally friendly game changer solutions. Halide Perovskites present the serious drawback related to the presence of toxic materials, i.e. lead, with the associated health and environment concerns that severely hamper their commercialization. So far, only a few viable alternatives to Pb have been found, which however lag behind in terms of power conversion efficiency. Here, a forward-looking perspective is developed presenting different potential strategies to overcome the environmental and health issues related to the use and release of lead for operative HP solar cells. The possible lead-leakages paths and related "remediation" tools are reviewed and possible strategies are put together to face a new era of lead containing HP devices. Finally, through a comparison with existing Lead-based technology, a comparative study is presented to provide the tools nowadays essential for a real evaluation of the impact of lead content to HP commercialization.

1. Introduction

The recent energy demand projections of the International Energy Agency (IEA) predict a growth of more than 25% by 2040 induced concomitantly by demographic growth and the urbanization.[1] According to IEA, the global electricity demand should increase at least of 60% due to the increased electricity market in a near future (e.g. predominance of electric cars on the market, development of internet of things). In the context of the global warming and in the frame of the 2015 Paris agreement, this inexorable growing energy demand must be fulfilled by sustainable sources of electricity, cheap enough to maintain industrial activities and people lifestyle and in sufficient quantity. Solar energy meets these criteria. Earth receives in one hour 174 PW which equals more than one year of worldwide energy consumption.[2,3] A great potential has been indeed recently foreseen for photovoltaics (PVs), considered the mainstream technology for the next five years by recent IEA report. In particular, PVs increased of 31% in 2018, showing the largest absolute generation growth (+136 TWh) of all renewables being on track to reach the Sustainable Development Scenario (SDS) level by 2030, which will require electricity generation from solar to increase 16% annually. Silicon PV is the leader of this segment. However, their fabrication is energy-intensive and generates CO_2 emissions as well as harmful chemical wastes (e.g. $SiCl_4$ leading to additional process and recycling costs estimated at 84 500 \$/ton).[4] To face the growing energy demand and push a new solution for green energy generation, a paradigm shift to a new portable, flexible, adaptable and low-cost thin film PV technology is needed. Recently, a new class of materials called Hybrid Perovskites (HPs) has emerged beating all expectations in the field of PVs. The typical structure of this family of materials is represented by the methylammonium lead iodide, $CH_3NH_3PbI_3$, one of the most emblematic HPs. The crystalline structure is defined by a three-dimensional (3D) organic-inorganic network of formula ABX_3 where A is an organic cation located at the center of the unit cell (e.g. $CH_3NH_3^+$), B a metal cation (e.g. Pb^{2+}, Sn^{2+}) and X a halide anion (e.g. Br^-, I^-). The astonishing evolution of the light conversion efficiency of HPs (PV cells) made them

one of the trendiest materials of early 21st century and keeps stimulating the scientific and industrial community. Over the last 10 years, HP-based PV cells have seen their conversion efficiency growing from 4 to 25% while those made of silicon required 60 years to reach similar results (from 4 to 29% of PV cell efficiency).[5,6] Furthermore, eco-friendly and cheap HP synthesis and PV processing are other seducing aspects that can overshadow the silicon technology. However, their commercialization is currently hampered because of their relatively low stability (upon moisture, air, UV light and moderate temperature) and the potential presence of toxic heavy metals (e.g. Pb) which can be released into nature during the degradation process.[7] While assessing the stability issue is deeply studied in the HP research community, showing interesting solutions to improve material resistance by proper material and interface engineering,[8] the latter has been less explored, despite the huge debate on it.

If the presence of toxic elements can, or not, impact the real widespread of the HP technology is nowadays question. Naturally, the two problems are strictly related: HP are unstable upon humidity and oxygen exposure, leading to material irreversible degradation back into the initial precursors (e.g. PbI_2 colloids). The mechanism involves a multi-step process leading to first material hydration followed by the expulsion of PbI_2, while the organic cation ($CH_3NH_3^+$) decomposes into methylamine and hydroiodic acid.[9,10] The simultaneous presence of oxygen and UV light leads to the formation of strong oxidizer O_2^- reacting with the photoexcited HP. This phenomenon results in the formation of water, PbI_2, CH_3NH_2 and I_2. Importantly, also thermal stress affects dramatically HP integrity. At low temperatures, $CH_3NH_3PbI_3$ releases I_2 and metallic lead clusters appear already at 40°C.[11] At higher temperatures ranging from 80 to 85°C, methylammonium iodide decomposes into volatile compounds (e.g. CH_3I, NH_3).[12,13]

Lead is currently a major concern within the HP community because of its notorious detrimental impact on the environment and population health; a problem that represents a barrier to further PV cell industrial development. Lead is known to be one of the most toxic heavy elements present in the environment. Because of its non-biodegradable nature, this metal persists in the

soil and accumulates increasing hazards. A recent study showed that the lead from methylammonium lead iodide degradation is ten times more efficiently absorbed by plants than other sources of lead (e.g. PbI_2) due in part, to the presence of the organic cation.[14] On the other side, the effects of acute and chronic Pb poisoning are well understood and documented: its assimilation in the body affects almost every organ. Pb compounds enter the soft tissues (liver, kidneys, etc.) through the bloodstream, interfering in the functions of enzymes and receptors by mimicking essential elements such as Ca, Zn and Fe. It eventually deposits into the bones as lead phosphate with a half-life of 20-30 years. Pb poisoning can also cause anemia, blood pressure increase, severe damage to the kidneys and neurological disorders (decreased intelligence and behavioural problems) upon exposure to values of 5 µg/dl or lower.[15–17]

Considering the release of lead during the HP degradation process, a tremendous effort from the scientific community has been focused on strategies to replace lead by Bi, Ge, Sb, In and Sn.[18,19] Despite the numerous studies already reported, efficiency still lag behind the conventional lead-based perovskite solar cells. It is to note that tin has been considered as an alternative candidate and because it is located in the same column of the periodic table as lead, has attracted great attention of researchers for its favorable electronic properties.[20] The effects of Sn are less established: acute toxicity is documented, whereas long-term effects such as neurotoxicity and carcinogenicity are still under debate.[21] However, B. Conings et al. have recently estimated the LC_{50} (Lethal Concentration for 50% of the population) at 0.09 and 0.83 mM for SnI_2 and PbI_2 respectively and demonstrated the higher toxicity of tin over lead due to increased acidification by formation of HI.[22] This result calls into question the advantages of Sn-based perovskites in terms of toxicity and environmentally safety highlighting the great difficulty to choose suitable metals and material composition to synthesize high-performance lead-free HPs.[23]

This turns into the question: if we consider that HP solar cells need lead to function, which strategies can be adopted to reduce the amount of the released lead? How effective should they be to foresee a possible implementation of lead-based solar cell in the market?

Here, we intend to put in perspective original alternatives to the issue of lead on current technologies already applied to technologies incorporating heavy metals. For the sake of clarity, the techniques for lead removal are firstly presented with the aim of collecting fragmented information which are available in different fields of research. Details on alternatives to the issue related to the lead removal from soil and water are then discussed in detail. These latter are then adapted and extended to HP PV systems. Finally, we criticize these methods as a function of the field reality followed by a perspective concerning lead issue for commercialization potential.

2. Current technologies for lead removal

2.1. Lead in soil: Remediation tools

Due to anthropogenic activities (utilization of pesticides and fertilizers, mining, combustion of fossil fuel), heavy metals are accumulating over time in the soil. In order to solve the contamination problem, different strategies have been put in place integrating remediation technologies. They may be classified as being based on physical, chemical or biological methods.

2.1.1. Physical remediation

Sanitizing or stopping the contamination of the soil can be carried out through physical remediation which encompasses different techniques such as soil replacement, isolation and thermal treatment **(Figure 1)**.[24] Soil replacement consists in mixing the polluted soil or recovering its surface with clean soil leading to the dilution of the heavy metals in the medium. To avoid the spread of the contamination, the area to contain can be isolated. This can be

achieved through the installation of barrier walls made of impermeable materials (e.g. cement, steel) preventing the pollutants from entering the groundwater.[25] The removal of heavy metals can also be carried out through thermal treatment. This latter consists in heating the subsurface to evaporate the contaminant. This involves different technologies such as electrical resistive heating, conductive heating and radio-frequency heating.[26] However, their use usually affects greatly the soil in terms of mineralogical composition and physicochemical properties.

2.1.2. Chemical remediation

The chemical remediation technologies involve in using chemical reactants to remove contaminants and include solidification/stabilization, vitrification, soil flushing/washing, and electrokinetics **(Figure 1)**.[25] Solidification/stabilization is composed of two steps, the physical encapsulation within a matrix (e.g. cement, asphalt, bitumen) followed by chemical reactions with the contaminant to reduce its mobility. For instance, bonemeal ($Ca_{10}(PO_4)_6(OH)_2$) can react with heavy metals to form metal phosphates with low mobility and bioavailability.[27] Vitrification implies to disperse glass precursors into the soil.[24,28] Then, the mixture is heated to a temperature ranging from 1400-2000°C leading to the formation of amorphous glass trapping in that way lead. The soil flushing/washing method relies on the removal of heavy metals with water[29] or solutions containing either saponin,[30] organic acids,[31] surfactants[32] or chelating agents.[33] EthyleneDiamineTetracetic Acid (EDTA) is an additive of choice due to its biocompatibility and its capture efficiency.[34] During the process, EDTA forms a complex with the metal helping its extraction and is then evacuated through a dynamical solution stream.[35] The decontamination is also possible by applying an electrical current, a process called electrokinetic remediation which includes electromigration, electroosmosis, electrophoresis and electrolysis.[36,37] This technique is also associated to the use of chelating agent to enhance the process efficiency.

2.1.3. Biological remediation

This type of remediation is based on the exploitation of the inherent capture properties of bioorganisms such as plants, bacteria, fungi, algae and enzymes **(Figure 1)**.[38] This strategy ensures the eco-friendly aspect of the technique and counter to physical and chemical remediations, is cost-effective. Phytoremediation is a branch of bioremediation concerning plants only **(Figure 1)**.[39] They can act in different ways such as absorbing heavy metals from soil and storing within the roots (phytoextraction)[40] or sequestrating them through a filtration process (phytofiltration).[39] The contaminants can also see their mobility and bioavailability reduced in the environment in the presence of plants (phytostabilization)[41] or in some cases, they can be first absorbed and then converted into their volatile forms (phytovolatilization).[39] The last possible process concerns the transformation of the heavy metals by integrating them into the plant metabolic process (phytodegradation).[39]

2.2. Lead in Water: Remediation tools

The contamination of water is nowadays a great concern causing the deprivation of drinkable water to about 1.2 billion of people. In the frame of this issue, different techniques were developed at large scale including precipitation, coagulation-flocculation, ionic exchange, adsorption and membrane separation **(Figure 2)**.[42]

2.2.1. Precipitation

This technique relies on the conversion of heavy metal ions into insoluble salts (e.g. hydroxide, carbonate, sulfide or phosphate) followed by their removal after sedimentation **(Figure 2a)**.[43] Simple and inexpensive, precipitation process is widely used but often requires additional treatments for complete decontamination. The common reagents leading to the precipitation are for instance, alkaline compounds commercially available industrially (lime or caustic soda), sulfides (hydrogen sulfide, sodium sulfide or ferrous sulfide) or carbonates (calcium carbonate or carbon dioxide). In specific conditions, it has been showed that the maximum Pb removal

efficiency through chemical precipitation induced by $Ca(OH)_2$ may reach 99.42%.[44] It is to note that organic precipitating agents designed for soft metal cations can also be used such as sodium dimethyldithiocarbamate and sodium thiocarbonate. In the case of 1,3-benzenediamidoethanethiol dianion, 99.4% of Pb was removed from a solution with a lead concentration of 3.61 ppm within 15 min for a stoichiometric molar ratio of 1:1.[45]

2.2.2. Coagulation-flocculation

This process aims to induce the destabilization of aggregates through their electrical neutralization and generally involves the use of ferric and aluminum salts **(Figure 2b)**. Coagulation consists in adding positively charged additives to reduce the surface negative charges of particles. Then, the flocculation is triggered by introducing anionic flocculant interacting with the positively charged aggregates to form bigger systems more easily to separate by filtration.[46] It is to note that in general, this process cannot remove entirely the heavy metal in wastewaters and therefore, requires additional treatment techniques.

2.2.3. Ionic exchange

The removal of heavy metals through ionic exchange process involves the use of solid ion exchange resin bearing for instance, functional groups ($-COOH$, $-SO_3H$) which can complex the metal cations after deprotonation **(Figure 2c)**.[47,48] The process ends with the separation of the resin from the solution followed possibly by its regeneration.[49] A plethora of examples can be found in literature.[50] For instance, the resin Purolite C100E can remove ≥90% of Pb from water, releasing at the same time Ca cations.[51] The regeneration is then possible with a solution of $Ca(NO_3)_2$. This method is particularly interesting for the reuse of the heavy metals and therefore their recycling.

2.2.4. Adsorption

The heavy metals can also be trapped by adsorbents endowed with high porosity, active sites and functional groups **(Figure 2d)**.[52] One of the main factors to take into account is the specific surface area. Therefore, the materials are generally designed in order to exhibit high surface/volume. An arsenal of adsorbents are industrially available including activated carbons,[53] zeolites[54] and metal oxides[55] and more recently carbon nanotubes (CNTs)[56] and graphene oxides (GOs)[57] have been considered as excellent candidates for the selective and efficient capture of heavy metals. Activated carbons may be prepared through calcination process from agricultural wastes (e.g. coconut tree banana pith).[58] They are generally inexpensive and proved, thanks to the presence of functional groups, their abilities to adsorb various contaminants (e.g. dyes and metal ions).[59] At 80°C and at optimum contact time of 60 min, activated carbon produced from African palm fruit showed efficient removal of toxic metals estimated at 99.235, 96.711, 95.35 and 97.750% for Cd, Cu, Ni and Pb respectively.[60] Zeolites (aluminosilicates minerals) are composed of SiO_4 and AlO_4 tetrahedra. The replacement of Si^{4+} with Al^{3+} induces the apparition of a negative charge in the lattice. This latter is compensated with a cation (e.g. Na, Ca, K) which can be replaced with others in solution such as Mn, Cd and Pb.[61] For instance, clinoptilolite, one of the most abundant natural zeolites adsorbs various heavy metals leading to a removal percentage estimated at 28, 32, 59, 75 and 99% for Ni, Cd, Zn, Cu and Pb respectively.[62] Metal oxide nanoparticles have the abilities to adsorb reasonably metal cations. Hematite (α-Fe_2O_3) nanoparticles, the most resistant iron oxide to corrosion, is capable of removing up to >99, 89, 94 and >99% of Zn, Cu, Cd and Pb present in water.[63] CNTs are an allotropic form of carbon forming cylindrical structure with an aromatic surface.[64] The pristine CNTs can be used for adsorption or can be functionalized either by grafting new functional groups or by oxidizing the material.[65] CNTs can show great Pb adsorption efficiency reaching nearly 100% at pH 7 but at lower pH values, this removal percentage decreases to 17 and 25% at pH 4 and 5 respectively caused by the gradual

protonation of the carboxylate groups grafted onto the CNT surface.[66] GOs are monolayer graphite oxides bearing epoxy, carboxyl and hydroxyl groups. This material exhibits a particularly strong affinity to metal ions following this trend: Pb > Cu >> Cd > Zn.[67] In addition to a strong selectivity, GOs exhibit an impressive maximal adsorption capacities estimated at 1119 mg.g^{-1} for Pb.

2.2.5. Membrane separation

Counter to the previous techniques for water decontamination, membrane separation is a one-step treatment process. This latter relies on the selective separation of heavy metals from water through a barrier **(Figure 2e)**. The main parameters to consider for the membranes are the pore size, surface charge, pore size distribution, hydrophobicity/hydrophilicity balance and functionalization. Various types of membrane technology may be integrated into the process such as ultrafiltration, dense and supported liquid membranes as well as electrodialysis.[68] For instance, poly-gamma-glutamic acid was used to treat water through ultrafiltration process and allowed removing more than 99.8% of Pb.[69] Reverse osmosis membrane is an example of dense membrane. For a mixture of different heavy metals in low concentration, this type of membrane allowed removing entirely Pb and Ni and partially Cr (89%) and Cu (49%).[70]

3. Challenges: Current Lead recovery strategies of potential interest for HP technology.

HP solar technology contains alkali metal lead and tin halides which have an environmental impact. The RoHS directive restricts the use of hazardous substances in electrical and electronic equipment and requires a possible reduction/substitution of heavy metals such as lead with safer alternatives. In particular, the risk of a Pb-washout from a damaged HP solar cell is high and proper encapsulation and remediation methods must be considered to mitigate potential leakage rate levels. The techniques already presented, used at large scale for the soil/water sanitizing or contamination reduction, can be potential source of inspiration and effective solutions for the

elaboration of new strategies to contain the deleterious effects of lead released by HP PV cells. The isolation of the lead source can be carried out through the deposition of impermeable barriers on the top of the material. Examples include polymers, glass or inert and biocompatible metal oxides **(Figure 3a)**. The membranes designed for the water treatment can also be exploited to concomitantly protect the HP PV cell from water (e.g. hydrophobicity) and selectively capture the released lead. Very recently, PD-10-DTTE-7, a hydrophobic conjugated polymer, was placed between the hybrid perovskite (MAPbI$_3$) and the hole transport layer (doped spiro-OMeTAD) to protect the PV cell from the action of water.[71] This additional layer provided concomitantly a greatly better stability in humid conditions but also higher power conversion efficiency (PCE) estimated at 18.83% (PCE without PD-10-DTTE-7 =17.51%). The covering of the top of the HP PV cell with a superhydrophobic polymer (Teflon) has also showed a great efficiency to protect HP. The initial PCE value only decreased of 5% after 30 days while in the case of the unprotected HP PV cell, this value dropped from 11.3 to 6.3% during the same period of time.[72] The in-situ stabilization of the formed lead can be achieved with additives such as chemicals reacting with this metal to form stable and insoluble compounds (e.g. phosphates, hydroxides, sulfates) or adsorbents to retain efficiently the metal (e.g. zeolites, graphene oxides, carbon nanotubes). These latter can be improved by combining them with chelating agents (e.g. EDTA). Resins are also of great interest due to their commercial availability and well-known efficiency to retain lead within the system. As mentioned before, the by-products of the HP degradation may be cations (molecular level) or even colloids (nano/micro-scale level). In this last case, it might be considered to destabilize them through the neutralization of their surface charge with non-neutral electrical barrier (e.g. functionalized polymers). Biological materials can also be integrated to the device to prevent lead from going out. Enzymes with high affinity to this heavy metal can store it efficiently within a porous matrix. Different studies have already proved the compatibility between biological components and PV cells and therefore, this option deserves to be explored.[73]

Finally, as recently demonstrated, we can also develop identical recycling sector to this of lead-acid batteries for HP PV cells.[74] Each layer of PV cells can be isolated and be reused such as ITO glass (the most expensive component) but also PbI_2 generated during the degradation.

4. Future Direction and Strategies: Ecological Impact of Lead HP devices.

In this part, we focus on the necessary amount of lead for the electricity generated by HP PV cells, the degree of the potential lead contamination and the comparison with current lead-based technologies **(Figure 3b,c)**. For that purpose, we consider $CH_3NH_3PbI_3$ as HP for the elaboration of PV cells because of its notoriety and well-established high solar energy conversion efficiency. The amount of lead to generate 1 kWh has been estimated at 38 μg (considering HP layer thickness of 300 nm in PV cell and a PV plant lifetime of 25 years) which corresponds approximatively to 160 t/year to supply U.S. in electricity and 1000 t/year for the whole world.[75] In comparison, the amount of lead for electronic solder is estimated at 6200 t/year[76] and over 1 million t/year for the lead-acid batteries designed for automotive industry.[77] In this last case, lead is mainly recovered by recycling process. However, during this latter, more than 40 000 t/year of lead are released into the environment and additional 70 000 t/year of lead waste generated by lead mining and battery manufacturing.[77] Even considering the entire dissolution of $CH_3NH_3PbI_3$, the overall amount of released lead for the worldwide electricity demand is much lower than this related to current lead-based technologies (1000 t/year vs 110 000 t/year for HP PV cell and battery technology respectively). Another aspect to take into account is the local soil contamination and the law regulations related to this heavy metal. A recent study explored a scenario where HP PV cells are under rain.[78] Through the climatic simulation experiments, the lead concentration in the first centimeters of the soil layer below the HP PV cell has been estimated at about 70 ppm. Usually, lead concentrations range from < 10-30 ppm (clean soil) to 50-200 ppm and even more (urban soil).[78] Therefore, the lead contamination due to HP seems to be acceptable and the metal concentration tends to

decrease under rain which dilutes it in the soil leading to an average value of approximatively 20 ppm.[78] According to U.S. Environmental Protection Agency, the maximum level of lead concentration is set at 400 and 1200 ppm for bare soil in play areas and urban soil in non-play areas respectively.[79] However, it has been showed that to preserve 99% of people from an excess of lead blood concentration of 100 µg/L, the maximum tolerated lead concentration in soil should be below 300 ppm.[80] Therefore, in the worse scenario assuming the entire HP dissolution, the final lead concentration in soil matches widely with the recommended values.

5. Conclusions and Outlook

This Perspective has highlighted the issue related to the presence of toxic elements in HP solar cells and their potential release as current barrier to the market. Potential strategies to overcome this issue has been discussed in the frame of the existing know-how developed for current in market lead-containing technologies. In the context of a potential lead contamination, soil and water contamination and remediation effects have been reviewed. These latter can be adapted and extended to HP PV systems, providing technological solution and hints for researcher and technologists exploring the potential of HP commercialization thanks to a comparative study with existing know-how in current lead-based technologies.

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References

[1]   *World Energy Outlook 2018*, International Energy Agency (IEA), Paris, **2018**.

[2]   V. Smil, *General Energetics: Energy in the Biosphere and Civilization*, Wiley, New York, **1991**.

[3]   H. L. Zhang, J. Baeyens, J. Degrève, G. Cacères, *Renew. Sustain. Energy Rev.* **2013**, *22*, 466.

[4]   E. Kabir, P. Kumar, S. Kumar, A. A. Adelodun, K.-H. Kim, *Renew. Sustain. Energy Rev.* **2018**, *82*, 894.

[5]   J.-P. Correa-Baena, M. Saliba, T. Buonassisi, M. Grätzel, A. Abate, W. Tress, A. Hagfeldt, *Science* **2017**, *358*, 739.

[6]   G. Grancini, *Photoniques* **2019**, 24.

[7]   G. Schileo, G. Grancini, *J. Phys. Energy* **2020**, *2*, 021005.

[8]   Z. Yang, B. H. Babu, S. Wu, T. Liu, S. Fang, Z. Xiong, L. Han, W. Chen, *Sol. RRL* **2020**, *4*, 1900257.

[9]   J. Huang, S. Tan, P. D. Lund, H. Zhou, *Energy Environ. Sci.* **2017**, *10*, 2284.

[10]   J. Yang, B. D. Siempelkamp, D. Liu, T. L. Kelly, *ACS Nano* **2015**, *9*, 1955.

[11]   E. J. Juarez-Perez, L. K. Ono, M. Maeda, Y. Jiang, Z. Hawash, Y. Qi, *J. Mater. Chem. A* **2018**, *6*, 9604.

[12]   B. Conings, J. Drijkoningen, N. Gauquelin, A. Babayigit, J. D'Haen, L. D'Olieslaeger, A. Ethirajan, J. Verbeeck, J. Manca, E. Mosconi, F. D. Angelis, H.-G. Boyen, *Adv. Energy Mater.* **2015**, *5*, 1500477.

[13]   E. J. Juarez-Perez, Z. Hawash, S. R. Raga, L. K. Ono, Y. Qi, *Energy Environ. Sci.* **2016**, *9*, 3406.

[14]   J. Li, H.-L. Cao, W.-B. Jiao, Q. Wang, M. Wei, I. Cantone, J. Lü, A. Abate, *Nat. Commun.* **2020**, *11*, 310.

[15]   R. Rubin, D. S. Strayer, Eds. , *Rubin's Pathology: Clinicopathologic Foundations of Medicine*, Wolters Kluwer/Lippincott Williams & Wilkins, Philadelphia, **2008**.

[16]   R. Z. Sokol, N. Berman, *Toxicology* **1991**, *69*, 269.

[17]   A. L. Wani, A. Ara, J. A. Usmani, *Interdiscip. Toxicol.* **2015**, *8*, 55.

[18]   S. Ghosh, B. Pradhan, *ChemNanoMat* **2019**, *5*, 300.

[19]   E. Greul, M. L. Petrus, A. Binek, P. Docampo, T. Bein, *J. Mater. Chem. A* **2017**, *5*, 19972.

[20]   Q. Zhang, F. Hao, J. Li, Y. Zhou, Y. Wei, H. Lin, *Sci. Technol. Adv. Mater.* **2018**, *19*, 425.

[21]   A. Babayigit, A. Ethirajan, M. Muller, B. Conings, *Nat. Mater.* **2016**, *15*, 247.

[22]   A. Babayigit, D. Duy Thanh, A. Ethirajan, J. Manca, M. Muller, H.-G. Boyen, B. Conings, *Sci. Rep.* **2016**, *6*, DOI 10.1038/srep18721.

[23]   R. Kour, S. Arya, S. Verma, J. Gupta, P. Bandhoria, V. Bharti, R. Datt, V. Gupta, *Glob. Chall.* **2019**, *3*, 1900050.

[24]   Z. Yao, J. Li, H. Xie, C. Yu, *Procedia Environ. Sci.* **2012**, *16*, 722.

[25]   A. Jankaitë, S. Vasareviėius, *J. Environ. Eng. Landsc. Manag.* **2005**, 6.

[26]   B. Song, G. Zeng, J. Gong, J. Liang, P. Xu, Z. Liu, Y. Zhang, C. Zhang, M. Cheng, Y. Liu, S. Ye, H. Yi, X. Ren, *Environ. Int.* **2017**, *105*, 43.

[27]   M. E. Hodson, É. Valsami-Jones, J. D. Cotter-Howells, *Environ. Sci. Technol.* **2000**, *34*, 3501.

[28]   A. Navarro, *Minerals* **2012**, *2*, 473.

[29]   G. Dermont, M. Bergeron, G. Mercier, M. Richer-Laflèche, *J. Hazard. Mater.* **2008**, *152*, 1.

[30]   J. P. Maity, Y. M. Huang, C.-W. Fan, C.-C. Chen, C.-Y. Li, C.-M. Hsu, Y.-F. Chang, C.-I. Wu, C.-Y. Chen, J.-S. Jean, *J. Environ. Sci.* **2013**, *25*, 1180.

[31]   J.-O. Kim, Y.-W. Lee, J. Chung, *KSCE J. Civ. Eng.* **2013**, *17*, 1596.

[32]   X. Mao, R. Jiang, W. Xiao, J. Yu, *J. Hazard. Mater.* **2015**, *285*, 419.

[33]   W. Jiang, T. Tao, Z.-M. Liao, *Open J. Soil Sci.* **2011**, *01*, 70.

[34]   J. Qiao, H. Sun, X. Luo, W. Zhang, S. Mathews, X. Yin, *Chemosphere* **2017**, *167*, 422.

[35]   D. Leštan, C. Luo, X. Li, *Environ. Pollut.* **2008**, *153*, 3.

[36]   Q. Luo, X. Zhang, H. Wang, Y. Qian, *Chemosphere* **2005**, *59*, 1289.

[37]   D. Cabrera-Guzmán, J. T. Swartzbaugh, A. W. Weisman, *J. Air Waste Manag. Assoc.* **1990**, *40*, 1670.

[38]   M. Kapahi, S. Sachdeva, *J. Health Pollut.* **2019**, *9*, 191203.

[39]   A. Cristaldi, G. O. Conti, E. H. Jho, P. Zuccarello, A. Grasso, C. Copat, M. Ferrante, *Environ. Technol. Innov.* **2017**, *8*, 309.

[40]   A. Mahar, P. Wang, A. Ali, M. K. Awasthi, A. H. Lahori, Q. Wang, R. Li, Z. Zhang, *Ecotoxicol. Environ. Saf.* **2016**, *126*, 111.

[41]   S. Yang, B. Liao, Z. Yang, L. Chai, J. Li, *Sci. Total Environ.* **2016**, *562*, 427.

[42]   S. Bolisetty, M. Peydayesh, R. Mezzenga, *Chem. Soc. Rev.* **2019**, *48*, 463.

[43]   L. K. Wang, D. A. Vaccari, Y. Li, N. K. Shammas, in *Physicochem. Treat. Process.* (Eds.: L.K. Wang, Y.-T. Hung, N.K. Shammas), Humana Press, Totowa, NJ, **2005**, pp. 141–197.

[44]   D. Kavak, *Desalination Water Treat.* **2013**, *51*, 1720.

[45]   M. M. Matlock, B. S. Howerton, D. A. Atwood, *Ind. Eng. Chem. Res.* **2002**, *41*, 1579.

[46]   J. Bratby, *Coagulation and Flocculation in Water and Wastewater Treatment*, IWA Publ, London, **2006**.

[47]   Z. Hubicki, D. Koodynsk, in *Ion Exch. Technol.* (Ed.: A. Kilislioglu), InTech, **2012**.

[48]   R. A. Silva, K. Hawboldt, Y. Zhang, *Miner. Process. Extr. Metall. Rev.* **2018**, *39*, 395.

[49]   A. Azimi, A. Azari, M. Rezakazemi, M. Ansarpour, *ChemBioEng Rev.* **2017**, *4*, 37.

[50]   A. Dąbrowski, Z. Hubicki, P. Podkościelny, E. Robens, *Chemosphere* **2004**, *56*, 91.

[51] A. Lalmi, K.-E. Bouhidel, B. Sahraoui, C. el H. Anfif, *Hydrometallurgy* **2018**, *178*, 287.

[52] F. Fu, Q. Wang, *J. Environ. Manage.* **2011**, *92*, 407.

[53] R. M. Taylor, R. W. Kuennen, *Environ. Prog.* **1994**, *13*, 65.

[54] P. K. Pandey, S. K. Sharma, S. S. Sambi, *J. Environ. Chem. Eng.* **2015**, *3*, 2604.

[55] J. Yang, B. Hou, J. Wang, B. Tian, J. Bi, N. Wang, X. Li, X. Huang, *Nanomaterials* **2019**, *9*, 424.

[56] V. K. Gupta, O. Moradi, I. Tyagi, S. Agarwal, H. Sadegh, R. Shahryari-Ghoshekandi, A. S. H. Makhlouf, M. Goodarzi, A. Garshasbi, *Crit. Rev. Environ. Sci. Technol.* **2016**, *46*, 93.

[57] X. Liu, R. Ma, X. Wang, Y. Ma, Y. Yang, L. Zhuang, S. Zhang, R. Jehan, J. Chen, X. Wang, *Environ. Pollut.* **2019**, *252*, 62.

[58] K. Kadirvelu, M. Kavipriya, C. Karthika, M. Radhika, N. Vennilamani, S. Pattabhi, *Bioresour. Technol.* **2003**, *87*, 129.

[59] A. Belayachi, B. Bestani, A. Bendraoua, N. Benderdouche, L. Duclaux, *Desalination Water Treat.* **2016**, *57*, 17557.

[60] S. Abdulrazak, K. Hussaini, H. M. Sani, *Appl. Water Sci.* **2017**, *7*, 3151.

[61] H. Ferch, *Chem. Ing. Tech.* **1980**, *52*, 366.

[62] S. M. Shaheen, A. S. Derbalah, F. S. Moghanm, *Int. J. Environ. Sci. Dev.* **2012**, 362.

[63] H. J. Shipley, K. E. Engates, V. A. Grover, *Environ. Sci. Pollut. Res.* **2013**, *20*, 1727.

[64] M. Terrones, A. R. Botello-Méndez, J. Campos-Delgado, F. López-Urías, Y. I. Vega-Cantú, F. J. Rodríguez-Macías, A. L. Elías, E. Muñoz-Sandoval, A. G. Cano-Márquez, J.-C. Charlier, *Nano Today* **2010**, *5*, 351.

[65] J.-G. Yu, X.-H. Zhao, L.-Y. Yu, F.-P. Jiao, J.-H. Jiang, X.-Q. Chen, *J. Radioanal. Nucl. Chem.* **2014**, *299*, 1155.

[66]   M. A. Atieh, O. Y. Bakather, B. Al-Tawbini, A. A. Bukhari, F. A. Abuilaiwi, M. B. Fettouhi, *Bioinorg. Chem. Appl.* **2010**, *2010*, 1.

[67]   R. Sitko, E. Turek, B. Zawisza, E. Malicka, E. Talik, J. Heimann, A. Gagor, B. Feist, R. Wrzalik, *Dalton Trans.* **2013**, *42*, 5682.

[68]   N. Abdullah, N. Yusof, W. J. Lau, J. Jaafar, A. F. Ismail, *J. Ind. Eng. Chem.* **2019**, *76*, 17.

[69]   I. Hajdu, M. Bodnár, Z. Csikós, S. Wei, L. Daróczi, B. Kovács, Z. Győri, J. Tamás, J. Borbély, *J. Membr. Sci.* **2012**, *409–410*, 44.

[70]   E. Dialynas, E. Diamadopoulos, *Desalination* **2009**, *238*, 302.

[71]   X.-X. Gao, D.-J. Xue, D. Gao, Q. Han, Q.-Q. Ge, J.-Y. Ma, J. Ding, W. Zhang, B. Zhang, Y. Feng, G. Yu, J.-S. Hu, *Sol. RRL* **2019**, *3*, 1800232.

[72]   I. Hwang, I. Jeong, J. Lee, M. J. Ko, K. Yong, *ACS Appl. Mater. Interfaces* **2015**, *7*, 17330.

[73]   R. W. Bradley, P. Bombelli, S. J. L. Rowden, C. J. Howe, *Biochem. Soc. Trans.* **2012**, *40*, 1302.

[74]   A. Binek, M. L. Petrus, N. Huber, H. Bristow, Y. Hu, T. Bein, P. Docampo, *ACS Appl. Mater. Interfaces* **2016**, *8*, 12881.

[75]   D. Fabini, *J. Phys. Chem. Lett.* **2015**, *6*, 3546.

[76]   U.S. Department of the Interior, United States, Department of the Interior, *Minerals Yearbook: Metals and Minerals 2013.*, **2018**.

[77]   J. DeCicco, J. Kliesch, American Council for an Energy-Efficient Economy, *ACEEE's Green Book: The Environmental Guide to Cars and Trucks, Model Year 2001*, American Council For An Energy Efficient Economy, Washington, D.C., **2001**.

[78]   B. Hailegnaw, S. Kirmayer, E. Edri, G. Hodes, D. Cahen, *J. Phys. Chem. Lett.* **2015**, *6*, 1543.

[79]   *Hazard Standards for Lead in Paint, Dust and Soil (TSCA Section 403)*, United States
Environmental Protection Agency (EPA), **2019**.

[80]   B. G. Wixson, B. E. Davies, *Environ. Sci. Technol.* **1994**, *28*, 26A.
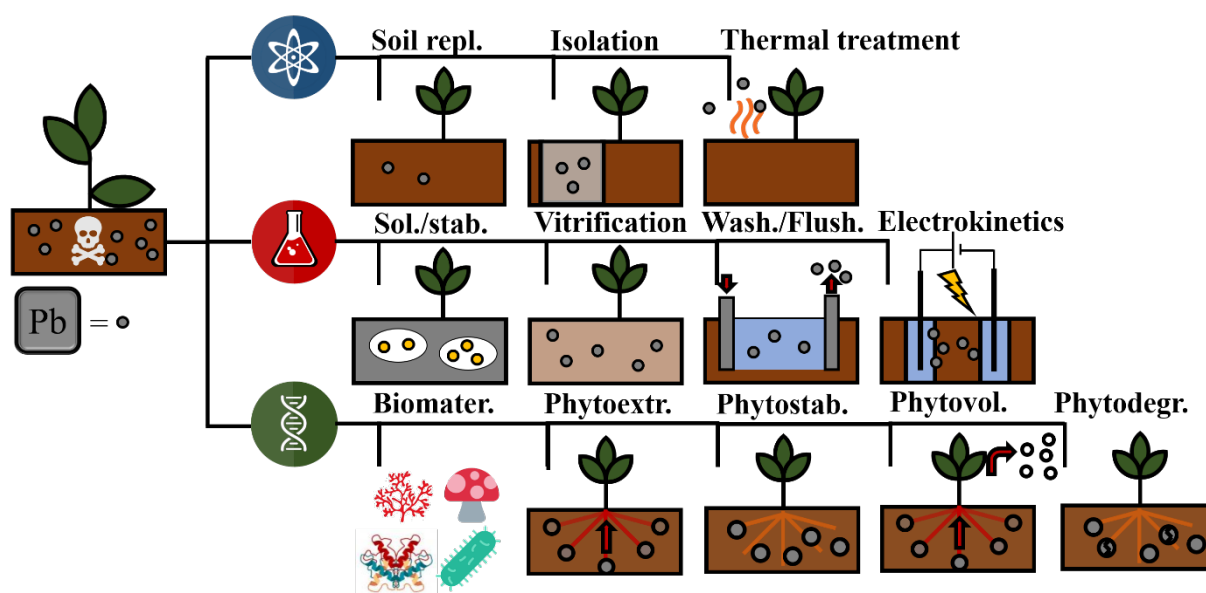
Figures

Figure 1: Lead in soil: remediation tools. Remediation technologies including physical (soil replacement, isolation and thermal treatment), chemical (solidification/stabilization, vitrification, soil washing/flushing and electrokinetics) and biological (biomaterials, phytoextraction, phytostabilization, phytovolatilization and phytodegradation) remediations. Grey and yellow spheres refer to lead cations and additives respectively.
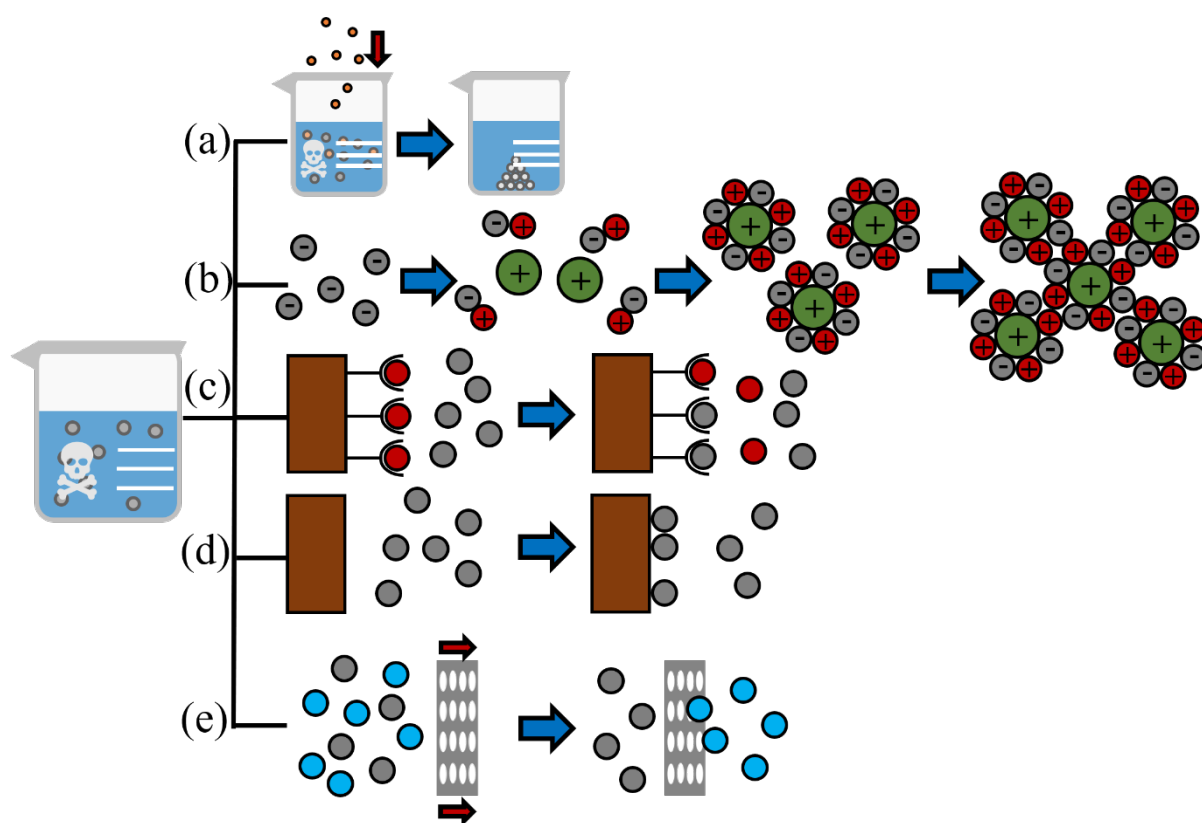
Figure 2: Techniques for lead removal from water. They include **(a)** precipitation, **(b)** coagulation-flocculation, **(c)** ionic exchange, **(d)** adsorption and **(e)** membrane separation processes. Orange and yellow spheres represent reactants for the precipitation and the precipitated salt respectively. Grey(-), red(+) and green(+) spheres represent lead particles, additives and aggregates respectively. Red, grey and blue spheres are protons, lead and water molecule respectively.
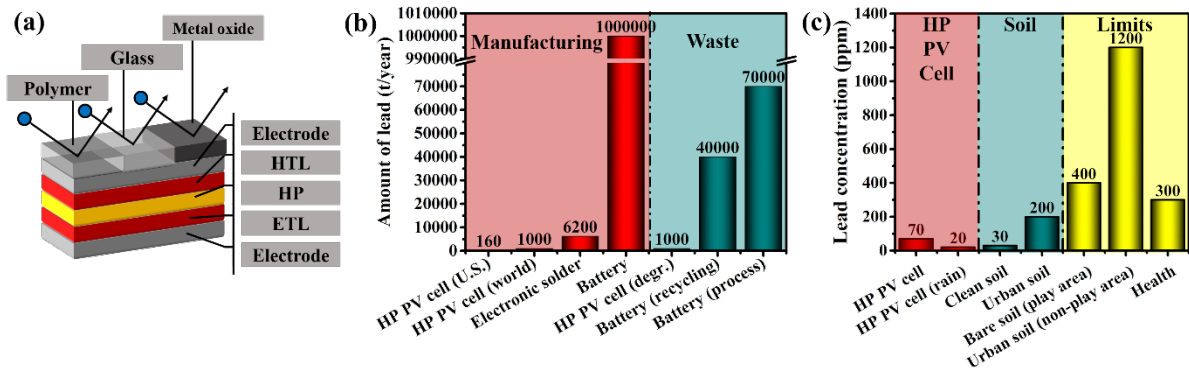
Figure 3: Strategies for Lead collection. (a) Illustration of HP PV cell three types of protective layers on the top made of either polymer, glass or metal oxide. **(b)** Amount of lead for the manufacturing and generated lead waste of HP PV cells, electronic solders and batteries. **(c)** Lead concentration in soil and guideline values.

The table of contents

In this article, a forward-looking perspective is given to develop new approaches for the issue related to lead in Hybrid Perovskites. The currently used remediation tools for the sanitization of soil and water are described and discussed to transfer these technologies to Hybrid Perovskite Photovoltaic cells. Finally, the impact of lead content is assessed in comparison with existing lead based-technologies.

Keyword Hybrid perovskite, lead, toxicity, remediation, soil, water, photovoltaics, toxicity

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Dealing with Lead in Hybrid Perovskite: a Challenge to Tackle for a Bright Future of

This Technology?
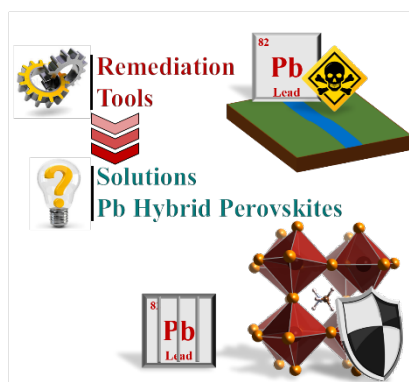
Giulia is Associate Professor in Chemistry at University of Pavia, leading the *PVsquared2* team and the European ERCStG Project "HYNANO", aiming at the development of advanced hybrid perovskites materials and innovative functional interfaces for efficient, cheap and stable photovoltaics. She is author of 91 peer-reviewed scientific papers (h-index=44, >14'000 citations). Recently, she received the USERN prize in Physical Science, the Swiss Physical Society Award in 2018 for Young Researcher and the IUPAP Young Scientist Prize in Optics. She is currently *USERN Ambassador for Italy* and board member of the *Young Academy of Europe*. More can be found at https://pvsquared2.unipv.it.

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More can be found at https://pvsquared2.unipv.it.